

Vapor and Gas Permeability of Asymmetric Membranes

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Synopsis

The membrane with continuously varying and pressure-dependent local permeability P may show a dependence of transport property for gases and vapors on the direction of flow. Such an asymmetry occurs only if the deviation of local permeability from ideality varies from layer to layer. In mathematical formulation, this means that the local permeability is an irreducible function of location and pressure, i.e., not a product of a function of location and a function of pressure. The membrane permeability is higher if the side with greater deviation from ideal, i.e., constant permeability, is exposed to the higher pressure. For two simple cases the currents in both directions and their ratio at constant pressure difference were calculated. It turns out that the asymmetry of permeability increases with increasing deviation from ideality up to a maximum, after which the membrane tends to return to symmetry. An additional result of this investigation is the conclusion that Fick's law, i.e., the proportionality of the diffusion current to the negative concentration gradient is inapplicable not only to inhomogeneous membranes but also to homogeneous not ideal membranes.

INTRODUCTION

The asymmetric gas and vapor permeability of composite membranes was studied theoretically and experimentally by Rogers, Stannett, and Szwarc.¹ They found that the combination of Ethocell 610 and nylon 6 membranes has a higher permeability for water vapor if the nylon film faces the vapor and the Ethocell film faces the vacuum. The former film has a permeability constant P increasing rapidly with vapor pressure, while the latter film exhibits a nearly constant P . The effect observed is in excellent agreement with their theoretical prediction that a membrane composed of two films, the permeability constant of one increasing rapidly with pressure while the permeability constant of the second increases only slightly (or not at all), will be more permeable if the first film is exposed to the high pressure than if the gradient of pressure is reversed.

The treatment of membranes with continuously variable composition which might show a permeability dependence on the flux direction is suggested by these authors on the basis of flow rate equation

$$j = \alpha(d\mu/dx) \quad (1)$$

where α is a constant throughout the whole membrane and μ is the chemical potential

$$\mu = -RT \log p \quad (2)$$

where p is the pressure of the gas in equilibrium with the particular layer of the membrane. From eqs. (1) and (2) they deduce that p changes linearly through the membrane, falling from the highest value p_0 on one side ($x = 0$) to 0 on the other side ($x = l$) of the membrane. If the solubility of such a membrane varies linearly with the depth x , it may happen that at some stage the gas flows against the gradient of concentration, although not against the gradient of chemical potential.

But they did not calculate the dependence of permeability of such a membrane on the flux direction. Since one can produce membranes with continuously varying composition,^{2,3} it seems worthwhile to investigate the conditions under which such films may exhibit an asymmetric permeability for vapors and gases. In that which follows, the problem will be formulated quite generally and the conclusions checked on two very simple examples.

GENERAL THEORY

In a membrane with continuously varying composition, the sorption S and the diffusion constant D are expected to be continuously varying functions of location x and pressure p of the gas in equilibrium with the particular layer of the membrane. The irreversible thermodynamics yields for the flow of gas the equation

$$j = - (c/f) \text{grad } \mu = -(c/f)(d\mu/dx) \quad (3)$$

where c is the local concentration of gas

$$c = c(x,p) = S(x,p)p \quad (4)$$

and f is the local resistance against the transport of a mole of gas or vapor

$$f = f(x,p) = [RT/D(x,p)]. \quad (5)$$

The coefficient c/f is not a constant but a continuously varying function of x and p . The chemical potential of the ideal gas reads

$$\mu = \mu^0 + RT \ln p \quad (6)$$

where μ^0 is a constant of the gas or vapor. By introducing expressions (4) to (6) in the flow eq. (3), one obtains

$$j = -S \cdot D(dp/dx) = -P(dp/dx) \quad (7)$$

$$P(x,p) = S(x,p) D(x,p). \quad (7a)$$

The solutions of eq (7) satisfying the boundary conditions at $x = 0$ and $x = l$, being $p = p_0$ and $p = 0$ for the flow from left to right (j_+) and $p = 0$ and $p = p_0$ for the flow in the opposite direction (j_-), yield the currents j_+ and j_- , respectively, as functions of applied pressure p_0 .

The solutions are obtained by a straightforward integration if $P(x,p)$ is a product of a function of x and a function of p . One has in such a case

$$i = -P(x,p)(dp/dx) = -f_1(x) \cdot f_2(p)(dp/dx), \tag{8}$$

yielding

$$i \frac{dx}{f_1(x)} = -f_2(p) dp \tag{9}$$

$$j_+ \int_0^l \frac{dx}{f_1(x)} = \int_0^{p_0} f_2(p) dp = -j_- \int_l^0 \frac{dx}{f_1(x)}. \tag{9a}$$

The currents j_+ and j_- are equal. This result agrees with that obtained for the liquid permeability of membranes under a pressure gradient.⁴ The membrane is symmetric if the pressure dependence of permeability, i.e., of the product of sorption and diffusion, is the same throughout the membrane irrespective of the local variation of permeability at zero pressure ($p \rightarrow 0$). In mathematical formulation in such a case, the permeability P is a reducible function of x and p as shown in eq (8).

TWO SPECIAL CASES

In order to demonstrate the possibility of the existence of asymmetric membranes, let us consider two extremely simple cases of irreducible local permeability:

I.
$$P = P_0(1 + \alpha x + \beta p)$$

II.
$$P = P_0(1 + \alpha xp).$$

With positive nonvanishing coefficients α , β , and a , the permeability of the first membrane is more pressure dependent at $x = 0$ than at $x = l$, and the opposite is true for the second membrane. In both cases the permeability at zero pressure is higher at $x = l$ than at $x = 0$. This situation is best demonstrated in Figure 1, where for a fictitious linear decrease or increase

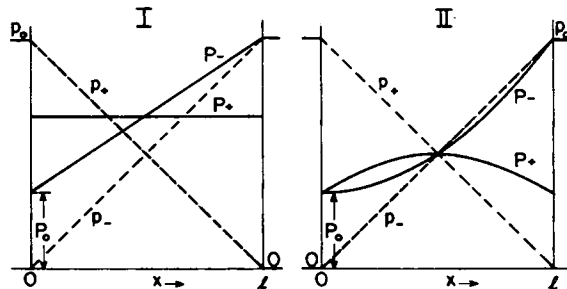


Fig. 1. Local permeabilities $P_+(x,p)$ and $P_-(x,p)$ for cases I and II under the arbitrary assumption that the pressure drops (p_+) or increases (p_-) linearly with x (broken lines).

of pressure through the membrane, the local permeabilities P_+ and P_- are plotted for $al = \beta p_0 = 1$ (I) and $alp_0 = 1$ (II). In the first case the permeability at $z = 0$ is twice as high for $p = p_0(P_+)$ than for $p = 0(P_-)$ while at $x = l$ the ratio of these permeabilities is only $3/2$, P is $3P_0$ for $p = p_0(P_-)$ and $2P_0$ for $p = 0(P_+)$. In the second case, the permeability (P_-) at $x = 0$ is constant, independent of p , and at $x = l$ it is P_0 for $p = 0(P_+)$ and $2P_0$ for $p = p_0(P_-)$. One hence expects a higher gas or vapor permeability of the membrane if in the first case the high pressure is at $x = 0$ ($j_+ > j_-$) and if in the second case it is at $x = l$ ($j_- > j_+$).

The schematic representation of local permeability in Figure 1 permits even a more detailed analysis. Since the pressure gradient is inversely proportional to the permeability, the current is inversely proportional to the average of inverse permeability:

$$j = \frac{p_0}{\int_0^l dx/P(x,p)} \quad (10)$$

That means that the areas with low permeability are more important and affect more the current than those with high permeability. The pressure drop in case I₊ for $al = \beta p_0$ is constant throughout the membrane so that the representation in Figure 1 indeed yields the true local permeability. If the flow is reversed (I₋), most of the pressure drop is concentrated in the low permeability area at low x , thus yielding a current j_- smaller than j_+ . If one changes βp_0 from 0 to ∞ , the ordinates $P_0(1 + \beta p_0)$ at $x = 0$ (I₊) and $P_0(1 + al + \beta p_0)$ at $x = l$ (I₋) are going up from P_0 and $P_0 + al$, respectively, to ∞ , while the other intercepts, P_0 at $x = 0$ (I₋) and $P_0(1 + al)$, at $x = l$ (I₊) remain unchanged. Both straight lines representing the local permeabilities P_+ and P_- for the fictitious case of linear drop or increase of p with x are identical for $\beta p_0 = 0$, have almost the maximum difference at $\beta p_0 = al$, and become increasingly similar with $\beta p_0 \gg al$. One hence expects $j_+ = |j_-|$ at $\beta p_0 = 0$, the maximum difference between them and therefore the maximum dissymmetry $j_+/|j_-|$ close to $\beta p_0 = al$, and a decrease of asymmetry for $\beta p_0 > al$. In the limit of very large $\beta p_0/al$, an almost identical current will flow in both directions, and the membrane will be again symmetric as in the case of vanishing βp_0 .

In case of II₊, the local permeability is slightly larger than in that of II₋ in the first half of the membrane and substantially smaller in the second half. That immediately yields $|j_-| > j_+$ for nonvanishing positive a . As a consequence of the above-mentioned averaging of inverse permeability, however, the extremely high permeability values of II₋ in the second half of the membrane in the case of very large ap_0 may be less important than the low values in the first half. If that is indeed so, one may expect that the asymmetry of the membrane in case II will reach a maximum at a finite ap_0 value and subsequently decrease to a lower limit without ever reaching 1. The membrane is not expected to become symmetric at large ap_0 .

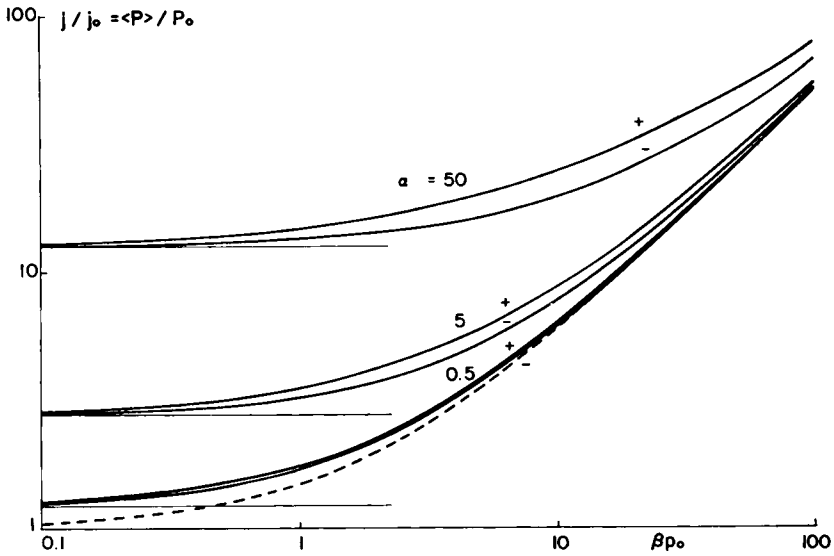


Fig. 2. Relative currents $j/j_0 = \langle P \rangle / P_0 = l/p_0 A$ vs. βp_0 for $\alpha l = 0.5, 5,$ and 50 (case I). Thin horizontal lines represent the relative currents $j_{\beta=0}/j_0 = P_{\beta=0}/P_0 = \alpha l / \ln(1 + \alpha l)$ for the membrane with pressure-independent permeability. Broken line represents the relative current $j_{\alpha=0}/j_0 = P_{\alpha=0}/P_0 = 1 + \beta p_0 / 2$ for the homogeneous nonideal membrane.

Case I. The solution of the flow eq. (7) reads

$$1 + \alpha x = C e^{-\alpha p/A} - \beta p + \frac{\beta A}{\alpha} \tag{11}$$

yielding for the currents j_+ and $|j_-|$ the transcendental equations

$$e^{\alpha p_0/A_+} = 1 + \frac{\alpha l - \beta p_0}{1 + \beta p_0 - \beta A_+/\alpha}$$

$$e^{\alpha p_0/A_-} = 1 + \frac{\alpha l + \beta p_0}{1 + \beta A_-/\alpha} \tag{12}$$

$$A_+ = P_0/j_+$$

$$A_- = P_0/|j_-|.$$

The calculated values of relative permeabilities

$$\langle P \rangle / P_0 = j/j_0 = l/p_0 A \tag{13}$$

are plotted in Figure 2 versus the dimensionless pressure parameter βp_0 for $\alpha l = 0.5, 5,$ and 50 . The thin horizontal lines represent the values

$$P_{\beta=0}/P_0 = \alpha l / \ln(1 + \alpha l) \tag{14}$$

for the limit $\beta = 0$, i.e., the permeability of the membrane in the case of no pressure dependence. In this limit, $\beta p_0 = 0$, the local permeability is

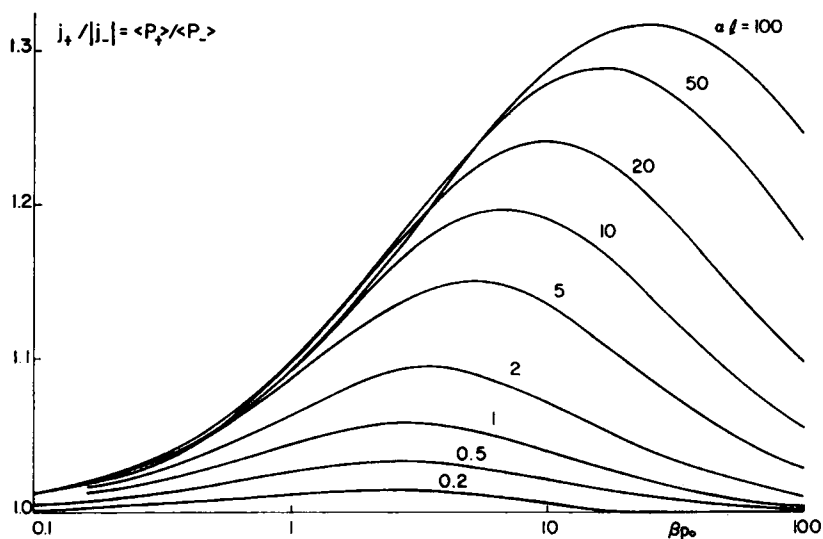


Fig. 3. Asymmetry $j_+ / |j_-| = \langle P_+ \rangle / \langle P_- \rangle$ vs. βp_0 for different values of αl .

independent of p . In spite of inhomogeneity of composition, as measured by αl , the membrane does not exhibit any directionality, $P_+ = P_- = P_{\beta=0}$.

The asymmetry of permeability $P_+ / P_- = j_+ / |j_-|$ is plotted in Figure 3 versus βp_0 with αl as parameter. One notices that the asymmetry of the membrane has the expected sign. But it is small. The membrane is symmetric for $\beta p_0 = 0$, i.e., for a pressure-independent permeability and also for very small pressure. The asymmetry increases with increasing asymmetry of composition (αl) and pressure dependence (βp_0) up to a maximum which, very roughly, is located close to the point where $\alpha l \sim \beta p_0$. The existence of the maximum and the subsequent drop in asymmetry are the consequences of the fact that, with increasing βp_0 , the importance of the term αx in the local permeability is rapidly diminishing. The membrane becomes more symmetric with increasing nonlinearity contribution to the pressure dependence. The limiting permeability for $\alpha l = 0$,

$$P_{\alpha=0} / P_0 = 1 + \beta p_0 / 2, \quad (15)$$

is plotted in Figure 2 as dotted curve. The asymmetry of permeability decreases with increasing βp_0 to the same extent as the permeability curves approach this limiting permeability.

The existence of the maximum in the asymmetry is a consequence of the special choice of permeability dependence on x and p . Since the choice was made more on the grounds of mathematical considerations to have the simplest, i.e., linear, dependence on x and p and not on the basis of any real membrane, one must not conclude that actual membranes will exhibit exactly the properties of case I in the whole pressure range. One can guess that the region between $\beta p_0 = 0$ and the maximum asymmetry may describe pretty well the general trend of membrane directionality while the

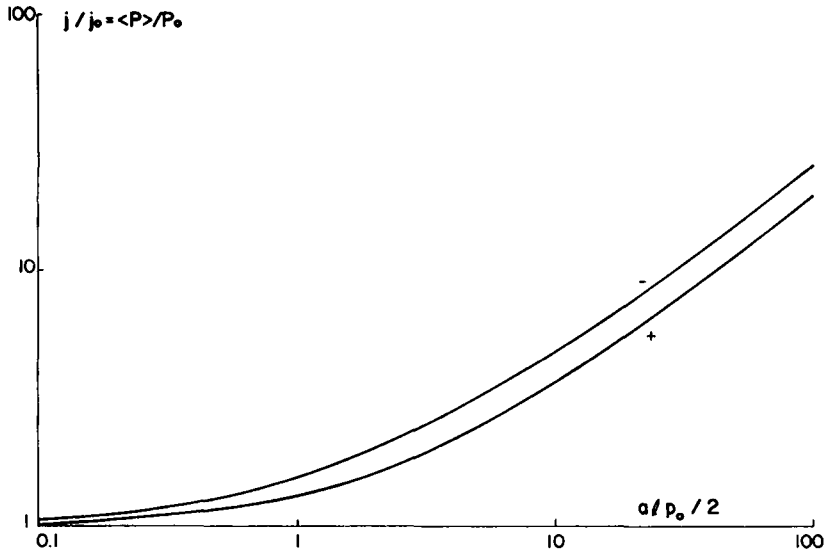


Fig. 4. Relative currents $j/j_0 = \langle P \rangle / P_0 = l / A p_4$ vs. $al p_0 / 2$ (case II).

maximum and the subsequent drop very likely do not represent properties of a true membrane.

Case II. The solution of the flow eq. (7) reads

$$x = \left(C - A \int_0^p e^{Aat^{2/2}} dt \right) e^{-Aap^{2/2}}, \tag{16}$$

yielding for the currents j_+ and $|j_-|$ the equations

$$\begin{aligned} \lambda_+ &= \int_0^{u_+} e^{t^2} dt \\ \lambda_- &= e^{u_-^2} \int_0^{u_-} e^{-t^2} dt \end{aligned} \tag{17}$$

$$\begin{aligned} \lambda_{\pm} &= l(a/2A_{\pm})^{1/2} \\ u_{\pm} &= p_0 (aA_{\pm}/2)^{1/2} \\ A_{\pm} &= P_0/|j_{\pm}|. \end{aligned}$$

The calculated values of relative permeability of the membrane

$$\langle P \rangle / P_0 = j/j_0 = \lambda/u \tag{18}$$

are plotted in Figure 4 versus $al p_0 / 2 = \lambda u$. The current $|j_-|$ turns out to be larger than j_+ . The asymmetry

$$|j_-|/j_+ = \lambda_- u_+ / \lambda_+ u_- \tag{19}$$

is plotted in Figure 5 versus $al p_0 = 2\lambda u$.

With small deviation of permeability from the zero value P_0 , i.e., with small $al p_0$, the currents in opposite directions are nearly equal, and the

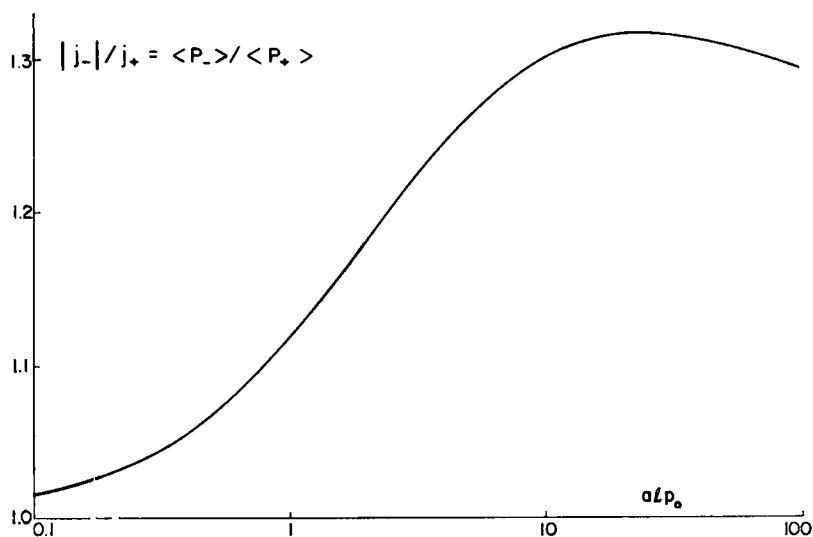


Fig. 5. Asymmetry $|j_-|/j_+ = \langle P_- \rangle / \langle P_+ \rangle$ vs. alp_0 .

membrane asymmetry is small. With increasing alp_0 , the difference between j_+ and $|j_-|$ and the asymmetry $|j_-|/j_+$ are rapidly increasing. The current is larger if the side $x = 0$ with $P = P_0$ faces the vacuum and the pressure is applied to the side $x = l$ with maximum pressure dependence of permeability $P = P_0(1 + alp_0)$ in complete agreement with the experience on the two-layer membrane.

The initial part of the curve $|j_-|/j_+$ is very similar to that for $\alpha l = 100$ of case I as far as the absolute values and the dependence on the deviation from constant local permeability, i.e., βp_0 and alp_0 , are concerned. There is again a maximum in the asymmetry curve, which means that the membrane becomes more symmetric with very large deviation of permeability from the constant zero value P_0 . But the decrease of asymmetry is substantially lower than in case I and does not continue down to 1. The membrane does not become symmetric again at very large ap_0 . One guesses that case II is a better model for a membrane with directionality than case I.

The existence of a maximum in the asymmetry is a little surprising, since in case II the nonlinearity of local permeability is always maximum at $x = l$ and nonexistent at $x = 0$. But a glance at Figure 1 shows that for j_+ there is a local permeability maximum in the interior of the membrane which enhances j_+ and thus reduces the asymmetry. Such a behavior makes case II not very much different from case I as far as the maximum of permeability is concerned. One may speculate that it is germane to all kinds of vectorized gas- and vapor-permeable membranes. But the subsequent drop of asymmetry to 1 seems to be a peculiarity of the case I and not a general property of asymmetric membranes.

CONCLUSIONS

From these two examples one can conclude that a membrane with continuously varying permeability exhibits directionality of the diffusion current if the pressure dependence of the local permeability is an irreducible function of pressure and location, i.e., the relative deviation from ideality $(P - P_{p=0})/P_{p=0}$ is a nonconstant function of location. This dependence of permeability on pressure and location can be caused by a nonideal sorption or diffusion, or by both. The higher permeability results if the side with higher relative deviation from ideality is exposed to the high pressure, i.e., to the gas or vapor, and the more ideal side to the vacuum. The absolute value of the ideal permeability, $P_{p=0}(x)$, i.e., the value at zero pressure, influences the absolute value but not the sign of directionality.

The actual membrane may exhibit a much stronger dependence of permeability on location and pressure than assumed in cases I and II. One can easily include such a dependence by introducing in the models x^n and p^m instead of x and p with n and m larger than 1. Such a substitution would increase the asymmetry. But it has no particular sense to proceed further with such calculations before one has indeed synthesized an asymmetric membrane with known composition and hence with known dependence of P on x and p . The present paper wants only to show under which conditions a membrane can exhibit an asymmetric permeability and how the asymmetry can be calculated from the dependence of permeability on location and pressure.

The asymmetry of membrane permeability for gases and vapors is in many respects similar to that of permeability for liquids under an applied pressure difference. In both cases the dependence of permeability on location and pressure must be an irreducible function of x and p ; that means it must not be expressible as a product of a function of x and a function of p . The membrane permeability is larger if the diffusion current flows from the side with greater relative deviation of local permeability from the ideal, i.e., constant value, to the side with smaller relative deviation. The absolute values of the ideal permeability influence the magnitude but not the sign of directionality.

But there are two important differences between the two cases. The first difference is the role of pressure. In the case of gas permeability, the pressure dependence of local permeability is derived from the sorption dependence on gas pressure and on the diffusion dependence on concentration which in turn, via sorption, can be expressed as a function of gas pressure. In the case of liquid permeability, the pressure dependence arises from the compaction of swollen and hence very compressible membrane under the applied pressure which is about 10 atm. No conspicuous effect of this type is expected in the gas permeation as long as the pressure difference is some small fraction of 1 atm and the membrane is dry, exhibiting very small compressibility. Secondly, the anisotropy of membrane permeability is a steadily increasing function of applied pressure difference in the

case of liquids permeating through the swollen membrane. With gas permeation, however, a maximum of asymmetry is obtained with a subsequent decrease and eventually complete disappearance at sufficiently high applied gas pressure.

One can make an additional conclusion about the theoretical treatment of diffusion through membranes. Equation (3) becomes identical with Fick's law and yields the same eq. (7) if the sorption coefficient S is a constant independent of pressure and location, i.e., for an ideal homogeneous membrane. Because no polymer membrane is truly ideal one must conclude that Fick's law is, strictly speaking, inapplicable for the description of diffusion in such membranes. Even in the case of a homogeneous membrane the diffusion constant D_F derived from permeability on the basis of Fick's law turns out to be

$$D_F = D/(1 + d \ln S / d \ln p) \quad (20)$$

i.e., different from the true diffusion constant D . By good luck in most papers and review articles about gas diffusion through polymer membranes the term dS/dp in derivation of eq. (7) from Fick's law was forgotten as if S were constant in spite of the fact that the authors discussed at length and even included graphs showing the dependence of S on p . This mathematical error apparently saved Fick's law in polymer membrane field. The situation becomes much worse in the case of inhomogeneous membranes where Fick's law yields

$$j = -D(dc/dx) = -D[S(dp/dx) + p(dS/dx)] \quad (21)$$

and consequently a nonvanishing current

$$j_0 = -Dp(dS/dx) \quad (22)$$

even in the case that there is no pressure gradient across the membrane in striking contradiction with experience and thermodynamics.

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