

Pressure-dependent permeation of noble gases (He, Ne, Ar, Kr, Xe) through thin membranes of oriented polypropylene (OPP) studied by mass-spectrometry

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Abstract

A mass spectrometric method has been used to study transmission of noble gases (He, Ne, Ar, Kr, Xe) through thin polymer membranes of OPP and PET. The transmission of gas originating from a confined volume in a gas cell through the membrane is measured by a mass spectrometer. Due to depletion of gas inside the gas cell, transmission decreases as function of time, which is taken as measure for permeation. For the smaller noble gases helium and neon gas transmission is found to be an exponential function of time indicating a pressure independent permeability for PET and OPP. For the permeation of heavier noble gases xenon, krypton and - to a lesser extent - argon through OPP a pressure dependent permeability was found. A model takes into account the higher solubility for bigger gas atoms as they have a higher probability to stay in cavities of the free volume of the polymer.

There is good agreement between experimental and calculated data. Sensitivity of the mass spectrometric method is discussed for argon isotopes ^{40}Ar , ^{38}Ar and ^{36}Ar and shows an instrumental detection limit of less than 0.1%.

Keyword: gas permeation, mass spectrometer, polymer membrane, noble gas

I. Introduction

Polymer membranes are used as barrier films to prevent gas permeation (applications include food packaging, organic light emitting diodes, proton conductors in fuel cell) or to separate individual components of gas mixtures. In order to optimize barrier and selectivity properties, a much better understanding of gas permeation through polymer membranes is necessary. For such studies, noble gases as permeants offer the advantage of a range of atomic sizes while being chemically inert and having reduced interaction with the polymer. Only a few measurements have been published about Kr and Xe permeation through polymers so far¹²³⁴⁵.⁶ In many systems (polymer and permeant gas) permeability is a pressure dependent quantity.⁷ This is the case for krypton permeation through polypropylene (PP) too, where studies in the pressure range up to 100 bar⁴ have shown that permeability is pressure dependent.

We have used a mass spectrometric method⁸ to study the transmission of inert gases through membranes of oriented polypropylene (OPP) and polyethylene terephthalate (PET). Using a fixed volume of gas which depletes during permeation, this method offers the advantage of measuring pressure dependent permeation data. Permeability for neon and argon estimated with a mass spectroscopic method was found to be in good agreement with control experiments.⁸ In this article we will focus on the pressure dependence of permeability at low gas pressures for permeation of noble gases through OPP and PET.

II. Experiments

There are a number of experimental methods to measure permeation through polymer membranes.⁹ The mass spectrometric method used in this study has been described in detail elsewhere.⁸ Figure 1 shows the principle of measurement where a small container (gas cell) is filled with the gas of interest, covered with a polymer membrane, sealed and then introduced into a UHV system. After the gas cell has been positioned to face a mass spectrometer it records partial pressure as function of time, which is a decreasing function due to depletion of gas in the gas cell during permeation (..g. 1). In a simple model the time constant and geometric parameters of the gas cell can be used to calculate permeability.⁸ Prior to the experiment the gas of interest was admitted to the vacuum chamber and the mass spectrometer was adjusted to maximize its reading and to reproduce the correct intensity ratios between different isotopes. For the experiments we used quadrupole mass spectrometer systems with a channeltron detectors supplied by European Spectrometry Services (ESS).

The measured partial pressure vs. time curves have been corrected against total pressure measured with an ionization gauge, taking into account sensitivity factors.¹⁰ Due to the limited accuracy in sample positioning⁸ partial pressure may vary between experiments. We will therefore focus on estimating time constants of partial pressure decay as a function of time as these quantities are independent of experimental geometry. Control experiments have been carried out on a GTR 30-XR device (Yanaco Inc.) which uses a chromatographic principle for gas detection,¹¹ and with the pressure increase method using a Penning gauge (similar to¹²).

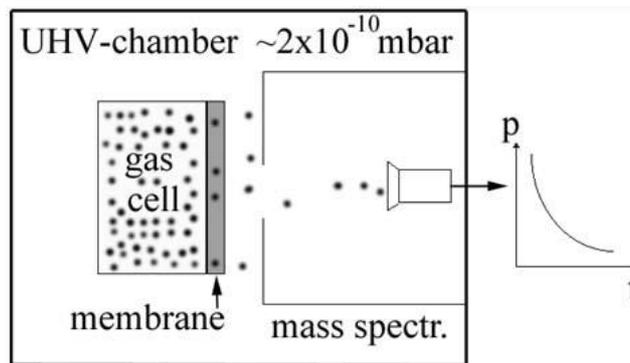


Figure 1: Principle of measuring gas transmission through thin membranes with a mass spectrometer. A vessel (gas cell) is introduced into the UHV system facing a mass spectrometer, and the partial pressure is measured as function of time.

The sensitivity of the mass spectrometric method can be illustrated by studying gas transmission of isotopes. Figure 2 shows the dependence of partial pressure on time for different isotopes of argon. The three naturally occurring isotopes ^{40}Ar , ^{36}Ar and ^{38}Ar have an abundance ratio of approximately 1600:6:1, which corresponds to 99.6%, 0.34% and 0.06%.¹³ In Fig. 2 even the rare isotopes can be clearly distinguished from the background. Experiments reproduce the abundance ratio to a good approximation (Fig. 2). Although the determination of a time constant from the less abundant isotopes ^{36}Ar and ^{38}Ar has a bigger error margin than ^{40}Ar (mainly due to noise and background), all three isotopes show a similar slope in logarithmic representation of partial pressure as function of time (Fig. 2). Hence, the mass spectrometric method is capable of measuring time constants of partial pressure decay of Ar-species which contribute much less than 0.1% to the total pressure.

PET and OPP (biaxially drawn) membranes were used for the permeation experiments because of the great practical importance of these materials.¹⁴ At this stage of the investigation we have restricted the investigation to frequently used thicknesses of 20 μm for OPP and 12 μm for PET.

III. Results and discussion

A practical advantage of using noble gases for permeation experiments is the low background at their respective mass/charge values. This is an advantage because a low background leads to a better signal to noise ratio, and eliminates the need for background pressure correction and therefore permits a more accurate evaluation of the partial pressure as function of time. In the experiments we actually study the transmission of gas through membranes of one particular thickness. When discussing the matter in more general terms we will use gas permeation instead of transmission.

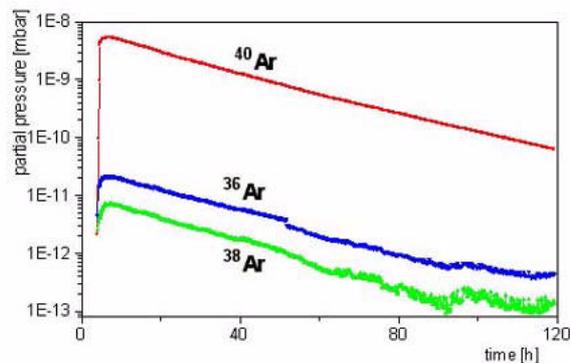


Figure 2: Partial pressure as function of time for permeation of isotopes ^{40}Ar , ^{36}Ar and ^{38}Ar through OPP 20 μm thick.

A. Transmission of helium and neon through OPP and PET

Figure 3 shows the dependence of mass-spectrometric estimated total pressure on time for permeation different noble gases through OPP. For helium and neon the relationship between pressure measured by the mass spectrometer and time is exponential (Eq. 3) and a pressure-independent permeability K can be calculated according to: $K = \lambda l$ with λ as pressure decay constant and l the length of the gas cell taken as a cylinder with cross section the same as the area of the membrane.⁸ For permeation through OPP this concept can be extended to include argon, although there is minor deviation from a single exponential behavior which will be discussed in the following chapter. Figure 4 shows partial pressure vs. time curves for transmission of He, Ne and Ar through PET. Helium and neon clearly show the exponential relationship.

Argon transmission through PET changes very slowly and therefore a quantitative study of gas transmission, which requires the measurement of change of this quantity is practically impossible. For the same reason transmission of Kr and Xe through PET is not amenable to study by this method. Table I compares the transmission coefficients obtained in our experiments with values from the literature. Given the different nature of the methods, the agreement is reasonable. Comparison of polymer samples is in general difficult because it is impossible to get identical samples due to structural fluctuations.

It is important to emphasize that the permeability is obtained from the decay of partial pressure which is a relative quantity and hence does not depend on the initial pressure inside the gas cell. Neither does permeability depend on the presence of other, non-interacting gases as we have shown for the permeation of air through OPP.⁸ This concept is similar to radioactive decay where the decay constant (and half life) does not depend on the amount of the radioactive substance and the presence of other elements.

Table I: Comparison between transmission rates measured by mass spec-

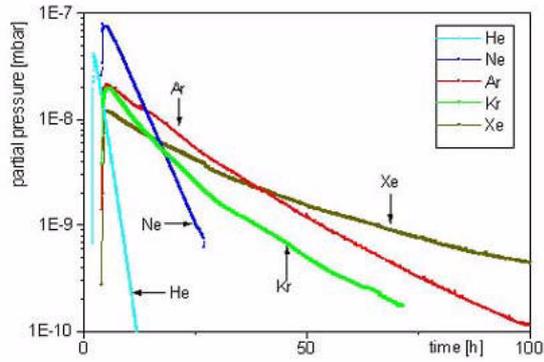


Figure 3: Partial pressure as function of time for He, Ne, Ar, Kr and Xe permeation through OPP 20 μm thick.

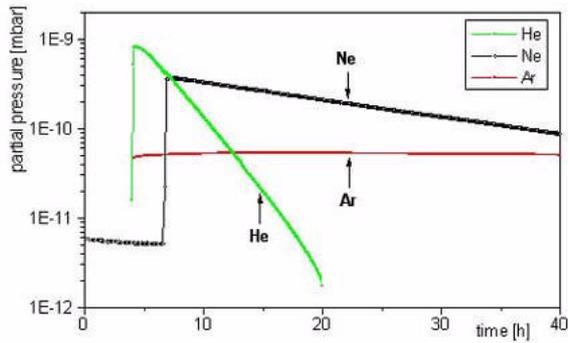


Figure 4: Partial pressure as function of time for He, Ne and Ar permeation through PET 12 μm thick.

trometry (@35±C) and control experiments (chromatographic method) and literature values.

		mass- spectrometry @35±C	control experiment @35±C	lit. ⁶
OPP 20 1m	He	38300	22300	38000 ^a
OPP 20 1m	Ne	13300	6700	-
OPP 20 1m	Ar	4100	2600	-
PET 12 1m	He	22000	7800	7630 ^{aa}
PET 12 1m	Ne	2500	900	-
PET 12 1m	Ar	-	100	-

^a (PP @33±C)

^{aa} (PET @25±C, 40% crystallinity)

B. Transmission of argon, krypton and xenon through OPP

Figure 3 shows the partial pressure vs. time curve for transmission of krypton and xenon through OPP (the partial pressure for the relevant gas is the sum over the partial pressures of the individual isotopes, see table II). The curves shown in ...g. 3 for krypton and xenon (and to a lesser extent argon) do not obey the single exponential relationship found for the lighter noble gases helium and neon⁸ which is in agreement with data of krypton permeability through polypropylene (PP).⁴ It means that for the heavier noble gases permeability is not a constant but rather a pressure dependent function. Permeation is generally considered to be determined by diffusion and sorption. As the bigger mass of heavy noble gases is unlikely to result in faster diffusion we will focus on solubility. Gas may be dissolved in the polymer matrix, for heavier noble gases we will consider the possibility of pore condensation. When gases enter small pores of nm-size, interaction between gas atoms and pore walls become important. This is known as pore condensation and may lead to a lower critical temperature with the critical point shift inversely proportional to the pore width^{15,16}. It has been suggested that a deep molecular potential well is formed where molecules tend to be adsorbed.¹⁷ The adsorption effects are much more pronounced for heavier gases such as krypton and xenon. When xenon is admitted to porous carbon (pore size ~1 nm) an increased proportion of Xe-dimers and Xe-trimers was observed even at sub-atmospheric pressures.¹⁷ For carbon micropores pressures of up to 1000 bar have been reported for Xe.¹⁸ Table II summarizes physical properties of noble gases. Krypton and xenon are more condensable than the lighter noble gases because of their rather high critical temperature.

Table II: Selection of physical properties of noble gases

	He	Ne	Ar	Kr	Xe
isotopes [□] [a.u.] (>0.1%) [■]	4	20,21,22	36,40	78,80,82- [■] 84,86	128- 132,134,136
kinetic diameter ^{□□} [nm] ¹⁹	0.26	0.275	0.34	0.36	0.396
critical temper- ature [K] ²⁰	5.2	44.4	150.8	209.4	289.7
critical pressure [bar] ²⁰	2.3	27.6	48.7	55.0	58.4

□ isotopes with more than 0.1% natural abundance

□□ intermolecular distance of closest approach for two molecules colliding with zero kinetic energy

Polymers such as OPP do not have pores similar to carbon as used in.¹⁸ However, in the "free volume" concept²¹ a similar argument can be applied. Our samples consist of crystalline and amorphous regions. Crystalline regions are believed to be impermeable and not contributing to solubility. In the amorphous regions there is inefficient packing of chains, the excess volume is called "free volume" and can be considered as cavities. The free volume allows conformation changes. This means the size of a single cavity of the free volume is in the range of up to a few interatomic distances. Table II shows that the kinetic diameters of noble gas atoms are of the order of magnitude of the cavities. There are very few atoms required in a cavity to reach the critical pressure. This should be considered as qualitatively as this macroscopic concept cannot be easily transferred to consider few atoms in a cavity. The picture of cavities in polymers is also used in theoretical calculations to model gas diffusion^{22, 23} In some respect, the concept presented here takes advantage of ideas from the dual-mode model developed for permeation through glassy polymers^{24, 25} We note that the experiments were carried out close to the glass transition temperature of OPP which implies relatively slow changes of conformation and hence a longer lifetime of cavities formed.

As long as the gas pressure is sufficiently high we expect condensation of Kr and Xe in cavities of OPP. This can be considered as opening an "additional track" for gas permeation because of the higher amount of gas dissolved in the polymer. The condensation probability depends on the number of molecules entering a cavity per time and hence on the pressure inside the gas cell. As the gas cell is depleted of gas in the course of the experiment the condensation probability decreases and the "additional track" contributes less and less to permeation.

We have stated before that the slope of the partial pressure vs. time curves for gases that do not condense in cavities (He, Ne) does not explicitly depend on the initial pressure inside the gas cell⁸ (the pressure in the gas cell, however, determines the position of the partial pressure vs. time curve with respect to the

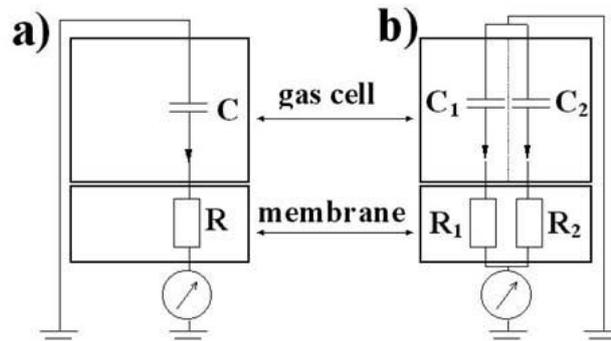


Figure 5: b) normal pathway through C_1 and R_1 and additional track through C_2 and R_2 which includes pore condensation

pressure axis). Components of mixtures permeate independently. This allows us to consider the amount of gas using the "additional track" separately from "normal pathway" (without cavity condensation). Figure 5b shows a "gedanken-experiment" where the gas in the gas cell is divided by the dotted line into a part using the "additional track" through R_2 and a part which permeates in a "normal pathway" through the polymer R_1 . Figure 5b shows the corresponding RC-circuit where the two capacitors C_1 and C_2 correspond to the two gas volumes inside the gas cell and the two resistors R_1 and R_2 correspond to the "normal pathway" and "additional track" permeation pathways. After some time, when the initial response of the circuit is negligible, the total current or total gas permeation takes the form:

$$p(t) = A_1 \exp(j \zeta_1 t) + A_2 \exp(j \zeta_2 t) \quad (1)$$

where p is the partial pressure, t the time and A_1 , A_2 , ζ_1 and ζ_2 are parameters. Figure 6 shows a good agreement between experimental data and the double exponential ...t for krypton and xenon permeation through OPP according to eq. (1). Fit parameters are summarized in table III. Minor deviations of argon from a single exponential behavior (...g. 3) can be explained by a second exponential function according to eq. (1) too. It appears that values ζ_2 given in table III correspond to permeation through the "additional" track.

This shows that a rather simple model can quantitatively account for pressure-dependent permeability. Figure 5a represents the situation where there is no cavity condensation due to a low critical temperature as in the case of He and Ne. The ratio A_1/A_2 (table III) can be taken as measure for the deviation of the curve shape from a single exponential behavior. In the case of light noble gas atoms the probability of gas atoms getting trapped in the cavities is very low, the cavities become "transparent". In this case we obtain a single exponential function with $A_1/A_2=0$ which is in agreement with our observations (see ...gs. 3 and 4). The deviation of argon from single exponential behavior in the partial pressure vs. time curve with an A_1/A_2 ratio of 0.07 is small but signi...cant.

The consideration of cavity condensation as reason for pressure-dependent permeability is supported by previous experimental results. A pronounced pres-

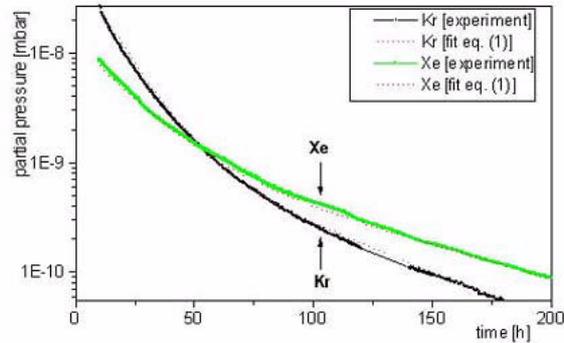


Figure 6: 20 μ m thick and curves fitted according to eq. (1).

sure dependency of permeability for various gases through PP was shown for gases with a high critical temperature, such as Kr, N₂O and CO₂ whereas gases with a low critical temperature (H₂, He, Ne, N₂, O₂, Ar) did not show such a behavior.⁴

Experimental observation points to the fact that the choice of polymer material has influence on the pressure dependence of permeability too. Between PP and LDPE a much less pronounced such dependency was found for LDPE⁴ which has an approximately 100°C lower glass transition temperature T_g . T_g itself does not determine the size of the pores but may indirectly influence the life-time of cavities as in polymers with lower T_g backbone motion is more restricted and a higher life-time can be expected. The exact mechanism of cavity formation is not well understood and other processes such as localized secondary relaxations may play a role.

The tendency of gases with a higher critical temperature to have a higher permeability at increased pressures was observed in silicone rubber²⁶ and polydimethylsiloxane (PDMS).²⁷ On the other hand side, a decreasing permeability through polysulfone was found for CO₂, which has a critical temperature comparable to Xe. Koros and Paul reported linear sorption isotherms for CO₂ in PET²⁴ above the glass transition temperature. These examples show, that for permeant gases other than noble gases permeability is influenced by chemical interaction between polymer and permeant too.

The time constant λ_1 given in table III decrease from He to Xe with the exception of Kr where the value is higher than for argon and xenon. This behavior might be caused by the complex interplay between enhanced sorption for heavier noble gases¹ (they are more condensable, see table II), and slower diffusion.³ These opposite contributions to permeability may be responsible for the high value for λ_1 in krypton. Whether this is indeed the case requires further study to reduce error margins of the experiments. A similar effect, however, has been observed in studies of noble gas permeation through polyethylene where neon showed the lowest permeability among the noble gases.³ Applying the

simple relationship between time constant and transmission rate $K = \lambda l^2$ a time constant λ of 1.9 day^{-1} for krypton at about 1 bar feeding pressure at 35°C corresponds to a gas transmission rate of $4800 \text{ cm}^3_{\text{STP}} = \text{m}^2/\text{day}/\text{bar}$ which is in reasonable agreement with a value of $2090 \text{ cm}^3_{\text{STP}} = \text{m}^2/\text{day}/\text{bar}$ that we have estimated in a control experiment by the pressure increase method under similar conditions. This calculation relies on the assumption of equal pressures inside the gas cell and in the mass spectrometer. In the case of a condensable gas a significant amount of gas is dissolved in the membrane and the permeation rate should be considered as a rough estimate only.

Table III: Fitting parameters for partial pressure vs. time curves for Kr and Xe permeation through OPP 20 μm thick according to eq. (1).

OPP 20 μm	$\lambda_1 [\text{day}^{-1}]$	$\lambda_2 [\text{day}^{-1}]$	$\frac{A_1}{A_2}$
Helium	15.3	-	0
Neon	5.3	-	0
Argon	1.6	0.24	0.007
Krypton	1.9	0.5	0.04
Xenon	1.4	0.35	0.08

Further study will be necessary to disentangle the complex relationship between the nature of the permeating gas, the structure and properties of the polymer, and other experimental conditions to come to a quantitative understanding of processes that determine permeation of a wide range of gases through polymers. The simple model introduced above neglects the case that gas atoms may jump between pathways. One possible way to get an improved model for permeation of heavy noble gases is to assume a pressure dependent activation energy.²⁸

IV. Conclusions

We have investigated the pressure-dependent transmission of noble gases through membranes of OPP and PET with a mass spectrometer. Helium and neon show an exponential decay of partial pressure as function of time for OPP and PET which indicates pressure-independent permeability. In extension to this model we suggest that permeation of heavier noble gases (krypton, xenon and -to a lesser extent- argon) through OPP is strongly influenced by interaction with cavities in the free volume (sorption) of the polymer. In these cases permeability becomes a pressure-dependent quantity. This behavior can be explained quantitatively in analogy with a simple electrical RC-circuit which reproduces the experimental data in good approximation with a sum of two exponential functions. Gas transmission coefficients determined by mass spectrometer show reasonable agreement with those obtained by other methods. Mass spectrometry is very sensitive to small amounts of less abundant isotopes of noble gases.

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