

Study of Counter Diffusion in Isostatic Permeameters

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Abstract : The counter-diffusion of two gaseous substances permeating a polymeric membrane has been investigated both experimentally and theoretically. The aim of the study was to find mutual effects, if any, that could influence the permeability and diffusivity data. The experimental data were obtained with an isostatic permeameter operating at ambient pressure and 303 K; helium, nitrogen, carbon dioxide methane were used as permeating gas at different partial pressure; helium or nitrogen as equilibrating or carrier gas. No evident mutual effect of the counter-diffusing gas was observed. The theoretical analysis gave some insight into the phenomena and it was concluded that at near-atmospheric pressures, and in the absence of swelling phenomena no mutual interaction exists. On a theoretical basis any mutual interaction between diffusing and counter-diffusing gases could only occur: i) at high pressures, when the free movement of permeating gas molecules within the polymer is hindered by the counter-diffusing gas; ii) when a large part of the free volume fraction is occupied by the counter-diffusing gas; iii) swelling phenomena modify the structure and free volume fraction of the polymer.

Keywords :

Introduction

Since the first permeation measurements, many experimental devices have been proposed to determine permeability and diffusivity, the aim being to obtain high repeatability and reproducibility of data [1-3]. Actually the permeability data of polymeric materials ranges around five or six order and this justifies the efforts made to find devices able to give highly accurate measurements within such a large range of values.

Basically, the various devices that usually

operate under isothermal conditions measure the rate of variation of:

- volume at constant pressure [4-7];
- pressure at constant volume, [8-9];
- composition variation for constant pressure and volume [10].

The experimental details and operating tricks of each device have been described in detail by various authors.

Also a gravimetric method has been used; this is based on weight variation vs. time of a sample hanging in a given atmosphere. From the rate of the adsorption-desorption phenomena it is possible to evaluate the diffusion coefficient and the adsorption constant of the polymer [1,11-13].

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Today many of these devices are no longer used and are of historical interest.

For what concerns the operating conditions, the various devices can be divided into two groups:

- isostatic devices, where the hydrostatic pressure on the two sides of the membrane is practically the same: the pressure of the permeating gas on one membrane face being equal to the pressure of an inert gas on the other face. No mechanical stress acts on the membrane, except compression but only at high pressure. In this case the driving force is due to the difference in the partial pressure of the permeating gas across the membrane, while the inert gas, with an opposing pressure gradient, usually permeates in the opposite direction. These devices can operate in both closed and flowing conditions [14].
- non-isostatic devices, where the driving force of permeation acts as a hydrostatic pressure on one side of the membrane, the permeating gases being present at higher pressure on one side. In order to reduce strain, the membrane is usually supported on a porous material that increases the mechanical resistance.

In recent years greater interest has been shown in isostatic devices due to their convenience, sensitivity and suitability for permeability evaluations.

Isostatic conditions are usually obtained by using inert gases, such as helium, nitrogen, hydrogen etc., on the permeated side. In fact the transport data from such devices are in good agreement with data using non-isostatic devices, nevertheless it might, in some cases, be thought that the counter-diffusion of the gas used to equilibrate pressure on the two sides of the membrane could interfere with the permeating gas itself, and thus influence the final results.

The *modus operandi* of the isostatic device varies, being either a differential procedure, by instantaneous flow analysis of permeate gas, or an integral procedure, by analysing the accumulated permeating gas on the permeating side [15].

The first procedure is suitable for highly permeable materials. The permeability of the mate-

rials can be directly measured from the limiting value of the permeation rate (stationary flow procedure) while the diffusion coefficient can be determined from the half-time of the limiting value of permeation [3]. The latter is done according to the procedure of Roger, Buritz, Alper [17], that is based on the change in permeate flow over time in non stationary conditions, or that of Fedel and co [3]. who evaluated the time lag of the membrane through numerical integration of the experimental data.

The second procedure (integral procedure) is usually applied to low permeating materials; indeed the permeate is accumulated within a closed (well-defined) volume, allowing the measurement of permeate concentration. Thus the increase in concentration of the permeant can be assessed as a function of time and used to evaluate the asymptotic flow rate; this, in turn, allows the evaluation of permeability from slope, and the time lag value from the intercept with the time axis.

The aim of this work was to study, both experimentally and theoretically, counter-diffusing phenomena in gas permeation.

Experimental

Details of the apparatus

The isostatic-measuring device was designed and developed in our laboratory. It allows the permeability measurements either in transient or stationary conditions, in flow or closed volume procedure [15]. Figure 1 shows a schematic diagram of the apparatus.

The isostatic permeameter is composed of two half-cells separated by a polymeric flat membrane, the one being studied: one half-cell (usually the upper one, called the permeating compartment) has either the purge gas or the permeating gas flowing through it; the second half cell (usually the lower one, called collecting compartment) collects the permeated gas. An external pump, in line with the sampling valve that is connected to a gas-chromatographic analyser and the collecting compartment, allows a thorough

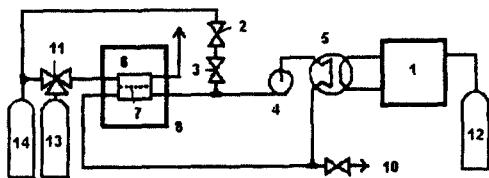


Fig. 1. Schematic flow diagram of the modified apparatus. 1) Gas-chromatograph-2) input valve-3) manometer-4) circulating pump 5) automatic sampling valve-6) permeation cell-7) membrane-8) thermostat-9) exit valve-10) to flow controller-11) three way valve-12) carrier gas (helium cylinder)- 13) permeating gas cylinder-14) helium cylinder.

mixing of the permeated gas with the equilibrating gas; the circulating flow eliminates any concentration polarisation on the lower membrane surface (on the upper surface the flow rate of the permeating gas does not allow the formation of any concentration polarisation). The modifications made to the apparatus allow it to operate with either closed permeate volume, i.e. to accumulate the permeate in the collecting compartment, or a stream flow, i.e. a flowing gas that purges into the ambient the permeate from the collecting compartment. Permeation measurements can be performed in both transient and stationary conditions. The closed volume procedure is suitable with low permeating rate, the open flow one for high permeating rate. In both procedures the measurements of permeate concentration as a function of time allow to evaluate the membrane diffusion coefficient, using time lag value determined from transient state data, and membrane permeability, from stationary state data.

The guidelines for our permeameter are:

a) the flow rate of the permeating gas in the permeating compartment (upper in Figure 1) must be quite high when the helium (present for purging) is switched off, and the switching time, from helium to permeating gas, as low as possible in order to have a negligible system time lag in the permeating compartment. The helium feeding the permeameter is usually used to either clean the two half-cells or, in differential procedure, as a flowing gas to remove the permeate (with closed volume procedure it is

present in the circulating loop); it is this gas that counter diffuses the permeating gas;

b) the flow rate of the gas circulating in the collecting compartment must be high enough to have a well-mixed system and a negligible time lag between the membrane and the analytical system. This target was obtained by reducing the overall volume of the system, i.e. collecting compartment, circulating loop, connecting lines, the control and the regulating valves; the total volume of the system was about 25 cc;

c) the volume of the gas-chromatographic sampling valve, in line with the circulating loop, was kept to the minimum, 20 μL for the integral procedure, 70 μL for the differential;

d) the carrier gas for the gas-chromatographic analysis is usually the same as in the circulating loop.

Both the gas chromatograph and the permeameter are fed by gas cylinders; there is a timer-operated six-way sampling valve on line with the circulating loop; both half-cells operate at atmospheric pressure; the hydrostatic pressure difference between the two half-cells is a few cm of water, unavoidable due to the re-circulating pump.

In principle this equipment could operate at pressure higher than the atmospheric one.

Preliminary operations

a) Determination of the collecting compartment and loop volume: a correct evaluation of the membrane time lag requires the knowledge of the collecting volume. Moreover the composition of the gas in the sampling valve must be the same as in the collecting compartment; thus it is necessary the system be well mixed. To evaluate system volume and mixing efficiency the usual procedure for testing CSTR (continuous stirred tank reactor) was followed. A metal sheet was used instead of a membrane to separate the upper and the lower half-cells of the system was operated in flow condition. After purging the collecting compartment with a gas stream of known rate, a given amount of a marker gas, i.e.

nitrogen, methane etc, was introduced into the compartment under continuous flow of purging gas. At the same time, the timer connected to the sampling valve was activated. For a well-mixed system the following decay law holds:

$$C = C^0 \exp^{-t/\theta}$$

where:

$\theta = V/F$, the ratio between the volume of the collecting-circulation loop (V), and the flow rate (F) of the flowing gas; C, the actual concentration of the tracer in the system, and C^0 the initial one; t time.

For a well-stirred system, by plotting the logarithm of the measured tracer concentration, C, against time, t, a straight line is obtained; the slope of the straight line is $1/\theta$ and the intercept is $\ln C^0$. From the value of θ and $\ln C^0$, evaluated from the initial amount m of the tracer and the purge gas flow rate, it is possible to obtain two estimated values of V that must coincide for different amounts of m^0 and F. This provides a self-validity test for the experimental run. The system was tested with many different helium flow rates F and an initial amount m^0 of the tracer. It is important to note that also for very low values of F the system is always well mixed: this suggests that also operating in closed conditions the system is well mixed. The evaluated volume of the half-cell and circulating loop was 25 mL.

Materials and test runs

At the beginning of a run, after a complete purge of the two compartments with the equilibrating gas, a stream of the permeating gas was introduced into the permeating compartment. The transport gas is either allowed to flow into the collecting compartment for the flow procedure, or its flow is stopped when the accumulation procedure is used.

A gas chromatograph with a timer operated sampling valve was used to analyse the permeated gas. Various columns, depending on the

gas to be revealed, were used. The appropriate carrier gas, He or N_2 , was chosen for the gas chromatographic analysis so as to enhance and separate the signals of the permeating and equilibrating gases. Each analysis must be no longer than 300-400 s, always lower than the sampling time. The carrier and equilibrating gas can be the same; actually only the equilibrating gas counter can diffuse in the permeating cell.

Two sets of runs were performed using two different membranes.

With the first membrane, a commercial film of polypropylene (thickness 150 μ), the permeability to mixtures was evaluated.

The following mixtures (volume % of the first gas in parenthesis) were tested:

N_2 /He (100, 72, 40, 20%); CO_2 /He (100, 67, 40, 20, 10%), the carrier, equilibrating and diluent gas being helium;

CO_2 / N_2 (100, 68, 45, 21, 10%); the carrier, equilibrating and diluent gas being nitrogen;

He (100%); equilibrating gas - CO_2 ; carrier gas - N_2 .

N_2 (100%); equilibrating gas - CO_2 ; carrier gas - He.

The second set of runs was performed with a polycarbonate-polyurethane membrane (PTMC 1093-PU; thickness 150 μ) prepared by reacting poly(tetramethylene)carbonate diols (MW 1093) and toluendiisocyanate: details of its preparation and characterisation are given in (16); the permeating gas was methane mixed with helium, used also as equilibrating gas (CH_4 /He = 12.2; 22.8; 36.5; 55.3; 75.3; 95; 100%). The carrier gas was helium. For each mixture at least three test runs were performed in order to make a statistical analysis of the results. Methane was used due to its relatively lower permeability, compared with other gases.

Permeability of helium

In order to have an independent measure, helium permeability was tested by a volumetric device (ASTM 1434), consisting of an open to air calibrated flange (0.5 cm) connected on one side

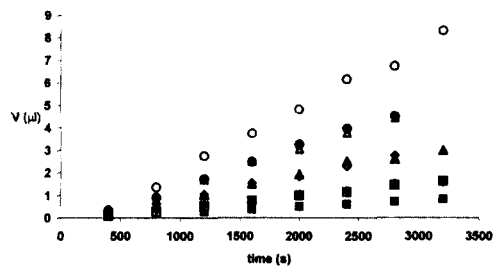


Fig. 2. Total permeated volume (μl of CO_2) vs. time (s) for various mixtures of CO_2 -He. Counter-diffusing gas: He. Membrane: polypropylene. Permeating mixtures CO_2 %: \triangle 100; \square 67; \circ 40; \diamond 20; * 10. Full symbols: duplicated runs.

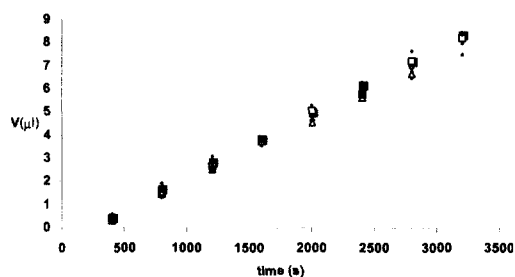


Fig. 3. The same as Figure 2. All the data are normalised to the same driving force (standard pressure of 1 atm., 101.311 kPa.) by considering the partial pressure of permeating gas.

to a helium cylinder and on the other to a calibrated capillary tube (0.8 mm ID). Between the flange and the capillary, where the membrane was put, there is an intermediate zone that allows, through a rubber sealed side tube, the introduction of a drop of a liquid (usually methylethylcheton) used to reveal flow rate in the capillary. A valve and a manometer regulate the upper side pressure, while the lower side is at atmospheric pressure. After imposing a pressure drop P across the membrane, the measure of the permeating gas flow rate in the capillary, of the thickness and the surface area of the membrane, allows to calculate the permeability.

Results

Polypropylene membrane

The permeability of polypropylene to Helium, according to ASTM 1434, was $14(\pm 2) \cdot 10^{-10}$ (STP $\text{cm}^3/(\text{cm} \cdot \text{cm Hg} \cdot \text{s})$). Figure 2 shows, as an example, the results obtained in our apparatus for the permeation of mixtures CO_2 -He, with He as equilibrating gas: the values of the total permeated CO_2 volume vs. time, for different volume concentrations of the feed stream, are reported: all runs were at least duplicated. As can be seen all the lines converge to the same time lag, independently of mixture composition, while the slope of the lines depends on the mixture composition. The same data are reported in normalised form

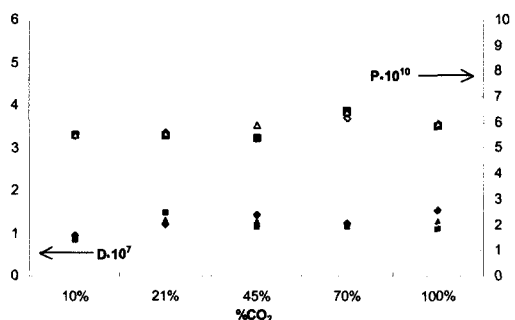


Fig. 4. Experimentally evaluated data for P and D as a function of permeating gas composition. Permeating mixture: CO_2 - N_2 ; collecting gas He. Membrane: polypropylene. Some runs have been duplicated: mean value of duplicated runs.

(Figure 3), i.e. by considering the composition of the mixtures: all the lines have, within the limits of the experimental error, the same slope and the same time lag. All the mixtures analysed present similar behaviour.

Figure 4 shows the values of P and D for the mixtures CO_2 -He vs. composition.

Table 1 summarises the results for all the studied mixtures. It can be seen that, within the limits of experimental error, the values for P and D are independent of the composition the permeating gas and of the nature of the counter diffusing gas.

The obtained results show that in polypropylene, a typical semi-crystalline polymer, the counter-diffusing gas has no influence on perme-

Table 1. Permeability, diffusivity and solubility data of various gases in a polypropylene membrane.

Permeant/ Equilibrating gas	$P \cdot 10^{10}$ (STPcm ³ / (cm · cmHg · s))	$D \cdot 10^7$ (cm ² / s)	$S \cdot 10^3$ (STPcm ³ / (cm ³ · cmHg))
N ₂ / He	0.39 ± 0.05	1. ± 0.1	0.44
N ₂ (*) / CO ₂	0.38 ± 0.01	0.8 ± 0.1	0.5
CO ₂ / He	6.1 ± 0.2	1.6 ± 0.4	4.
CO ₂ / N ₂	5.8 ± 0.5	1.4 ± 0.1	4.1
He(*) / CO ₂	14.0 ± 0.2	230 ± 17	0.06
He (**)	14.0 ± 0.2		

(*) Only pure gases were used.

(**) Obtained according to ASTM 1434.

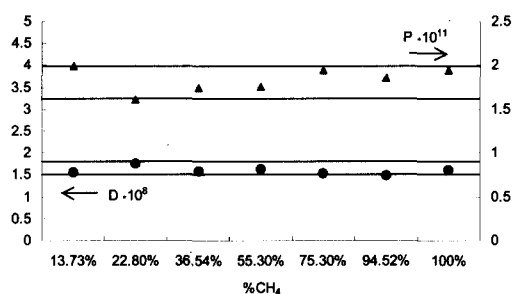


Fig. 5. Experimentally evaluated data for P and D as a function of permeating gas composition. Permeating mixture : CH₄-He ; collecting gas He. Membrane: PTMC 1093-PU. As a result of the statistical analysis of all replicated data the confidence limits are reported.

ability and diffusivity, even though the gases have a quite different critical temperature, solubility and molecular weight (4 for helium and 44 for carbon dioxide). Moreover, as expected, also the gas used to achieve the isostatic conditions has no influence on the calculated solubility coefficients.

PTMC1093-PU membrane

This glassy, highly permeable, polymer was subjected to a deep study, in the methane/helium mixture, the permeability test runs being replicated many times in order to make a thorough statistical analysis. Figure 5 shows the values of methane permeability as a function of permeating mixture composition.

Also in this case the values resulting from

changes in the driving force, for both the permeating gas and the counter-diffusion gas, are independent of the permeation rate of the counter diffusing gas.

The values for methane are:

$P = (1.6 \pm 1) \cdot 10^{-11}$ (STPcm³ / cm² · cmHg · s) and
 $D = (1.8 \pm 1) \cdot 10^{-8}$ (cm² / s).

Analysis of the results

The mean value of the permeability, either of the permeating gas *i* or the counter diffusing gas *j*, is given by the relation:

$$\bar{P}^v = \frac{J^v \delta}{(P_\alpha y_\alpha^v - P_\beta y_\beta^v)} \quad (1)$$

the apex stands for *i* or *j*; the permeation flow of gas *v* is J^v and the term in the denominator is the difference between the partial pressure of gas *v* on the two sides, α and β of the membrane, and y^v is the molar fraction in gas phase for a strictly isostatic apparatus:

$$P_\alpha = P_\beta; \quad y_\alpha^i = 1; \quad y_\alpha^j = 0; \quad y_\beta^i = 0; \quad y_\beta^j = 1.$$

By assuming that in the non-porous polymeric membrane the diffusion is Fickian and the adsorption-solution equilibrium state condition is established on both faces of the membrane, the one-dimensional transport through the membrane under steady conditions may be described by Fick's first law:

$$J^v = -D^v(T, \pi, v^i, v^j) \frac{dv^v}{dx} \quad (2)$$

J^v is the volumetric flux; D^v is the diffusion coefficient which in general is a function of the volume concentration of the penetrants; v^v the local volume concentration of penetrant v (volume of penetrant at normal condition/polymer volume); T is the isothermal diffusion temperature; π is the hydrostatic pressure on the system; x is the co-ordinate in the diffusion direction.

According to Cohen and Turnbull [18], Fujita [19] and Doolittle [20] D^v is a function of the available free volume fraction Φ_f of the polymer. For a dilute solution D^v can be written as:

$$D^v = RT A_D^v \exp\left(-\frac{B_D^v}{\Phi_f}\right) \quad (3)$$

where R is the universal gas constant; A_D^v and B_D^v are characteristic parameters that depend on the size and shape of the penetrant molecule v , but are usually assumed independent of temperature and penetrant concentration. Let Φ_r be the free volume fraction of the pure polymer ($v^v = 0$) in a reference temperature T_r and hydrostatic pressure π_r , in absence of any swelling; the free volume fraction of the pure polymer Φ^v as a function of temperature and pressure is given by the relation:

$$\Phi^v = \Phi_r + \lambda_T(T - T_r) + \lambda_\pi(\pi - \pi_r) \quad (4)$$

λ_T and λ_π are respectively the thermal expansion coefficient and the compressibility coefficient of the pure polymer. In the presence of any dissolved materials, or penetrants, the free volume fraction of the polymer could change. This change can be expressed in terms of volume concentration of penetrant v^v :

$$\gamma^v = \left(\frac{d\Phi_f}{dv^v}\right)_{T, \pi, v} \quad (5)$$

γ^v can be positive, with an increase in free volume, when polymer swelling occurs, or

negative if the species do not change the total free volume, due to absence of interaction with the polymer, but occupies the free polymer volume so that some of the free volume is no longer available for the free movement of permeating molecules.

Therefore the free volume fraction of the polymer in the presence of diffusing and counter diffusing penetrant can be written as:

$$\Phi_f = \Phi^v + \gamma^i v^i + \gamma^j v^j \quad (6)$$

In the previous equation a linear relationship must be assumed between the penetrant concentration and the free volume variation of the polymer; this simplifying hypothesis implies:

- the swelling phenomena are linear with the volume concentration of the penetrant;
- the partial molar volume of the components diffusing into the polymer are equal to their molar volume.

In stationary conditions, the permeation flux J^i for the component i , across a membrane of thickness δ , is given by the expression:

$$J^i = -\frac{RT A_D^i}{\delta} \int_{v_a^i}^{v_b^i} \exp\left(\frac{-B_D^i}{\Phi^v + \gamma^i v^i + \gamma^j v^j}\right) dv^i \quad (7)$$

The solution of the integral may be performed if a relation between v^i and v^j can be found. A simple way is to assume that the adsorption rate is greater than the diffusion rate within the polymer i.e. all the penetrants are in local adsorption equilibrium. In this case a relation can be found between the volume concentration. A simple adsorption equation for low concentration of penetrants, i.e. for low values of v^v , is the Henry law:

$$v^v = S^v P y^v \quad (8)$$

S^v is the solubility coefficient of the component v ; p the total pressure and y^v the molar fraction of the adsorbing gases. Under the conditions of

Henry law validity a linear relationship can be assumed for the concentration of the component within the membrane, along the co-ordinate x position in the direction of diffusion. On the basis of this hypothesis:

$$\begin{aligned} v^i &= P_\alpha S^i y_\alpha^i - \frac{S^i}{\delta} (P_\alpha y_\alpha^i - P_\beta y_\beta^i) x \\ v^j &= P_\alpha S^j y_\alpha^j - \frac{S^j}{\delta} (P_\alpha y_\alpha^j - P_\beta y_\beta^j) x \end{aligned} \quad (9)$$

the relation between v^j and v^i can be obtained by solving the first equation with respect to the co-ordinate x , and substituting the obtained value in the second equation:

$$v^j = \frac{S^j}{S^i} (P_\alpha y_\alpha^i - P_\beta y_\beta^i) \frac{v^i - P_\alpha S^i y_\alpha^i + P_\alpha S^j y_\alpha^j}{P_\alpha y_\alpha^i - P_\beta y_\beta^i} + P_\alpha S^j y_\alpha^j \quad (10)$$

or:

$$v^j = m v^i + P_\alpha (S^j y_\alpha^j - m S^i y_\alpha^i) \quad (11)$$

where :

$$m = \frac{S^j (P_\alpha y_\alpha^i - P_\beta y_\beta^i)}{S^i (P_\alpha y_\alpha^i - P_\beta y_\beta^i)} \quad (12)$$

For a strictly isostatic apparatus the hydrostatic pressure acting on the two faces of a membrane is the same, $p_\alpha = p_\beta$, so the pressure on the membrane will be simply indicated by p ; moreover if it works in optimal conditions the upstream partial pressure of the diffusing component is equal to the total pressure while its downstream partial pressure is zero; the opposite holds true for the counter diffusing gas, i.e.: $y_\alpha^i = 1; y_\alpha^j = 0; y_\beta^i = 0; y_\beta^j = 1$.

With this condition the following relations holds for v^i :

$$\begin{aligned} m &= -\frac{S^j}{S^i} \\ v^j &= p_\alpha S^j - \frac{S^j}{S^i} v^i \end{aligned} \quad (13)$$

The previous integral [7] may be written in the following simplified form:

$$j^i = \frac{RT A_D^i}{\delta} \int_{v_\beta^i}^{v_\alpha^i} \exp\left(\frac{-B_D^i}{\phi^1 + \gamma v^i}\right) dv^i \quad (14)$$

where:

$\phi^1 = \phi^0 + \gamma^i P_\alpha (S^j y_\alpha^j - m S^i y_\alpha^i)$; $\gamma = \gamma^i + \gamma^j m$; v_α^i and v_β^i are the volume concentrations of the penetrant i at the polymer surfaces α and β , respectively.

The integral may be solved by parts. Let:

$$Y^v = -\frac{B_D^v}{\phi^1 + \gamma v^v} \quad (15)$$

then:

$$j^i = \frac{RT A_D^i}{\delta} \left(\frac{B_D^i}{\gamma}\right) \left[-\frac{e^{Y_\alpha^i}}{Y_\alpha^i} + \frac{e^{Y_\beta^i}}{Y_\beta^i} + \ln \frac{Y_\alpha^i}{Y_\beta^i} + \left[\sum_{n=1}^{\infty} \frac{Y_\alpha^i - Y_\beta^i}{n * n!} \right] \right] \quad (16)$$

The previous equations might be simplified by suitably developing them in series, as shown in the appendix. The resulting simplified form of flux J^v for both of the penetrants is :

$$\begin{aligned} j^i &= \frac{RT A_D^i}{\delta} \left(\frac{B_D^i}{\gamma}\right) \frac{(Y_\alpha^i - Y_\beta^i) e^{Y_\alpha^i}}{Y_m^2} \\ j^j &= \frac{RT A_D^j}{\delta} \left(\frac{B_D^j}{\gamma}\right) \frac{(Y_\beta^j - Y_\alpha^j) e^{Y_\beta^j}}{Y_m^2} \end{aligned} \quad (17)$$

For the diffusing component i the permeation equation is obtained by substituting equation [17] in equation [1]:

$$\bar{P}^i = \frac{RT A_D^i}{P_\alpha y_\alpha^i - P_\beta y_\beta^i} \left(\frac{B_D^i}{\gamma}\right) \frac{(Y_\alpha^i - Y_\beta^i) e^{Y_\alpha^i}}{Y_m^2} \quad (18)$$

By explicating the Y_α^i and developing in series the resulting function, as reported in the appendix, the previous equation becomes:

$$\bar{P}^i = RTA_D^i \bar{S}^i e^{-\frac{B_D^i}{\Phi^1} \gamma^v} \frac{B_D^i}{\Phi^2} \quad (19)$$

where:

$$\bar{S}^v = \frac{V_a^v - V_\beta^v}{P_a Y_a^v - P_\beta Y_\beta^v}$$

is the mean solubility coefficient of the component v.

The obtained equation is similar to those obtained by other authors for diffusion at high pressure (21) or mixture permeation (22).

It is easy to verify that for γ^v equals zero, the permeation equation reduces to the standard form in terms of free volume fraction Φ^1 .

In the case of a strictly isostatic permeator the mean permeability is:

$$\bar{P}^i = RTA_D^i S^i e^{-\frac{B_D^i}{\Phi^0 + P\gamma^j S^j} \frac{B_D^i P(S^i \gamma^i + S^j \gamma^j)}{2(\Phi^0 + P\gamma^j S^j)^2}} \quad (20)$$

The solubility coefficient S^i of the permeating component i is equal to that on the pure component side; in any case, the last exponential term is very small, therefore the term equals one. Moreover if $P\gamma^j S^j \ll \Phi^0$ the permeability data of component i are not influenced by the counter diffusion of component j. This condition is always verified when :

- the permeating pressure in the isostatic apparatus is not high;
- the solubility of the counter diffusing component j is low, as is usually the case since the isostatic condition is obtained by using permanent gases that have a very low solubility in polymers;
- the effect of the counter diffusing gas volume concentration on the free volume fraction of the polymer is low, i.e. when no swelling phenomena is induced by the counter diffusing gas, and when the volume occupied by the molecules is negligible with respect to the free volume of the polymer.

All these conditions are usually verified in an isostatic permeameter. A case where these conditions are not verified is reported in (23).

Now let us consider the terms present in (20). First of all, according to Williams, Landel and Ferry [24], the free volume fraction is equal to 0.025 for all polymers at the glass transition temperature. Even though this is not really true for all polymers and can be considered only a rough approximation, the real value is certainly not far away and would increase little with temperature.

With regard to the term B_D^v , this is a well-discussed subject and it is normally accepted that its value is in the range 0.5-1.

γ^v has been defined by equation [5] : its value is a function of the local composition; nevertheless it is possible to calculate the limiting value in the case of a strictly isostatic system and in absence of swelling phenomenon. Actually in this case on the two side of the membrane only pure gas are present so the amount of dissolved gas v^v can be assumed equal to the gas solubility at the equilibrium pressure.

When the temperature of the diffusing gas is much greater than the critical temperature no swelling phenomenon is present, therefore there is only the decrease in free volume due to the diffusing gas has to be considered.

Under the previous conditions the value of γ is 1.

Due to the high inner pressure of the polymer it is reasonable to assume that the diffusing gas volume within the polymer is in the order of the critical volume, that is, for compounds in the vapour phase under room conditions, in the range 60-200 cc/gmole.

In Table 2 the value of $v^j = p\gamma^j S^j$ for the considered gases are reported .

From the previous Table 2 it results that helium and nitrogen can be used without any problem as equilibrating gases in the isostatic permeating apparatus while it is not suggested the use of carbon dioxide, owing to the significant variation of the free volume due to the volume of the molecules.

Table 2. Degree of occupancy of the free volume evaluated from solubility data.

Gas	Solubility 10^3 (stp cm^3/cm^3 cmHg)	Critical Volume (cm^3)/mole	$v^i 10^3$ (cm^3/cm^3 polym)	% of free volume filling
N ₂	0.44	90	1.34	5,4
	0.5		1.53	6.1
CO ₂	4.0	94	13	50
	3.7		12	47
He	0.06	57.8	0.12	0.5

Indeed the data reported in Table 1 doesn't evidence any effect of counter diffusing carbon dioxide on permeating gas (N₂ and He); to explain these results one has to remark that in the experimental condition adopted carbon dioxide behaves as a vapour, allowing possible swelling phenomenon. This consideration is supported by the high solubility coefficient value. Therefore there is a compensation between the decrease of free volume due to the absorption of the equilibrating gas and the swelling phenomena. In any case the use of carbon dioxide as equilibrating gas is non recommended.

Conclusion

The present investigation provides a theoretical insight into membrane transport phenomena in the presence of a counter diffusion process.

Experimental evidence and theoretical analysis highlight that permeability and diffusivity of counter diffusing gas are independent of hydrostatic pressure, at least when the counter-diffusing gases are poorly soluble and there are thus no swelling phenomena. This is the case of helium and nitrogen. Indeed from the solubility data of these gases in polymers it results that only a small part of the free volume is occupied by these counter-diffusing gases, and there is therefore no hindrance to the free movement of the permeant molecules.

This is not the case of carbon dioxide that may have some effects when used as equilibrating gas owing to its high very high solubility. Nevertheless the reported experimental data don't evidence any important effects, probably owing to swelling phenomena produced by carbon dioxide.

The theoretical analysis suggests that the permeation of mixture of vapours or gases at high pressure may not be evaluated from the permeation data of pure gases if the solubility of data are high since the degree of occupancy of the free volume may hinder the free movements of the molecules.

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Appendix

The maximum value of the ratio Y_a^i/Y_β^i for the operating conditions of a isostatic apparatus is:

$$\frac{Y_a^i}{Y_\beta^i} = \frac{\phi_f + \gamma^i S^i p}{\phi_f + \gamma^j S^j p} \cong 1$$

If the solubility of penetrants, j, and I are similar, this ratio equals one.

$$\text{Let: } v_m^v = \frac{v_a^v + v_\beta^v}{2} \quad Y_m^v = \frac{-B_D^v}{\phi^1 + \gamma v_m^v}$$

$$\sum_{n=1}^{\infty} \frac{Y_a^n - Y_\beta^n}{n * n!} \cong \frac{(Y_a - Y_\beta)}{Y_m} e^{Y_m}$$

The series converge absolutely and can be approximated with the expression at the second term.

$$\frac{e^{Y_a^v}}{Y_a^v} - \frac{e^{Y_\beta^v}}{Y_\beta^v} = (Y_a^v - Y_\beta^v) e^{Y_m^v} \frac{Y_m^v - 1}{Y_m^v}$$

term.

$$J^v = \frac{RTA_D}{\delta} \left(\frac{B_D^v}{\gamma} \right) \frac{(Y_\alpha^v - Y_\beta^v)}{Y_m^v} e^{Y^v}$$

Moreover:

$$Y^v = -\frac{B_D^v}{\Phi^1 + \gamma v^v} \quad [Y^v]' = \frac{B_D^v \gamma}{(\Phi^1 + \gamma v^v)^2}$$

$$Y^v = -\frac{B_D^v}{\Phi^1 + \gamma v_m^v} + (v^v - v_m^v) \frac{B_D^v \gamma}{(\Phi^1 + \gamma v_m^v)^2}$$

$$Y_m^v = -\frac{B_D^v}{\Phi^1} + \gamma v_m^i \frac{B_D^v}{\Phi^{12}}$$

$$Y_\alpha^i - Y_\beta^i = \frac{B_D^i \gamma (v_\alpha^i - v_\beta^i)}{(\Phi^1 + \gamma v_m^i)^2}$$

Symbols

A_D, B_D	characteristic parameters (Eq. 3)
C	concentration
D	diffusivity
F	volume flow rate
J	volumetric permeation flow.
m	see eq. [12]
p	pressure
P	permeability
R	gas constant
S	solubility
t	time
T	temperature
v	volume concentration
V	system volume
y	molar fraction in gas phase
Y	see eq. [15]
x	position co-ordinate in diffusion direction.

Greek symbols

α	one surface of the membrane
β	other surface of the membrane
d	membrane thickness
λ_T	thermal expansion coefficient
λ_κ	compressibility coefficient
Φ	free volume fraction

γ	change of free volume fraction vs. dissolved gas volume fraction (Eq. 5)
π	hydrostatic pressure
θ	residence time.

Apex

$^{\circ}$	initial value
-	mean value
i, j, v	component i, j, or anyone.

Subscript

r	reference state
f	free

References

1. J. Crank and G. S. Park, "Diffusion in Polymers", Academic Press, London, (1968).
2. S. Hwang and K. Kammermeyer, "Membrane in Separations", Wiley, New York, (1975).
3. R. M. Felder and G. S. Huvard, "Method of Experimental Physics", vol. 16, Chapter 17, Academic Press, New York, (1980), pp 315-377.
4. K. K. Hsu, S. Natary, R. M. Thorogood and P. S. Puri, *J. Membrane Sci.*, **79**, 1 (1993).
5. S. A. Stern, T. F. Sinclair and P. J. Greis, "An improved permeability apparatus of the variable-volume type", Issue of modern plastic (1964).
6. S. A. Stern, P. J. Gareis, T. F. Sinclair and P. H. Mohr, *J. Appl. Polym. Sci.*, **7**, 2035 (1963).
7. A. S. T. M. D1434-82, "Standard method for determining gas permeability characteristic of plastic film and sheeting".
8. A. S. T. M., "1976 Annual book of ASTM Standards, Part 35", Philadelphia, (1976) 463.
9. D. W. Brubaker and K. Kammermeyer, *Ind. Eng. Chem.* **44**, 1465 (1952).
10. H. Yasuda, *J. Appl. Polym. Sci.*, **14**, 2839 (1970).
11. Crank, "The Mathematics of Diffusion, Oxford University Press", Oxford, (1956).

12. M. Fels and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 523 (1970).
13. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).
14. Lyssy, Analytical Gas Permeability Tester GPM-200, Technical Report GPM-200/E/2/11.81.
15. L. Zanderighi, F. Bianchi, R. Monga and M. Pegoraro, *La Chim. & Ind.* **72**, 147 (1990).
16. N. Cao, M. Pegoraro, F. Bianchi, L. Dilandro and L. Zanderighi, *J. App. Polym. Sci.*, **48**, 1931 (1993).
17. W. A. Rogers, R. S. Buritz and D. Alper, *J. Appl. Phys.*, **25**, 868 (1954).
18. M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 14 (1959).
19. H. Fujita, *Fortschr. Hochpolymer Forsch. (Advan. Polymer Sci)* **3**, 1 (1961).
20. A. K. Doolittle, *J. Appl. Phys.* **22**, 1471 (1951).
21. S. -M. Fang and S. A. Stern, *Chem. Eng. Sci.*, **30**, 773 (1975).
22. M. Fels and R. Y. Huang, *J. Macromol. Sci.-Phys.* **B5(1)**, 89 (1971).
23. W. R. Viet and Y. -S. Jiang, *J. Membrane Sci.*, **38**, 1 (1988).
24. M. L. Williams, R. F. Landel and J. D. Ferry, *J. Chem. Phys.*, **31**, 1164 (1959).