PARTITION AND FRICTION IN MEMBRANES

J. A. M. SMIT

PARTITION AND FRICTION IN MEMBRANES

STELLINGEN

I

Het gedachtenexperiment van Bresler en Wendt bewijst geenszins, dat de reciprociteitsrelatie van Onsager niet toepasbaar zou zijn voor een eenvoudig lineair membraanproces.

E. H. Bresler en R. P. Wendt, J. Phys. Chem. **73** 1969) 264.
J. A. M. Smit en A. J. Staverman, ibidem **74** (1970) 996.

II

Katchalsky en Curran benaderen op een onjuiste wijze het begrip membraanselectiviteit, zoals deze in de reflectiecoëfficiënt van Staverman tot uitdrukking wordt gebracht.

A. Katchalsky en P. F. Curran, „Nonequilibrium Thermodynamics in Biophysics", Harvard University Press, Cambridge, Massachusetts 1967, formule (10-20).

III

Het schema van verschillende transportprocessen door membranen, dat door Lakshminarayanaiah in fig. 1. van zijn overzichtsartikel opgesteld wordt, is onvolledig.

N. Lakshminarayanaiah, Chem. Rev. **65** (1965) 491.

IV

De hoge positieve waarde van de activeringsentropie voor dipoolrelaxatie, welke door Srivastava aan de zuivere vloeistof N,N′-diethyleenaniline wordt toegekend, is niet in overeenstemming met zijn experimentele resultaten.

K. K. Srivastava, J. Phys. Chem. **74** (1970) 152.

V

De lineaire uitzettingscoëfficiënten van een reeks polystyreenkluwens in benzeen bij 20 °C zijn door Tanford onjuist berekend.

C. Tanford, Physical Chemistry of Macromolecules, Wiley and Sons Inc. N.Y. 1967, Tabel (23-6), formule (23-11), formule (9-22).

VI

Tung en Runyon onderschatten de invloed van de zoneverbreding, voorzover die veroorzaakt wordt door menging buiten de kolommen van de gelpermeatiechromatograaf.

L. H. Tung en J. R. Runyon, J. Appl. Polym. Sci. **13** (1969) 2397.

VII

Ekejiuba en Hallam houden bij de toekenning van C-Cl rekvibraties in chloor-*cyclo*pentaan niet voldoende rekening met een mogelijk conformatie-evenwicht in de vaste toestand.

I. O. C. Ekejiuba en H. E. Hallam, Spectrochim. Acta **26A** (1970) 59.
ibidem, **26A** (1970) 67.

VIII

Bij de interpretatie van veldemissiebeelden, zoals die gevonden worden bij de desorptie van koolmonoxyde van een platina tip, maken Lewis en Gomer gebruik van een aanvechtbare veronderstelling.

R. Lewis en R. Gomer, Nuovo Cimento Suppl. **5(2)** (1967) 506.

IX

De conclusie van Spitnik-Elson en Atsmon, dat de aan RNA verbonden eiwitten verschillend zijn van die, welke door NaCl vrijgemaakt zijn, volgt niet uit de door hen gevonden aminozuursamenstelling.

P. Spitnik-Elson en A. Atsmon, J. Mol. Biol. **45** (1969) 113.

X

Een duidelijke leemte in het werk van Dufourcq is, dat het volledig voorbijgaat aan de historisch georiënteerde stroming in de moderne clavecimbelbouw.

Norbert Dufourcq, Le Clavecin, Presses Universitaires de France, Paris, 1967.

J. A. M. Smit
29 april 1970

RECEPTIE NA AFLOOP DER PROMOTIE

IN HET UNIVERSITEITSGEBOUW

RAPENBURG 73, LEIDEN

PARTITION AND FRICTION IN MEMBRANES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKS-UNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS DR. J. GOSLINGS, HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 29 APRIL 1970 TE KLOKKE 15.15 UUR

DOOR

JAN ANTON MARIE SMIT

GEBOREN TE DORDRECHT IN 1935

1970

UITGEVERIJ WALTMAN – DELFT

PROMOTOR: PROF. DR. A. J. STAVERMAN

Aan Margreet

CONTENTS

CHAPTER 1

INTRODUCTION

The main purpose of our investigation has been to arrive at a better insight into the mechanism of permeation across solute-permeable membranes and to inquire into the possibilities of finding adequate quantities for distinguishing between the chemical and geometrical membrane properties. As such it follows the lines of the phenomenological membrane theories based on irreversible thermodynamics, as first developed by Staverman (1951) [37, 38, 39] and later applied and extended by Kedem and Katchalsky [17, 18, 19]. Within the framework of irreversible thermodynamics, or more precisely in the so-called "discontinuous theory", it is possible to describe the permeation process with the aid of a definite number of phenomenological coefficients [13]. The number of coefficients needed is restricted by virtue of the Onsager reciprocal relation. As a result one finds that the behaviour of, for instance, a membrane system where two permeating non-electrolytes are present, can be described by means of three characteristic, and also well-measurable, quantities. They are the filtration coefficient L_P, the reflection coefficient σ of Staverman and the solute permeability ω of Kedem and Katchalsky. Their only drawback is, however, that they actually refer to the system as a whole and not to some species, including the membrane, in particular.

Better characteristic coefficients, at least from a physical point of view, are the "friction coefficients" which describe the friction between two species i and k moving with different velocities. They result from the so-called "continuous theory of transport processes" [2, 7, 25, 32] which we shortly term the friction model. Whatever their merits may be in the field of free diffusion [8, 10], where concentrations can be measured as a continuous function of the distance, in membrane systems they cannot be measured directly because of the difficulty of determining local concentrations within the membrane. Nevertheless, there remains a possibility of coupling the continuous theory to the discontinuous theory, because both cover essentially the same phenomena but only on a different scale. This requires an integration across the membrane under rather idealized assumptions. A number of procedures for this integration have been proposed [4, 18, 21, 22, 40], some of which appear completely impractible. It would appear that the integration involves an important attendant aspect: the partition of the solute between the membrane phase and the external phase. Once the integrated transport equations are found, they can be compared immediately with the corresponding equations of the discontinuous theory. As a result of this confrontation one retains expressions relating the friction coefficients to the experimental quantities, but also involving partition coefficients which must be measured separately. Thus in general the evaluation of the friction coefficients requires additional measurements. Only in the case where two permeating components are present, it is sufficient, as appears later, to measure σ, L_P and ω for different compositions of the system. These are the basic ideas of the whole treatment worked out in the subsequent chapters.

In Chapter 2 we have developed the discontinuous theory, leading in the case of a two-component system to the equation of Staverman relating the apparent to the true osmotic pressure, and also to the well-known phenomenological equations of Kedem and Katchalsky in which the experimental quantities σ, L_P and ω appear. We have extended the theory so that it also covers the cases of a very dilute multicomponent system and the heterodisperse mixture of polymers. For both latter systems we have succeeded in deriving flow equations quite comparable, as far as their form is concerned, with the equations of Kedem and Katchalsky.

Chapter 3 is devoted to the friction model. The two-component system can be described by means of three friction coefficients and a single partition coefficient. The friction coefficients are a measure for the mutual friction between every unequal species present: membrane-solvent, membrane-solute and solute-solvent. The partition coefficient relates the solute concentration within the membrane to the solute concentration outside. The four characteristic quantities concerned can be evaluated from the three experimental quantities σ, L_P and ω when the concentration-dependence of L_P is particularly taken into account. When the partition coefficient deviates from unity, there is an indication that the membrane does not behave chemically indifferently. When, on the other hand, the membrane is chemically inert, information is gained about its geometry by comparing the friction between solute and solvent in free solution to the friction between the same components in the membrane. If, for a given membrane, with regard to a number of different solutes but always to the same solvent, these friction coefficients are equal except for a constant factor, there is a strong indication that only geometrical effects are involved, and that a purely geometrical character must be ascribed to this constant, like the porosity and the tortuosity of the membrane. Finally we introduce in this chapter two indicative quantities enabling us to make a clearer distinction between the "pore model" and the "solution model". They are the partition coefficient and the geometrical constant mentioned above.

In Chapter 4 we enter into more practical details. The systems used were: Vycor glass as membrane, water as solvent and penta-erythritol, mannitol, sucrose and raffinose as successive solutes. The practical measurements centred around the determination of σ, L_P and ω. In order to obtain a consistent set of experimental data it is advantageous to gather information as much as possible from a single experiment, or from several experiments in which the system is not subjected to external conditions which differ too greatly from each other. However it may be, the experimental confirmation of the Onsager reciprocal relations may be regarded as a proof of the reliability of the experimental procedure.

In Chapter 5 we have presented the results. In particular the description in terms of the friction model reveals differences in the behaviour of the systems concerned, which would have remained unnoticed in the conventional description in terms of σ, L_P and ω. Conclusions about the results of the whole work are once again summarized in Chapter 5 § 4.

CHAPTER 2

THE DISCONTINUOUS THEORY

§ 1. *The Phenomenological Equations*

Osmotic experiments are generally visualized as involving a membrane, separating two solutions, having the same solvent and solutes, which may however differ in concentration. In many cases the osmotic membrane shows a measurable permeability to the solutes as well as to the solvent and consequently flow coupling appears as an important phenomenon in membrane theory. More than many model theories, irreversible thermodynamics has proved to be a very useful approach to transport processes across membranes, because of its very general character as a phenomenological theory, which also fully accounts for possible cross or coupling effects. Within the framework of irreversible thermodynamics the isothermal transport process of matter across the membrane is commonly described by means of flow equations in which the particle fluxes appear as linear functions of the differences of generalized chemical potentials between the outer bulk phases. The equations considered here, which are designated hereafter as "phenomenological equations" cover only the stationary cases, close to equilibrium, where in any case linearity is supposed to be present. Though nothing is known from thermodynamics about the range in which this linearity prevails, it appears in practice to be rather wide. In the case of isothermally permeating non-electrolytes, the phenomenological equations take their usual form [37, 38]:

$$J_i = \sum_{k=0}^{n} L_{ik}(\Delta\mu_k + v_k \Delta P), \qquad (i = 0, 1, 2, \ldots, n) \tag{2-1}$$

with J_i the number of moles of component i passing the membrane per unit time, $\Delta\mu_k$ the concentration-dependent part of the chemical potential difference of species k, v_k the partial molar volume of component k and ΔP the pressure difference between the outer phases. The subscript 0 refers to the solvent, while the other indices indicate the various solutes present. The permeability coefficients L_{ik} relate the independent "fluxes" (J_i) to the independent "forces" ($\Delta\mu_k + v_k \Delta P$) and obey the Onsager Reciprocal Relations (ORR) [30, 31]:

$$L_{ik} = L_{ki}. \qquad (i \neq k) \tag{2-2}$$

The equations (2-1), given in the permeability form, may be brought just as well into the reciprocal form:

$$\Delta\mu_i + v_i \Delta P = \sum_{k=0}^{n} R_{ik} J_k, \qquad (i = 0, 1, 2, \ldots, n) \tag{2-3}$$

with the resistance coefficients satisfying the ORR:

$$R_{ik} = R_{ki}. \qquad (i \neq k) \tag{2-4}$$

Thus the L_{ik} and the R_{ik} form reciprocal symmetrical matrices. The diagonal elements stand for the straight effects, whereas the off-diagonal elements represent the cross effects. The "fluxes" and "forces", which are connected by the straight coefficients L_{ii} or R_{ii}, are referred to as being conjugated to each other. The sum of their products divided by the absolute temperature T represents the entropy sources strength or entropy production inside the system σ_t, and can be formulated as

$$T\sigma_t = \sum_{i=0}^{n} J_i(\Delta\mu_i + v_i\Delta P). \tag{2-5}$$

The equations (2-1) to (2-5) are the basic relations for the isothermal permeation of non-electrolytes across membranes and have been treated thoroughly by De Groot and Mazur [13] and recently by Katchalsky and Curran [16] in their textbooks.

The permeability coefficients L_{ik} as well as the resistance coefficients R_{ik} may be regarded as describing completely the behaviour of a given membrane system with a definite composition. Dealing with a $(n+1)$-component system we need not know $(n+1)^2$ L_{ik} coefficients, but only a reduced number of $\frac{1}{2}(n+1)(n+2)$ as a consequence of the ORR. Another attractive feature of the discontinuous theory is that neither specific knowledge of the interior of the membrane is required, nor has any model to be adopted in order to evaluate the L_{ik} or R_{ik}. As will be obvious later (Chapter 3), our investigation centers around the so-called friction coefficients, because of their physical interest. Therefore the R_{ik} matrix, having simple relationships with this coefficients, warrants more consideration in our treatment than the L_{ik} matrix. Now the resistance coefficients, as such, are not directly measurable, so we have to express them in experimental quantities. In this connection we have made it the purpose of this chapter to select the experimental quantities in such a way that they are easily measurable, further, that they may be generalized from a two-component to a multi-component system and finally, that they can reasonably be expected to be almost independent of concentration, at least in dilute solution. Moreover we shall derive flow equations containing only these experimental quantities, and thus more appropriate to practical use than the phenomenological equations. Starting from different formulations for the entropy production (§ 2) we shall deal first with the familiar two-component system (§ 3) and pass then to the more complicated multi-component system (§ 4). The possibilities and limits of the discontinuous theory are discussed for the various cases. Obviously we shall often revert to the basic work done in this field by Staverman [37, 38] and Kedem and Katchalsky [17].

§ 2. *The Proper Choice of "Fluxes" and "Forces"*

The choice of conjugated "fluxes" and "forces" is in some degree arbitrary. Indeed

new sets of independent fluxes and thermodynamic forces may be derived from the old sets, provided that it leaves the entropy production invariant with respect to its magnitude and dimension. Hence it seems to be wortwhile to examine the possible ways in which the entropy production can be formulated and to find out the very combinations of fluxes and forces which are most ideal from a practical point of view. Now the actually measured forces are the hydrostatic and the osmotic pressure. Therefore it is convenient to put the thermodynamic forces in the entropy production into pressure units, say dyne/cm^2 and, since the product $T\sigma_t$ stands in ergs/sec, the units of the fluxes turn out to be cm^3/sec. In other words, volume flows are conjugated to pressures, where the dimension is concerned.

In order to work this out further, we first rewrite (2-5) in the following manner:

$$T\sigma_t = J_0\Delta\mu_0 + \sum_{i=1}^{n} J_i\Delta\mu_i + J_v\Delta P, \tag{2-6}$$

with the volume flow defined as

$$J_v = \sum_{i=0}^{n} J_i v_i. \tag{2-7}$$

For vanishingly small $\Delta\mu$'s we shall be allowed to apply the Gibbs-Duhem relation:

$$\sum_{i=0}^{n} \bar{c}_i\Delta\mu_i = 0. \tag{2-8}$$

Now we want to generalize (2-8), by definition, to all those cases where finite $\Delta\mu$'s occur, indicating with the bar over the concentration c_i an averaging process over both concentrations of species i, present in the phases outside the membrane (for more details see Appendix I). Moreover we introduce the average volume fraction of component i, $\bar{\varphi}_i = \bar{c}_i v_i$, satisfying the familiar expression:

$$\sum_{i=0}^{n} \bar{c}_i v_i = 1. \tag{2-9}$$

Among the many possibilities for formulating the entropy production we will consider in particular two ways which we believe to be of interest. The first formulation is directly found by elimination of $\Delta\mu_0$ from (2-8) and (2-6), yielding

$$T\sigma_t = \sum_{i=1}^{n} \left(J_i - \frac{\bar{c}_i}{\bar{c}_0} J_0 \right) \Delta\mu_i + J_v\Delta P. \tag{2-10}$$

The second formulation, though less conspicious, is found along the following lines of reasoning. Elimination of $\bar{c}_0$ from (2-8) and (2-9) leads on the one hand to

$$\Delta\mu_0 = -v_0 \sum_{i=1}^{n} \bar{c}_i \left(\Delta\mu_i - \frac{v_i}{v_0} \Delta\mu_0 \right). \tag{2-11}$$

On the other hand, solving (2-7) for J_0, gives

$$J_0 = \frac{J_v}{v_0} - \sum_{i=1}^{n} \frac{v_i}{v_0} J_i. \tag{2-12}$$

Finally, insertion of (2-11) and (2-12) into (2-6) yields

$$T\sigma_t = \sum_{i=1}^{n} (J_i - \bar{c}_i J_v) \left(\Delta\mu_i - \frac{v_i}{v_0} \Delta\mu_0 \right) + J_v \Delta P. \tag{2-13}$$

Equations (2-10) and (2-13) are two different ways of writing the entropy production in terms of independent fluxes and independent thermodynamic forces. It is immediately seen from these equations that the new fluxes form linear combinations of the old fluxes, found in (2-5). Further, it is easy to show that the same is true for the new forces with respect to the old forces in (2-5). Now with regard to such linear transformations which are subjected to the condition of an invariant entropy production, Meixner [26] has pointed out that the ORR remain valid for the new phenomenological coefficients in the linear relationships between the new fluxes and forces. This statement enables us to apply henceforth the ORR without restrictions. It does not alter the fact, if we once more multiply a flux with a definite factor and divide the conjugated force by the same factor in order to get the quantities in the right dimensions. Hence we introduce the useful definitions:

$$(J_D)_i = \left(\frac{\bar{\varphi}_0}{\bar{c}_i} J_i - J_0 v_0 \right), \qquad (i = 1, 2, \ldots, n) \tag{2-14}$$

$$(\Delta\Pi_D)_i = \frac{\bar{c}_i}{\bar{\varphi}_0} \Delta\mu_i, \qquad (i = 1, 2, \ldots, n) \tag{2-15}$$

$$(J_C)_i = \left(\frac{J_i}{\bar{c}_i} - J_v \right), \qquad (i = 1, 2, \ldots, n) \tag{2-16}$$

$$(\Delta\Pi_C)_i = \bar{c}_i \left(\Delta\mu_i - \frac{v_i}{v_0} \Delta\mu_0 \right), \qquad (i = 1, 2, \ldots, n) \tag{2-17}$$

and bring (2-10) and (2-13) into the desired final form, reading respectively:

$$T\sigma_t = \sum_{i=1}^{n} (J_D)_i (\Delta\Pi_D)_i + J_v \Delta P \tag{2-18}$$

and

$$T\sigma_t = \sum_{i=1}^{n} (J_C)_i (\Delta\Pi_C)_i + J_v \Delta P. \tag{2-19}$$

Though at this point it will not yet be apparent why we have made a proper choice of fluxes and forces, we can even now make some statements about the character of these quantities. The total volume flow J_v actually represents the volume of bulk liquid which is transported per unit time and is, like its conjugated force, the hydrostatic pressure ΔP, a good measurable quantity. The flux $(J_D)_i$ is a measure of the flow of solute i relative to the solvent motion, whereas $(J_C)_i$ stands for the same, but relative to the bulk motion. Concerning the forces $(\Delta\Pi_D)_i$ and $(\Delta\Pi_C)_i$, we state that both, after summing them over all solutes, yield $-\Delta\mu_0/v_0$. Recalling the familiar expression of thermodynamics for the osmotic pressure difference

$$\Delta\Pi = -\frac{\Delta\mu_0}{v_0}, \tag{2-20}$$

we see that $(\Delta\Pi_D)_i$ and $(\Delta\Pi_C)_i$ actually represent those fractions of $\Delta\Pi$, which as conjugated forces of the diffusional flows mentioned above refer to solute i. We shall in any case be obliged in the following to find the relation of these forces to the osmotic pressure difference $\Delta\Pi$ in order to obtain meaningful equations.

§ 3. *The Two-component System*

The theory outlined in § 2, becomes considerably more simple if it is applied to a system with a single solute. Putting $n = 1$ into (2-7), (2-14) and (2-16), we arrive at the identity $(J_D)_1 \equiv (J_C)_1$. Analogously, it follows from (2-8), (2-15), (2-17) and (2-20) that $(\Delta\Pi_D)_1 = (\Delta\Pi_C)_1 = \Delta\Pi$. Dealing with a single solute we are allowed to drop the parentheses and the index 1 as a lumber of notation. Then, according to (2-19), the entropy production must satisfy

$$T\sigma_t = J_C\Delta\Pi + J_v\Delta P. \tag{2-21}$$

In the linear approximation the fluxes and forces are related to each other by

$$J_C = L_C\Delta\Pi + L_{CP}\Delta P, \tag{2-22}$$

$$J_v = L_P\Delta P + L_{PC}\Delta\Pi. \tag{2-23}$$

The ORR reads in this notation

$$L_{PC} = L_{CP}. \tag{2-24}$$

Let us first examine the sign of the phenomenological coefficients, appearing in (2-22) and (2-23). Insertion of (2-22) and (2-23) into the expression for the entropy production (2-21) gives

$$T\sigma_t = L_C\Delta\Pi^2 + (L_{CP} + L_{PC})\Delta P\Delta\Pi + L_P\Delta P^2 > 0. \tag{2-25}$$

The fact, that the entropy production is positive definite, causes the right-hand side of (2-25) to be positive, whatever the value of $\Delta\Pi$ or ΔP may be. So, by taking these quantities respectively equal to zero, we conclude that L_P and L_C are positive. This result enables us to state that

$$(\sqrt{L_P}\Delta P + \sqrt{L_C}\Delta\Pi)^2 > 0. \tag{2-26}$$

With the help of (2-26) and (2-25), it can be shown that a positive definite entropy production requires still another condition, which becomes

$$L_P L_C - \tfrac{1}{4}(L_{PC} + L_{CP})^2 \geqslant 0. \tag{2-27}$$

By virtue of the ORR the inequality (2-27) is reduced to

$$L_P L_C - L_{CP}^2 \geqslant 0. \tag{2-28}$$

By considering (2-28), it is obvious that L_{CP} may be negative, positive or zero.

We now call attention to the question of which measurable quantities fit best in the theory developed hitherto. In fact we can distinguish two different permeation experiments, differing in the external conditions imposed on the system. A permeation experiment characterized by a constant hydrostatic pressure difference with $\Delta\Pi = 0$ is well-known as ultrafiltration. Another experimental situation is found in the so-called osmotic experiment, showing the characteristics of a fixed $\Delta\Pi$ ($\neq 0$) with an additional condition $\Delta P = 0$ or $J_v = 0$.

In general, ultrafiltration causes an observable separation of solute molecules from the solvent molecules, because the former are more "reflected" from the membrane than the latter. Thus the solute flow lags behind the bulk motion, as can be expressed by the inequality $J_1 < \bar{c}_1 J_v$. This effect can be formulated with more refinement, as has been done by Staverman [37], who has introduced the reflection coefficient σ, which accounts for the selectivity of the membrane. It is defined as

$$\sigma = \left(1 - \frac{J_1}{\bar{c}_1 J_v}\right)_{\Delta\Pi=0} = -\left(\frac{J_C}{J_v}\right)_{\Delta\Pi=0}. \tag{2-29}$$

Its significance is clarified as follows. If $J_1/\bar{c}_1 = 0$, all the solute is reflected and $\sigma = 1$ according to (2-29). In fact this occurs, when the membrane is semi-permeable. However, if $J_1 = \bar{c}_1 J_v$, solute and solvent are reflected to the same degree, which means, that $\sigma = 0$. In that case the membrane shows no selectivity at all and is completely permeable. In all intermediate cases the solute is more reflected than the solvent, corresponding to $0 < \sigma < 1$ and the membrane is to a certain extent permeable for the solute. An interesting case arises, when $J_1 > \bar{c}_1 J_v$ or σ becomes negative. Indeed negative values of σ have been observed by Talen and Staverman [43]. The following

explanation can be given for this phenomenon. In dilute solution the ratio $(J_1 v_1)/J_v$, being actually the transport number of the solute, reduces to

$$\frac{J_1 v_1}{J_v} = \frac{\varphi_1^* u_1}{\varphi_0^* u_0}, \tag{2-30}$$

where φ_1^* and φ_0^* stand for average volume fractions inside the membrane and u_1 and u_0 are the corresponding velocities. The internal concentrations may be related to those outside the membrane by the partition coefficient χ according to

$$\frac{\varphi_1^*}{\varphi_0^*} = \chi \frac{\bar{\varphi}_1}{\bar{\varphi}_0}. \tag{2-31}$$

Introducing respectively (2-30) and (2-31) into (2-29) and using the approximation $\bar{\varphi}_0 = 1$, can be written in terms of velocities, reading

$$\sigma = \left(1 - \chi \frac{u_1}{u_0}\right)_{\Delta\Pi = 0}. \tag{2-32}$$

From (2-32) we conclude that when $\chi \gg 1$ (solute adsorption within the membrane), σ becomes negative. Such phenomena occur clearly in the experiments reported by Talen and Staverman. The catastrophic decrease of the reflection coefficient to negative values suggests that χ increases rapidly in high dilution. Though this is an exceptional case, it may inspire us to take into consideration the influence of the partition coefficient on membrane selectivity, and not to ignore that even small deviations of χ from unity may have a large effect on the reflection coefficient. In fact one might equally well claim that it is precisely the case $\chi = 1$ which is exceptional. If, indeed, $\chi = 1$, we arrive by virtue of (2-32) at the expression for σ, given by Katchalsky and Curran [16]:

$$\sigma = \left(1 - \frac{u_1}{u_0}\right)_{\Delta\Pi = 0}. \tag{2-33}$$

Both equations (2-32) and (2-33) show that the rate of reflection is closely related to the ratio of the velocities of the solute and the solvent and also, as is seen from the former equation, to the partition coefficient.

During an ultrafiltration experiment it is quite possible to follow the bulk motion, induced by a hydrostatic pressure difference. Then the volume of the bulk liquid, transported through the membrane per unit time and pressure i.e. the filtration coefficient L_P can be determined. Its definition is

$$L_P = \left(\frac{J_v}{\Delta P}\right)_{\Delta\Pi = 0}. \tag{2-34}$$

At first sight one would think that membrane selectivity did not emerge clearly in this quantity. However, it will appear later that from the way in which L_P depends on concentration – as indeed it does to a slight extent –, we are informed about the nature and magnitude of the partition coefficient.

Experiments under osmotic conditions furnish even more information about the permeability properties of the membrane than ultrafiltration. Whereas ultrafiltration yields the filtration coefficient L_P and the reflection coefficient σ, an osmotic experiment provides us with three independent experimental quantities, which is just the number required to describe the two-component system completely. In order to hold the system in an at least quasi-stationary state, one will try to keep the concentration difference across the membrane constant as close as possible. Obviously this succeeds better in the osmotic state with $J_v = 0$ than in the state with $\Delta P = 0$. The reason is that the presence of a volume flow does itself lead to an extra change of concentration in the outer bulk phases. Hence it is advantageous to study the state with $J_v = 0$ rather than the state with $\Delta P = 0$. Now the hydrostatic pressure difference, which makes the bulk volume flow vanish, can be considered to counterbalance what we shall call the "apparent osmotic pressure" ΔP^*. This is formulated as

$$\Delta P^* = (\Delta P)_{J_v=0}. \tag{2-35}$$

As opposed to this situation, the volume flow J^*, still remaining when $\Delta P = 0$, will be termed by us the "apparent osmotic flow", obeying the definition

$$J^* = (J_v)_{\Delta P=0}. \tag{2-36}$$

Further, by a "real osmotic flow" is meant the flow J_{osm}, which is equal to $-L_P\Delta\Pi$ and which becomes identical to J^* in the case of a semi-permeable membrane. Finally we follow Kedem and Katchalsky [17] in defining the very useful solute permeability ω according to

$$\omega = \left(\frac{J_1}{\Delta\Pi}\right)_{J_v=0} = \left(\frac{\bar{c}_1 J_C}{\Delta\Pi}\right)_{J_v=0}. \tag{2-37}$$

The filtration coefficient L_P, the reflection coefficient σ, and the solute permeability ω play a major role in our treatment. The applicability of Fick's first law to a solute permeating a membrane implies that ω turns out to be reasonably independent of concentration. From a mechanical point of view the same conclusion may be drawn with respect to L_P. With regard to σ it seems to be plausible to assume a certain independency of concentration, if one considers the solute transport number, $(J_1 v_1)/J_v$ with $\Delta\Pi = 0$, to be proportional to $\bar{\varphi}_1$, as a first approximation. However we stress that we can only guess and hope that it is so. Only practical data will disclose, and perhaps justify, the operational value of these quantities.

So far we have not yet considered the fact, that the ORR give rise to relations amongst distinct experimental quantities. In this connection it is convenient to write the experimental quantities in terms of the phenomenological coefficients appearing in (2-22) and (2-23). Applying the definition of σ, (2-29), to (2-22) and (2-23) we have

$$\sigma = -\frac{L_{CP}}{L_P}. \tag{2-38}$$

In conformity with what is stated about the sign of L_P and L_{CP}, σ can be positive, negative or equal to zero. On the other hand we obtain from (2-35) and (2-23)

$$\Delta P^* = -\frac{L_{PC}}{L_P}\Delta\Pi. \tag{2-39}$$

Now, as was first pointed out by Staverman [37], the effects (2-38) and (2-39) are interconnected by virtue of the ORR (2-24) according to

$$\frac{\Delta P^*}{\Delta\Pi} = \sigma. \tag{2-40}$$

In a quite analogous way, it can be shown that

$$\frac{J^*}{J_{\text{osm}}} = \sigma. \tag{2-41}$$

In (2-40) and (2-41) we meet with an interesting consequence of the ORR, which introduces an entirely new proportion to the whole phenomenology. It means, in fact, that distinct physical quantities, measured in different states, are not unrelated, but are linked together by virtue of the ORR. Thus in this way the reflection coefficient σ, resulting from an ultrafiltration, is related to an apparent osmotic pressure difference ΔP^* or to an apparent osmotic flow J^*, measured under totally different condition, namely an osmotic experiment. It will be obvious upon consideration of (2-40) and (2-41) that here a way is found, however indirect, for determining the osmotic pressure difference $\Delta\Pi$ with a membrane permeable for the solute. For this purpose one has to measure σ in an ultrafiltration on the one hand and on the other hand ΔP^* in an osmotic experiment (2-40). Instead of ΔP^* one might measure also J^* osmotically and σ and L_P by an ultrafiltration, (2-41) leading also to an evaluation of $\Delta\Pi$. Talen and Staverman [42] have taken advantage of this principle to determine the molecular weight of sucrose with a membrane highly permeable for this solute.

Just as the reflection coefficient σ, the solute permeability ω can also be written in terms of the phenomenological coefficients. Applying its definition (2-37) to (2-22), (2-23) and (2-24), we obtain, after some arrangement

$$\omega = \bar{c}_1 \frac{L_P L_C - L_{CP}^2}{L_P}. \tag{2-42}$$

Recalling that L_P must be positive and comparing further (2-42) with (2-28), we conclude that

$$\omega \geqslant 0. \tag{2-43}$$

The sign of equality in (2-43) refers to the case where the membrane is semi-permeable ($\sigma = 1$) and prevents the solute from permeating.

From a practical point of view it is convenient to replace the set L_P, L_{CP} and L_C by the experimental quantities σ, L_P and ω in the flow equations (2-22) and (2-23). The procedure to be followed is: Apply the ORR (2-24) on (2-23) and insert (2-38) into the same equation, yielding

$$J_v = L_P(\Delta P - \sigma \Delta \Pi). \tag{2-44}$$

Further, first eliminate ΔP from (2-22) with the help of (2-23), apply the ORR (2-24) to this result and finally use (2-16), (2-38) and (2-42), which after rearrangement leads to

$$J_1 = \omega \Delta \Pi + \bar{c}_1(1-\sigma)J_v. \tag{2-45}$$

The equations (2-44) and (2-45), first derived by Kedem and Katchalsky [17] are more appropriate than the set (2-22) and (2-23) because of their operational form. Irrespective of their practical convenience, we have other reasons to present them here. First, they can be generalized to multi-component systems, which is the subject of the following section. Secondly, they form good starting points for the derivation of the equations relating the physically interesting resistance coefficients R_{11}, R_{10} and R_{00} to σ, L_P and ω. In order to show this, we solve (2-44) and (2-45) for $\Delta \Pi$ and ΔP, which becomes respectively

$$\Delta \Pi = \left\{\frac{1-(1-\sigma)\bar{\varphi}_1}{\omega v_1}\right\} J_1 v_1 - \left\{\frac{(1-\sigma)\bar{\varphi}_1}{\omega v_1}\right\} J_0 v_0, \tag{2-46}$$

$$\Delta P = \left\{\frac{1}{L_P} + \sigma\frac{1-(1-\sigma)\bar{\varphi}_1}{\omega v_1}\right\} J_1 v_1 + \left\{\frac{1}{L_P} - \frac{\sigma\bar{\varphi}_1(1-\sigma)}{\omega v_1}\right\} J_0 v_0, \tag{2-47}$$

where the total volume flow has been written out in the volume flows of its constituting components in accordance with (2-7) for $n = 1$. The relation of $\Delta \Pi$ to $\Delta \mu_0$ and $\Delta \mu_1$ can be obtained from (2-20) and (2-15), when these equations are applied to the particular case where $n = 1$. Making use of this, we write

$$\Delta \mu_0 + v_0 \Delta P = \left[\frac{1}{L_P} - \frac{(1-\sigma)\{1-(1-\sigma)\bar{\varphi}_1\}}{\omega v_1}\right] v_1 v_0 J_1 + \left[\frac{1}{L_P} + \frac{(1-\sigma)^2\bar{\varphi}_1}{\omega v_1}\right] v_0^2 J_0, \tag{2-48}$$

$$\Delta \mu_1 + v_1 \Delta P = \left[\frac{1}{L_P} + \frac{\{1-(1-\sigma)\bar{\varphi}_1\}^2}{\omega v_1 \bar{\varphi}_1}\right] v_1^2 J_1 + \left[\frac{1}{L_P} - \frac{(1-\sigma)\{1-(1-\sigma)\bar{\varphi}_1\}}{\omega v_1}\right] v_1 v_0 J_0. \tag{2-49}$$

Now the equations (2-48) and (2-49) correspond exactly, as far as their form is concerned, to the set (2-3) with n taken equal to 1. By comparing the two sets we obtain immediately

$$\frac{R_{10}}{v_1 v_0} = \frac{1}{L_P} - \frac{(1-\sigma)\{1-(1-\sigma)\bar{\varphi}_1\}}{\omega v_1}, \tag{2-50}$$

$$\frac{R_{00}}{v_0^2} = \frac{1}{L_P} + \frac{(1-\sigma)^2\bar{\varphi}_1}{\omega v_1}, \tag{2-51}$$

$$\frac{R_{11}}{v_1^2} = \frac{1}{L_P} + \frac{\{1-(1-\sigma)\bar{\varphi}_1\}^2}{\omega v_1 \bar{\varphi}_1}. \tag{2-52}$$

We can already give a prognosis as to how the resistance coefficients will depend on concentration, starting from the assumption, that σ, L_P and ω are almost constant. In the range of small concentrations the factor $\{1-(1-\sigma)\bar{\varphi}_1\}$ will be about 1. It means that in this range R_{10} will be approximately constant, R_{00} will increase and R_{11} will decrease with increasing average concentration.

Let us draw some final conclusions concerning the two-component system.

1. Within the framework of the discontinuous theory it is possible to describe the behaviour of the membrane system as a whole in terms of the measurable quantities σ ($\leqslant 1$), L_P (> 0) and ω ($\geqslant 0$). If only the selective properties of the membrane are of interest, an osmotic experiment ($\Delta\Pi \neq 0$) is sufficient to provide us with these three quantities, but then it is supposed that the osmotic pressure difference $\Delta\Pi$ is known. This can be illustrated with the flow equations (2-44) and (2-45). Assuming a constancy of σ, L_P and ω (which seems completely plausible for a single experiment where only small changes of concentrations are allowed), we expect straight lines, if J_v is plotted versus ΔP in accordance with (2-44). From slope and intercept L_P and σ may be calculated, provided that $\Delta\Pi$ is known. Equation (2-45), under the condition of J_v equal to zero, is the basis for the determination of ω. The experimental verification of (2-44) involves measurements of pressures and volume flows only, the verification of (2-45) involves measurements of changes of composition. We stress that it is recommendable to determine σ, L_P and ω in this way rather than σ and L_P in an ultrafiltration and ω separately in an osmotic experiment. The relatively high pressures applied in ultrafiltration may enhance preferential adsorption or bring the membrane in a state, differing from that prevailing in the osmotic experiment. In fact, dealing with the ORR, we have silently assumed that, though the external conditions are different, the membrane itself will remain in the same state, i.e. its selective properties are not allowed to vary with the external conditions imposed on the system.
2. If the molecular weight of the solute is unknown, or the ORR has to be tested, as well as an osmotic experiment an ultrafiltration must also be performed. The

latter yields only σ and L_P and not ω and does not therefore provide full information about the selectivity of the membrane. Nevertheless, ultrafiltration retains its value as a complementary measurement besides the osmotic measurements. In our opinion every investigation into the selective properties of the membrane has to be preceded by a test of the ORR.

3. The question may rise whether the experimental quantities σ, L_P and ω are the most appropriate quantities to describe membrane behaviour. In any case the use of the permeability coefficients L_{11}, L_{10} and L_{00}, following from first principles of irreversible thermodynamics (2-1), seems less appropriate, since they turn out to be very dependent on concentration [42, 15]. This also holds true to a lesser extent with regard to the resistance coefficients, where at least R_{10} is expected to be constant. Finally, about all these coefficients, at least within the scope of the discontinuous theory, it may be said that they tell us nothing of what actually happens within the membrane. The specific influence of the membrane is not immediately evident from them. With this we have reached the limits of the discontinuous theory, which, indeed simple in the mathematical sense, does not inform us about the essential nature of the permeation process.

§ 4. *The Multi-component System*

Though a system with a single solute is particularly worth examining because of its simplicity, one is often interested in systems in which more permeating solutes are involved. So it is important to know how far the theory developed for two-component systems may be generalized to multi-component systems. Moreover, what is valid for a two-component system, need not necessarily be true for a multi-component system. Hence an analysis in this field, or at least a first approach, seems to be meaningful. In particular we shall focus our treatment on the derivation of flow equations which contain overall quantities and actually represent an extension of the familiar equations of Kedem and Katchalsky viz. (2-44) and (2-45). As such they have not yet been presented. The following two cases will be discussed:

1. The highly dilute multi-component system.
2. A heterodisperse mixture of polymers.

Case 1. Starting from (2-19), we may write quite generally the basic linear relationships according to

$$(J_C)_i = \sum_{k=1}^{n} (L_C)_{ik}(\Delta\Pi_C)_k + (L_{CP})_i \Delta P, \qquad (i = 1, 2, \ldots, n) \tag{2-53}$$

$$J_v = L_P \Delta P + \sum_{k=1}^{n} (L_{PC})_k (\Delta\Pi_C)_k, \tag{2-54}$$

with the ORR:

$$(L_{PC})_i = (L_{CP})_i, \qquad (i = 1, 2 \ldots, n)$$
$$(L_C)_{ik} = (L_C)_{ki}. \qquad (i \neq k = 1, 2 \ldots, n) \tag{2-55}$$

In high dilution the difference between $(J_C)_i$ and $(J_D)_i$ becomes vanishingly small and the same is true for the difference between $(\Delta\Pi_C)_i$ and $(\Delta\Pi_D)_i$. Exactly as in the case of the two-component system, it makes no difference whether we use the "*C*-transformation" or the "*D*-transformation", formulating the flow equations. Here, we restrict ourselves to the set (2-53) to (2-55), which agrees with the set (2-22) to (2-24). On the analogy of (2-38) and (2-42) we define

$$\sigma_i = -\frac{(L_{CP})_i}{L_P}, \qquad (i = 1, 2, \ldots, n) \tag{2-56}$$

and

$$\omega_{ik} = \bar{c}_i \frac{L_P(L_C)_{ik} - (L_{CP})_i(L_{CP})_k}{L_P}. \qquad (i, k = 1, 2, \ldots, n) \tag{2-57}$$

With the use of (2-56) and (2-57) we eliminate the phenomenological coefficients from (2-53) and (2-54) and find with the help of (2-16), after some rearrangement,

$$J_i = \sum_{k=1}^{n} \omega_{ik}(\Delta\Pi_C)_k + \bar{c}_i(1-\sigma_i)J_v \qquad (i = 1, 2, \ldots, n) \tag{2-58}$$

and

$$J_v = L_P\left\{\Delta P - \sum_{k=1}^{n} \sigma_k(\Delta\Pi_C)_k\right\}. \tag{2-59}$$

Instead of (2-58), indicating the number of moles of solute i passing the membrane per unit time, we might equally well have written the number of cm^3 of solute i permeating through the membrane per unit time according to

$$J_i v_i = \sum_{k=1}^{n} \omega'_{ik}(\Delta\Pi_C)_k + \bar{\varphi}_i(1-\sigma_i)J_v, \qquad (i = 1, 2, \ldots, n) \tag{2-60}$$

where we have used the abbreviation

$$\omega'_{ik} = v_i\omega_{ik}. \tag{2-61}$$

As a next step we have to relate $(\Delta\Pi_C)_k$ to the osmotic pressure difference $\Delta\Pi$. Assuming the solution to be highly dilute with respect to each solute and every $\Delta\mu_k$ to be vanishingly small, we obtain from (2-17)

$$(\Delta\Pi_C)_k = \bar{c}_k\Delta\mu_k = RT\Delta c_k = \Delta\Pi_k \tag{2-62}$$

with R the gas constant and T the absolute temperature and the latter sign of equality referring to the definition of the partial osmotic pressure $\Delta\Pi_k$, i.e. the osmotic pressure difference between both compartments separated by the membrane, caused solely by the concentration difference of solute k. Moreover, when we impose on the system the condition that the same distribution of solutes must exist in both outer bulk phases, then $\Delta\Pi_k$ is related to $\Delta\Pi$, as can be shown easily, by

$$\Delta\Pi_k = \frac{\bar{c}_k}{\bar{c}_s}\Delta\Pi, \tag{2-63}$$

where $\bar{c}_s$ denotes the total average solute concentration.

Now the last step we have to make before arriving at the final result, is the introduction of some adequate definitions, which considerably simplify the notation. Therefore we assign by agreement that the overall quantity a_s means

$$a_s = \sum_{k=1}^{n} a_k, \tag{2-64}$$

while the subscript s refers to the whole solute and k to the single solute k. Further a_s may stand in this connection for:

$\bar{c}_s$ = the average concentration of the whole solute in moles per unit volume,
$\bar{\varphi}_s$ = the average volume fraction of the whole solute,
J_s = the flow of the whole permeating solute in moles per unit time,
$(\omega_s)_k$ = the permeability of the whole solute, caused by the partial osmotic pressure $\Delta\Pi_k$, in moles per unit time and pressure,
$(\omega'_s)_k$ = the same quantity as above, but then expressed in cm^3 per unit time and pressure.

Then the "number-average" quantity b_n represents by definition:

$$b_n = \sum_{k=1}^{n} \frac{\bar{c}_k b_k}{\bar{c}_s}, \tag{2-65}$$

standing respectively for:

M_n = the number-average molecular weight of the solutes,
σ_n = the number-average reflection coefficient,
v_n = the number-average molar volume of the solutes,
$(\omega_s)_n$ = the number-average solute permeability in terms of moles per unit time and pressure,
$(\omega'_s)_n$ = the same quantity as above, but here expressed in cm^3 per unit time and pressure.

Finally we introduce the "weight-average" b_w by

$$b_w = \sum_{k=1}^{n} \frac{\bar{\varphi}_k b_k}{\bar{\varphi}_s}, \tag{2-66}$$

being respectively:

σ_w = the weight-average reflection coefficient,
$(\omega_s)_w$ = the weight-average solute permeability in moles per unit time and pressure,
$(\omega_s')_w$ = the weight-average solute permeability in cm^3 per unit time and pressure.

After elimination of $(\Delta\Pi_C)_k$ from the set (2-58) to (2-60) by means of (2-62) and (2-63) and then performing the summation of this set with the help of the definitions given by (2-64) and (2-65), we find in a straight-forward way

$$J_s = (\omega_s)_n \Delta\Pi + \bar{c}_s(1-\sigma_n)J_v, \tag{2-67}$$

$$\sum_{k=1}^{n} J_k v_k = (\omega_s')_n \Delta\Pi + \bar{\varphi}_s(1-\sigma_w)J_v, \tag{2-68}$$

$$J_v = L_P(\Delta P - \sigma_n \Delta\Pi). \tag{2-69}$$

The equations (2-67) to (2-69) show a striking resemblance to the equations (2-44) and (2-45), due to Kedem and Katchalsky, especially with respect to their form. Indeed they account for the "overall behaviour" of the total solute present. Since, however n separate solutes are present within the solute as a whole, a new aspect arises from the occurrence of both number-average and weight-average quantities in this case, contrary to the two-component case in which the solute is uniform. Evidently the fact that $J_s v_n$ does not equal $\sum_{k=1}^{n} J_k v_k$ is the origin of the different averages appearing in (2-67) to (2-69).

It must be said that the set (2-67) to (2-69) only shows its full significance if the relevant transport coefficients are indeed experimentally measurable. Therefore we shall consider how these coefficients must be measured. First we note that L_P can be evaluated by an ultrafiltration in just the same way as already described, for the two-component case. Another quantity following directly from ultrafiltration experiments is the weight-average reflection coefficient σ_w. When we term the inner and outer compartments respectively α and β and take the applied pressure difference ΔP equal to $P^\alpha - P^\beta$, we can express σ_w in terms of the infinitesimally small changes of solute volume fraction φ_s and of the volume V of the bulk liquid in at least one compartment, say the α compartment (the β compartment can always be chosen so large that the change of concentration within it is negligible). As is shown in Appendix II, we may write

$$\sigma_w = \left(1 - \frac{\sum_{k=1}^{n} J_k v_k}{\bar{\varphi}_s J_v} \right)_{\Delta\Pi=0} = -\left(\frac{\mathrm{d} \ln \varphi_s^\alpha}{\mathrm{d} \ln V^\alpha} \right)_{\Delta\Pi=0}. \tag{2-70}$$

Now it is quite possible, if perhaps somewhat difficult, to measure the small variation of φ_s and V under ultrafiltration conditions, yielding thus σ_w according to the last member of (2-70). Analogously (Appendix II) we derive for the number-average reflection coefficient

$$\sigma_n = \left(1 - \frac{J_s}{\bar{c}_s J_v}\right)_{\Delta\Pi=0} = -\left(\frac{\mathrm{d}\ln c_s^{\alpha}}{\mathrm{d}\ln V^{\alpha}}\right)_{\Delta\Pi=0}. \tag{2-71}$$

Since in the concentration c_s^{α} the number of moles of solute is involved, it is obvious that the last member of (2-71) cannot be evaluated from measurement of the total solute volume concentration alone. The conclusion is that σ_n cannot be measured independently by ultrafiltration. The auxiliary measurements required make us rule out ultrafiltration as a technique for the determination of σ_n. The obvious way to get information about this quantity is an osmotic experiment ($\Delta\Pi \neq 0$) in which the chosen hydrostatic pressure difference $(\Delta P)_{J_v=0}$ causes the total volume flow to vanish. Just as in (2-40), σ_n may be found from the ratio of the measured apparent osmotic pressure difference ΔP^* and the true osmotic pressure difference $\Delta\Pi$, which must be known beforehand, by setting $J_v = 0$ in (2-69).

The solute permeabilities $(\omega_s)_n$ and $(\omega_s')_n$ can be measured only in the osmotic state characterized by the external conditions $\Delta\Pi \neq 0$, $J_v = 0$, and may be formulated as (Appendix II)

$$(\omega_s)_n = \left(\frac{J_s}{\Delta\Pi}\right)_{J_v=0} = -\frac{1}{RT}\left(\frac{V^{\alpha}V^{\beta}}{V^{\alpha}+V^{\beta}}\right)\left(\frac{\mathrm{d}\ln\Delta c_s}{\mathrm{d}t}\right)_{J_v=0}, \tag{2-72}$$

$$(\omega_s')_n = \left(\frac{\sum_{k=1}^{n} J_k v_k}{\Delta\Pi}\right)_{J_v=0} = -\frac{v_n}{RT}\left(\frac{V^{\alpha}V^{\beta}}{V^{\alpha}+V^{\beta}}\right)\left(\frac{\mathrm{d}\ln\Delta\varphi_s}{\mathrm{d}t}\right)_{J_v=0}. \tag{2-73}$$

The validity of (2-72) and (2-73) is based on the supposition that the permeation is so slow that the system may be considered to be in a quasi-stationary state. In order to measure the solute permeability, the very slow decay of concentration with time must be followed. Here also it is true that φ_s is more practically accessible than c_s. The solute permeabilities $(\omega_s)_n$ and $(\omega_s')_n$ are expected to be a function of the average solute concentration $\bar{c}_s$ or the average solute volume fraction $\bar{\varphi}_s$ in general. If not, a plot of $\ln\Delta c_s$ versus t or a plot of $\ln\Delta\varphi_s$ versus t will yield a straight line, indicating a constancy of the solute permeability with respect to the solute concentration.

Finally we conclude that in the case of a highly dilute multi-component system information is gained by an ultrafiltration experiment about the large molecules in particular (σ_w), whereas by an osmotic experiment it is about the small molecules

that we obtain information (σ_n). This discrepancy, not present in the case of a one-solute system, leads to the conclusion that what is quite well possible in the case of a one-solute system is not possible in the case of a multi-component system: i.e. the measurement of a molecular weight (M_n) by subjecting the solution to both an ultrafiltration and an osmotic permeation across the membrane.

Case 2. The permeation of a heterodisperse mixture of polymers through a membrane permeable for the solute may hold the attention now, because it is frequently met in practice. The problem of finding a good semi-permeable membrane is hard to solve, when one has to do with broad molecular distributions. Nevertheless, one is obliged to persist, when the number-average molecular weight M_n has to be measured with membrane osmometry. However, when the distribution itself is the subject of investigation, it is precisely a membrane admitting permeation which is suitable for the purpose, since it induces an easier passage for the small molecules than for the large ones, and this consequently has different effects on the number-average and weight-average transport coefficients. The discrepancy between these quantities must be related in some way or other to the width of the molecular weight distribution.

Dealing with a heterodisperse mixture of polymers, we are confronted with two aspects which complicate matters. First, since necessarily the dilution is not infinite, both transformations ('*C*' and '*D*') need not coincide, but can be applied separately. Further, even in high dilution, the interaction between the molecules must be taken into account. Staverman [39] has pointed out that it is possible to relate $\Delta\mu_k$ of each solute k to $\Delta\mu_0$ of the solvent, using the Flory-Huggins theory, provided that the solutions on both sides of the membrane are nearly equal with regard to the total solute concentration $\bar{c}_s$, and quite equal with regard to the solute distribution within the whole solute. His result may be written as

$$\frac{\Delta\mu_k}{\Delta\mu_0} = -\frac{\bar{c}_0}{\bar{c}_s} - \frac{\bar{c}_0}{\bar{c}_s}\left\{\frac{\bar{\varphi}_s\gamma(1-v_k/v_n)}{(\bar{\varphi}_0-\bar{\varphi}_s\gamma)}\right\}, \qquad (k = 1, 2, \ldots, n) \quad (2\text{-}74)$$

where γ is the abbreviation of $\gamma = 1-v_n/v_0(1-2\alpha)$, and α stands for the "interaction constant". Let us restrict ourselves in first instance to the "*C*-transformation", then we can translate (2-74) in our terms with the help of (2-17) and (2-20), reading

$$\frac{(\Delta\Pi_C)_k}{\Delta\Pi} = \bar{\varphi}_k + \bar{\varphi}_0\frac{\bar{c}_k}{\bar{c}_s} + \bar{\varphi}_0\frac{\bar{c}_k}{\bar{c}_s}\left\{\frac{\bar{\varphi}_s\gamma(1-v_k/v_n)}{(\bar{\varphi}_0-\bar{\varphi}_s\gamma)}\right\}. \quad (k = 1, 2, \ldots, n) \quad (2\text{-}75)$$

The equation (2-75) enables us to follow the same procedure with respect to the set (2-58) to (2-60) as has been done in case 1. It starts by eliminating $(\Delta\Pi_C)_k$ from (2-58)–(2-60) by means of (2-75), continues by summing the so obtained equations and arrives finally with the definitions (2-64)–(2-66) at

$$J_s = \left[\bar{\varphi}_s(\omega_s)_w + \bar{\varphi}_0(\omega_s)_n + \frac{\bar{\varphi}_0\bar{\varphi}_s\gamma}{\bar{\varphi}_0 - \bar{\varphi}_s\gamma} \left\{ (\omega_s)_n - (\omega_s)_w \right\} \right] \Delta\Pi + \bar{c}_s(1-\sigma_n)J_v, \tag{2-76}$$

$$\sum_{k=1}^{n} J_k v_k = \left[\bar{\varphi}_s(\omega_s')_w + \bar{\varphi}_0(\omega_s')_n + \frac{\bar{\varphi}_0\bar{\varphi}_s\gamma}{\bar{\varphi}_0 - \bar{\varphi}_s\gamma} \left\{ (\omega_s')_n - (\omega_s')_w \right\} \right] \Delta\Pi + \bar{\varphi}_s(1-\sigma_w)J_v, \tag{2-77}$$

$$J_v = L_P \left[\Delta P - \left\{ \bar{\varphi}_s\sigma_w + \bar{\varphi}_0\sigma_n + \frac{\bar{\varphi}_0\bar{\varphi}_s\gamma}{\bar{\varphi}_0 - \bar{\varphi}_s\gamma}(\sigma_n - \sigma_w) \right\} \Delta\Pi \right]. \tag{2-78}$$

Let us draw some conclusions from the transport equations derived above:

1. In general the small molecules count most in the value of σ_n, whereas it is precisely the large molecules which are important for the value of σ_w. On these grounds one would expect that always $\sigma_n < \sigma_w$. Following the same lines of reasoning, we expect the reverse to be true for the solute permeabilities; thus $(\omega_s)_n > (\omega_s)_w$, and similarly $(\omega_s')_n > (\omega_s')_w$.
2. The quotient of the apparent osmotic pressure and the real osmotic pressure being just the form in braces in (2-78) may be considered to be a sort of overall reflection coefficient depending clearly on the average solute concentration $\bar{c}_s$. Starting from the rather bold assumption that both σ_n and σ_w are independent of concentration, we expect, remembering the inequality $\sigma_n < \sigma_w$, that the overall reflection coefficient will decrease with increasing solute concentration. But even, when σ_n itself decreases with increasing solute concentration, and preliminary measurements seem to confirm this behaviour [14], the same concentration effect on the overall reflection coefficient is found again, and even more strongly still. However it may be, the overall reflection coefficient determined from an osmotic experiment ($\Delta\Pi \neq 0$, and $\Delta P^* = (\Delta P)_{J_v=0}$) becomes equal to σ_n in the limit of very small solute concentration, as follows from (2-78) in accordance with (2-69).
3. The forms in brackets in (2-76) and (2-77) may be understood as overall solute permeabilities. Assuming that the separate solute permeabilities are more or less constant (Fick's law), we expect that by virtue of the relevant inequalities mentioned in conclusion 1 the overall solute permeabilities increase with increasing solute concentration. This effect too, has been observed in preliminary measurements [14].
4. Recalling that σ_w can be determined by ultrafiltration and σ_n by osmotic measurements, we may calculate the quotient σ_w/σ_n providing us with information about the width of the molecular weight distribution. When it is known, or can be determined by calibration, how the reflection coefficient depends on the molecular weight, it must be possible to relate σ_w/σ_n to the familiar M_w/M_n ratio.

In the derivations so far, only the so-called "*C*-transformation" has been used. The same reasoning may be repeated for the "*D*-transformation", but this does not reveal

essentially new aspects, except that in the transport equations quantities appear which are defined in a somewhat different way. Because of the mathematical resemblance with the Kedem and Katchalsky equations we have preferred the "*C*-transformation" to the "*D*-transformation". However, on practical grounds one might decide which transformation yields better constant reflection coefficients and solute permeabilities at higher concentrations.

CHAPTER 3

THE FRICTION MODEL

§ 1. *Introduction*

The discontinuous theory provides us with a very general description of transport processes, irrespective of the membrane model adopted. It does not require any knowledge of what occurs within the membrane, except that the latter is homogeneous. It never involves complicated mathematics, but is always very simple in its formulation. It describes the whole transport process with a minimal number of transport coefficients, for instance, three for a two-component system. However, it must be noted that though the discontinuous theory yields L_p, σ and ω in the case of a two-component system it fails to give an interpretation of these coefficients in terms of the separate contributions of the permeating components and of the membrane. So it cannot explain or indicate what, for instance, is the influence of the membrane on the reflection coefficient and on the solute permeability. Nor can it give a decisive answer as to exactly what the influence of the solute is on the value of σ and ω. Evidently L_p, σ and ω do not refer separately to a special component or to the membrane, but to a complex combination of their contributions. Thus the very general concept of the discontinuous theory, however acceptable in itself, does not permit us to obtain information about the interior details of the membrane and does not reach far enough to penetrate into the mechanism of the transport process.

A promising approach which goes more to the root of the matter is found in the continuous description of transport processes with the aid of friction coefficients, as proposed by Onsager [32], Klemm [22], Laity [25] and Bearman [2]. Contrary to the discontinuous description, this theory covers the phenomena occurring locally within the membrane which is conceived as a separate continuous phase. The friction coefficients are well-defined physical quantities being a measure for the friction between the different species, including the membrane. As far as they refer to permeating components they may be compared with the friction coefficients resulting from free diffusion. In this way something can be predicted about their variation with composition. They have in any case the advantage of always referring to two specific components, what is not the case for the experimental quantities. Since they essentially describe the same phenomena as the experimental quantities, relationships will exist between the two sets. However, it must be noted that the friction coefficients result from a continuous theory and may be compared only with the experimental quantities after integration across the membrane phase of the local transport equations containing them. This step from microscopy to macroscopy is attended by mathematical complications which can be solved only by making some drastic assumptions. As will appear, the confrontation of both descriptions reveals, besides friction, still another aspect: the partition of solute between the membrane phase and the outer

phases. Both friction and partition are the very elements of permeation which do not clearly emerge from the discontinuous description, but which give the friction model a more intrusive character in a physical sense.

It is the object of this chapter to express the friction coefficients in terms of the experimental quantities, and vice versa, for a system consisting of a membrane and a mixture of two non-electrolytic permeants. Some authors [11, 18] have already provided relationships of this type, but never without making rather simplifying and hardly permissible assumptions in their derivations. We claim to have minimized the assumptions in our presentation with respect both to their number and to their significance.

§ 2. *The Differential and Integral Transport Equations*

The model to be discussed here is a homogeneous membrane phase separating two external phases under isothermal conditions. The external phases are kept at constant chemical potential of the solute. Mass transfer may only occur in the x-direction i.e. normal to the membrane. The membrane itself is considered to be composed of a lot of parallel layers normal to the transport direction and the position in space of each layer is indicated by its x-coordinate. The composition in a definite layer is assumed to be constant for all species, including the membrane. The concentrations c_i^* are expressed as the number of moles of species i per unit volume of membrane substance including the pore liquid, while the asterisk always refers to the membrane phase. The index i runs from 0 (solvent) over 1, 2, ..., $m-1$ (permeating solutes) to m (membrane). The average velocity of species i in a definite layer $u_i(x)$ is measured relative to a fixed point in space. If there is a stationary regime the flow densities $j_i\,(=c_i^* u_i)$ are independent of x and time t, in other words, no accumulation or depletion of permeating components may occur within the membrane. Further, under condition of a steady state the net force on a mole of species i in a certain layer will be zero:

$$\sum_{k=0}^{m} X_{ik} = 0, \qquad (i,k = 0, 1, 2, \ldots, m) \tag{3-1}$$

where the net force in (3-1) is considered to be composed of a driving force X_{ii} on a mole i equal to the gradient of the chemical potential in the isothermal case: $-\nabla\mu_i - v_i \nabla P$ and frictional forces on a mole i due to the relative velocity $u_i - u_k$ between the species i and k, termed X_{ik}. Following Klemm [22], we may write for the frictional forces in the linear approximation

$$X_{ik} = -r_{ik} c_k^* (u_i - u_k), \qquad (i,k = 0, 1, 2, \ldots, m) \tag{3-2}$$

by which the friction coefficients are defined. Since in a definite layer the total frictional force exerted by species k on species i must be equal and opposite to the total

force exerted by species i on species k by virtue of the principle of action = reaction:

$$c_i^* X_{ik} + c_k^* X_{ki} = 0, \qquad (i,k = 0,1,2,\ldots,m) \tag{3-3}$$

it follows from (3-2) that

$$r_{ik} = r_{ki}. \qquad (i \neq k = 0,1,2,\ldots,m) \tag{3-4}$$

As a consequence of (3-4) a local equilibrium of forces must exist following directly from (3-1) and (3-2) and reading

$$\sum_{i=0}^{m} c_i^* (\nabla \mu_i + v_i \nabla P) + c_m^* X_{mm} = 0. \qquad (i = 0,1,2,\ldots,m-1) \tag{3-5}$$

The relation (3-5) enables us to express the membrane force X_{mm} in the well-defined thermodynamic forces of the other components. With respect to the m permeants we may rewrite the balance between the thermodynamic and the frictional forces as represented by (3-1) as follows:

$$-\nabla \mu_i - v_i \nabla P + \sum_{k=0}^{m} X_{ik} = 0, \qquad (i = 0,1,2,\ldots,m-1) \tag{3-6}$$

which leads with the help of (3-2) to

$$-\nabla \mu_i - v_i \nabla P = \sum_{k=0}^{m} r_{ik} c_k^* (u_i - u_k), \qquad (i = 0,1,2,\ldots,m-1) \tag{3-7}$$

while X_{mm} is related to the other forces by means of (3-5). The equations (3-7) have already been presented in this form by many authors [2, 3, 22, 25]. Upon inspecting them it becomes clear that by virtue of (3-4) only a set of $\frac{1}{2}m(m+1)$ friction coefficients is required in the continuous description. Recalling that the number of permeating solutes n is equal to $m-1$, the required number of friction coefficients turns out to be $\frac{1}{2}(n+1)(n+2)$, namely exactly the number of resistance coefficients, as we have seen in Chapter 2. Further, we note that the friction coefficients are independent of the frame of reference chosen, i.e. independent of the coordinate system used for measuring the velocities, because neither the gradient of the chemical potential in the left side nor the difference in velocity in the right side of (3-7) depends on the choice of the coordinate system of measurement. Finally, we note that all coefficients of the type r_{ii} drop out of (3-7). Only the dissimilar species moving with different average velocities through a certain layer contributes as a result of their mutual friction to (3-7).

The set (3-7) may be simplified still farther. Since the ill-defined membrane concentration c_m^* always appears in the product $r_{im} c_m^*$, it is convenient to introduce the

abbreviation $f_{im} = r_{im}c_m^*$ into (3-7), being the friction coefficient of component i with the membrane. Furthermore, a membrane fixed in space means that u_m must be taken equal to zero. Finally, using the definition of the flow densities $j_i = c_i^* u_i$, we rewrite (3-7) in the form:

$$-\nabla\mu_i - v_i\nabla P = \frac{\sum_{k=0}^{m-1} r_{ik}c_k^* + f_{im}}{c_i^*} j_i - \sum_{k=0}^{m-1} r_{ik}j_k. \qquad i \neq k \ (i = 0, 1, 2, \ldots, m-1) \quad (3\text{-}8)$$

The equations (3-8) essentially describe the same phenomena as the equations (2-3), on the understanding however, that the former operate locally or on a microscopic level, whereas the latter do so integrally or on a macroscopic level. Direct confrontation of the continuous description with the discontinuous description is only possible after integrating the local equations (3-8). This operation gives rise to many problems and to differing results found by various authors [4, 18, 21, 40].

Before integrating (3-8) with respect to x across the membrane we suppose the following conditions to be fulfilled:

1. No jump may exist in the chemical potential of the solute at the boundaries of the membrane phase with the external phases [21]. It does not imply, however, that the same is true with regard to the solute concentration, or in other words, a partition of solute between the membrane phase and the outer phases is always possible and probable.
2. The flow densities are independent of x and thus constant throughout the membrane under steady-state conditions.

Assuming constant flow densities and continuous chemical potential of the solute we now integrate (3-8) with respect to x across the membrane thickness d, yielding [40]

$$\Delta\mu_i + v_i\Delta P = \frac{d}{A_m}\left\langle \frac{\sum_{k=0}^{m-1} r_{ik}c_k^* + f_{im}}{c_i^*} \right\rangle J_i - \frac{d}{A_m}\sum_{k=0}^{m-1}\langle r_{ik}\rangle J_k,$$

$$i \neq k \ (i = 0, 1, 2, \ldots, m-1) \qquad (3\text{-}9)$$

where we have denoted with the symbol $\langle\ \rangle$ the operation $(1/d)\int_0^d (\ )dx$ and have replaced j_i by J_i/A_m, A_m being the membrane surface. The equations (3-9) are given in the so-called integral form and are obtained by integration of the equations (3-8) appearing in the so-called differential form. The former equations are directly comparable with the set (2-3). In accordance with the fact that $n = m-1$ the relationships between the macroscopic resistance coefficients and the microscopic friction coefficients turn out to be

$$R_{ii} = \frac{d}{A_m}\left\langle \frac{\sum_{k=0}^{n} r_{ik}c_k^* + f_{im}}{c_i^*} \right\rangle, \qquad (i = 0,1,2,\ldots,n) \tag{3-10}$$

$$R_{ik} = -\frac{d}{A_m}\langle r_{ik}\rangle. \qquad i \neq k \ (i = 0,1,2,\ldots,n) \tag{3-11}$$

Some important conclusions may be drawn from (3-10) and (3-11):

1. The relation (3-4) which is based on the principle of action = reaction on a microscopic level implies, in view of (3-11), that $R_{ik} = R_{ki}$. Now this, precisely, is the ORR which is valid under the assumption of microscopic reversibility.
2. Evidently the resistance coefficients R_{ik} $(i \neq k)$ describe merely the friction between components i and components k as opposed to R_{ii} in which also the frictions with the membrane are involved.
3. It is important to know how the friction coefficients can be related to experimentally measurable quantities. In the particular case where only one permeating solute is present $(n = 1)$ the friction coefficient r_{10} accounting for the friction between solute and solvent is directly connected to experimentally measurable quantities. Indeed, by eliminating R_{10} from (3-11) and (2-50) we find

$$\frac{\langle r_{10}\rangle}{v_1 v_0} = \frac{A_m}{d}\left[\frac{(1-\sigma)\{1-(1-\sigma)\bar{\varphi}_1\}}{\omega v_1} - \frac{1}{L_p}\right]. \tag{3-12}$$

   The equation (3-12) shows a very attractive feature: it does not contain c_1^* which is difficult to determine. Even the external average solute volume fraction plays a minor role because mostly $(1-\sigma)\bar{\varphi}_1 \ll 1$. With the help of (3-12) a constancy of r_{10}, if present, is easily checked.
4. From (3-10) it becomes clear that the friction coefficients between the membrane and the other components are not simply determinable from the resistance coefficients. Auxiliary data or assumptions about the partition coefficients characterizing the ratios of the concentrations inside and outside the membrane must be available.

§ 3. *Partition of Solute between the Membrane Phase and the External Phases*

The concentrations appearing in (3-10) refer to values in the membrane and can be related to the external concentrations in the usual way by defining partition coefficients. Here we shall restrict ourselves to a system consisting of a membrane (m), solvent (0) and a single solute (1), and shall introduce a partition coefficient by strictly thermodynamic arguments.

We have already formulated the condition of the continuous chemical potential of

solute across the boundaries of the membrane phase with the external phases. When, under ordinary experimental conditions, the volume flow J_v is small, it can be shown (Appendix III) that the main part of the chemical potential is formed by μ_1 the concentration-dependent part of the chemical potential. So ignoring the influence of the pressure-dependent part of the chemical potential of solute, the condition of continuity is written

$$\mu_1^{\alpha} = \mu_1^{*\alpha}, \tag{3-13}$$

$$\mu_1^{\beta} = \mu_1^{*\beta}, \tag{3-14}$$

where μ_1^{α} is the concentration-dependent part of the chemical potential of the solute in the well-stirred α compartment, and $\mu_1^{*\alpha}$ is the corresponding quantity in the adjacent boundary layer within the membrane. μ_1^{β} and $\mu_1^{*\beta}$ have an analogous meaning but with respect to the β compartment and the β boundary. The chemical potential μ_1^{α} is given by the familiar expression:

$$\mu_1^{\alpha} = \mu_1^0 + RT \ln f_1^{\alpha} c_1^{\alpha}, \tag{3-15}$$

where the superscript 0 denotes the relevant value in the standard state, f_1^{α} represents the activity coefficient referring to the volume concentration, and RT has its usual meaning. With regard to the internal phase we want to express the concentrations in moles per unit volume including the membrane substance. Doing so we have quite analogously

$$\mu_1^{*\alpha} = \mu_1^{*0} + RT \ln f_1^{*\alpha} c_1^{*} (1-\varphi_m^{*})^{-1}, \tag{3-16}$$

with φ_m^{*} the volume fraction of the membrane substance and $(1-\varphi_m^{*})$ thus consequently the volume fraction of the pore liquid. By putting (3-16) equal to (3-15) in accordance with (3-13) we find, after some rearrangements,

$$\frac{c_1^{*\alpha}}{c_1^{\alpha}} = (1-\varphi_m^{*}) \frac{f_1^{\alpha}}{f_1^{*\alpha}} \exp \frac{\mu_1^0 - \mu_1^{*0}}{RT}. \tag{3-17}$$

Following the same lines of reasoning we obtain also

$$\frac{c_1^{*\beta}}{c_1^{\beta}} = (1-\varphi_m^{*}) \frac{f_1^{\beta}}{f_1^{*\beta}} \exp \frac{\mu_1^0 - \mu_1^{*0}}{RT}. \tag{3-18}$$

When the external concentration difference $c_1^{\alpha} - c_1^{\beta}$ is not too large we take approximately

$$\frac{f_1^{\alpha}}{f_1^{*\alpha}} = \frac{f_1^{\beta}}{f_1^{*\beta}}. \tag{3-19}$$

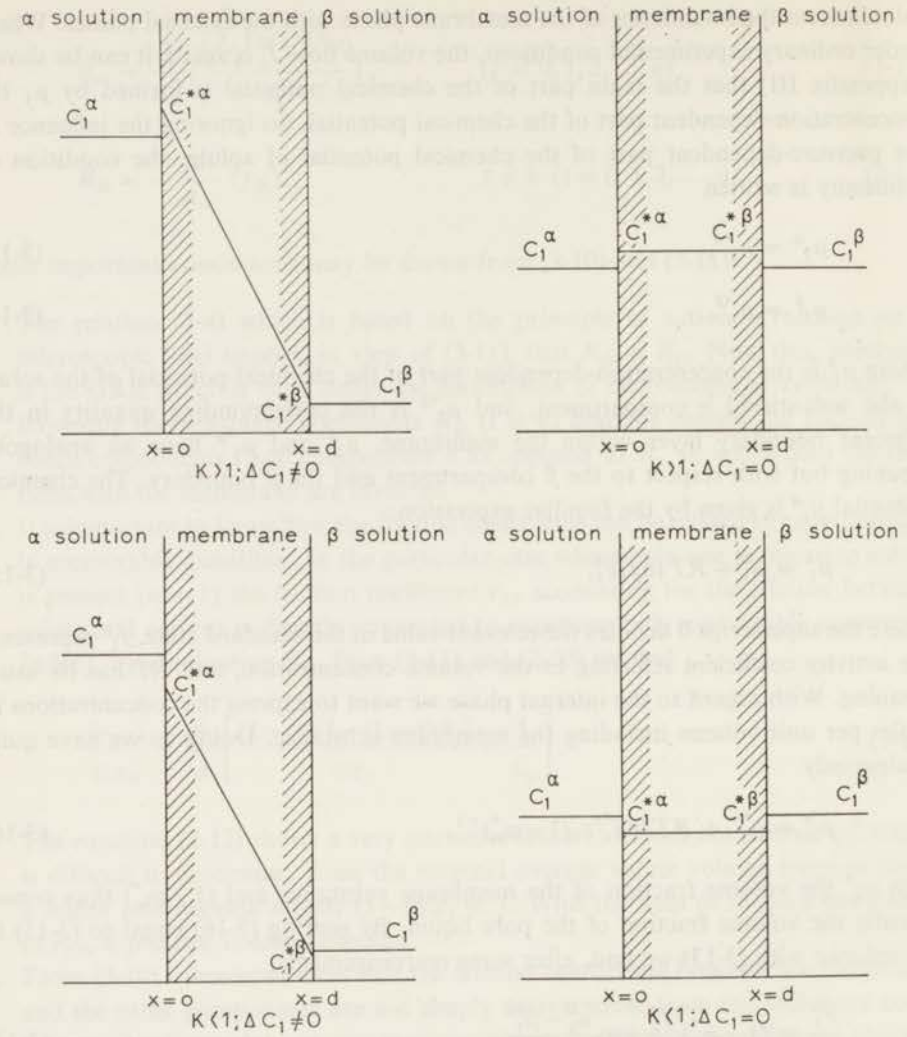

Fig. 3.1. Illustration of linear concentration profiles in the membrane for different internal and external conditions. There is a jump in the concentration at the boundaries when $K \neq 1$.

With this assumption (3-19) we are able to define a single partition coefficient K according to

$$K = \frac{f_1^{\alpha}}{f_1^{*\alpha}} \exp \frac{\mu_1^0 - \mu_1^{*0}}{RT} = \frac{f_1^{\beta}}{f_1^{*\beta}} \exp \frac{\mu_1^0 - \mu_1^{*0}}{RT}, \tag{3-20}$$

which with the help of (3-17) and (3-18) is simplified to

$$\frac{c_1^{*\alpha}}{c_1^{\alpha}} = \frac{c_1^{*\beta}}{c_1^{\beta}} = (1-\varphi_m^*)K. \tag{3-21}$$

Thus the concentrations in the boundary layers within the membrane are related to the external concentrations via the partition coefficient K. The first indication about the chemical interaction between the membrane and a permeant is given by the value of K. If $K > 1$ the membrane attracts the solute preferentially, if $K < 1$ it attracts the solvent with preference, and finally if $K = 1$ one may call the membrane chemically indifferent or inert, indicating that it does not show any preferential adsorption of some permeant.

Now from an operational point of view, it seems more convenient to work with an average concentration in the membrane $\langle c_1^* \rangle$, instead of with the boundary concentrations $c_1^{*\alpha}$ and $c_1^{*\beta}$. The former is in any case more easily measurable than the latter. However, $\langle c_1^* \rangle$ cannot be calculated without making an assumption about the concentration profile within the membrane. Let us suppose as a first approximation that the solute concentration is a linear function of the transport direction x. This is shown schematically for different internal and external conditions in Fig. 3.1. Then we may write

$$c_1^*(x) = \frac{c_1^{*\beta} - c_1^{*\alpha}}{d} x + c_1^{*\alpha} \tag{3-22}$$

Integrating both sides of (3-22) across the membrane thickness and dividing the result by d, we find for the average solute concentration in the membrane

$$\langle c_1^* \rangle = \tfrac{1}{2}(c_1^{*\alpha} + c_1^{*\beta}). \tag{3-23}$$

On the other hand, it can be shown from (3-22) that

$$\langle c_1^{*-1} \rangle = \frac{1}{(c_1^{*\alpha} - c_1^{*\beta})} \ln\left(\frac{c_1^{*\alpha}}{c_1^{*\beta}}\right). \tag{3-24}$$

Now it is worth comparing the results embodied in (3-23) and (3-24) with the expression found in Appendix I for the average external concentration $\bar{c}_1$, which reads

$$\bar{c}_1 = \frac{c_1^{\alpha} - c_1^{\beta}}{\ln\left(\frac{c_1^{\alpha}}{c_1^{\beta}}\right)} = \frac{\tfrac{1}{2}(c_1^{\alpha} + c_1^{\beta})}{\left\{1 + \tfrac{1}{3}\left(\frac{c_1^{\alpha} - c_1^{\beta}}{c_1^{\alpha} + c_1^{\beta}}\right)^2 + \tfrac{1}{5}\left(\frac{c_1^{\alpha} - c_1^{\beta}}{c_1^{\alpha} + c_1^{\beta}}\right)^4 + \ldots\right\}} \tag{3-25}$$

Using (3-21), (3-23), (3-24) and (3-25) we obtain respectively

$$\langle c_1^* \rangle = K(1-\varphi_m^*)\bar{c}_1 \left\{1 + \tfrac{1}{3}\left(\frac{c_1^{\alpha} - c_1^{\beta}}{c_1^{\alpha} + c_1^{\beta}}\right)^2 + \tfrac{1}{5}\left(\frac{c_1^{\alpha} - c_1^{\beta}}{c_1^{\alpha} + c_1^{\beta}}\right)^4 + \ldots\right\} \tag{3-26}$$

and

$$\langle c_1^{*-1} \rangle = \frac{1}{K(1-\varphi_m^*)\bar{c}_1}. \tag{3-27}$$

For small deviations of c_1^{α}/c_1^{β} from unity we are left in the right-hand side of (3-26) with only the first term of the series and retain

$$\langle c_1^* \rangle = K(1-\varphi_m^*)\bar{c}_1. \tag{3-28}$$

If large external concentration differences are present, we expect the ratio $\langle c_1^* \rangle/\bar{c}_1$ to be a function of c_1^{α}/c_1^{β}. If $c_1^{\alpha}-c_1^{\beta}$ equals $\frac{1}{3}(c_1^{\alpha}+c_1^{\beta})$, or $c_1^{\alpha} = 2c_1^{\beta}$, then the error in (3-28) is 4% only. An expression for $\langle c_0^* \rangle$, the average solvent concentration in the membrane, can also be derived. Remembering that everywhere in the membrane the sum of the volume fractions equals unity, we write

$$\langle c_1^* \rangle v_1 + \langle c_0^* \rangle v_0 + \varphi_m^* = 1. \tag{3-29}$$

Elimination of $\langle c_1^* \rangle$ from (3-28) and (3-29) leads to

$$\langle c_0^* \rangle = (1-\varphi_m^*)\frac{(1-K\bar{\varphi}_1)}{v_0}. \tag{3-30}$$

It must be noted that an imposed condition of nearly equal external concentrations on both sides of the membrane is so far reaching that it does not matter whether the concentration gradient of the solute is constant across the membrane or not. In the limit of a vanishingly small difference of the external solute concentrations, $\langle c_1^* \rangle^{-1}$ will be always equal to $\langle c_1^{*-1} \rangle$ making the constancy of the concentration gradient irrelevant. Nevertheless, by assuming a constant concentration gradient in the membrane we have shown clearly by (3-26) that finite concentration differences outside the membrane lead to a non-constant value of the ratio $\langle c_1^* \rangle/\bar{c}_1$, even if K is constant.

Summarizing, we may conclude that for ideal external solutions under conditions of small concentration differences, it is indeed possible to relate the average concentration of the components inside the membrane to those outside by means of a single partition coefficient. In the special case that all activity coefficients are equal to unity, or at least independent of concentration, K will be independent of the composition of the solutions.

§ 4. *The Relation between the Friction Coefficients and the Experimental Quantities*

However useful the friction coefficients may be for describing permeation, they can be applied practically only, if it is possible to express them in terms of experimentally measurable quantities. Dealing with a system consisting of a membrane, solvent and

a single solute we have to do this for three friction coefficients namely r_{10}, f_{1m} and f_{0m}. As we have already stated in § 2, the friction coefficient r_{10} representing the friction between solute and solvent yields no problems. The evaluation of f_{1m} and f_{0m} standing for the friction of respectively the solute and the solvent with the membrane requires still more assumptions than we have made already. Therefore we suppose further that the friction coefficients do not depend on x, which is, in fact, strictly true if the external concentration difference is vanishingly small. With the assumption above the expressions (3-10) and (3-11) can be developed further and become in the two-component case

$$R_{11} = \frac{d}{A_m}\left(r_{10}\left\langle\frac{c_0^*}{c_1^*}\right\rangle + f_{1m}\left\langle\frac{1}{c_1^*}\right\rangle\right), \tag{3-31}$$

$$R_{10} = -\frac{d}{A_m} r_{10}, \tag{3-32}$$

$$R_{00} = \frac{d}{A_m}\left(r_{10}\left\langle\frac{c_1^*}{c_0^*}\right\rangle + f_{0m}\left\langle\frac{1}{c_0^*}\right\rangle\right). \tag{3-33}$$

When, moreover, the solute concentration within the membrane is rather small, c_0^* may be taken in a good approximation equal to $\langle c_0^*\rangle$ everywhere in the membrane. Then using (3-27), (3-28) and (3-30) we have the following approximations:

$$\left\langle\frac{c_0^*}{c_1^*}\right\rangle \approx \langle c_0^*\rangle\langle c_1^{*-1}\rangle = \frac{1-K\bar{\varphi}_1}{K\bar{c}_1 v_0}, \tag{3-34}$$

$$\langle c_0^{*-1}\rangle \approx \langle c_0^*\rangle^{-1} = \frac{v_0}{(1-\varphi_m^*)(1-K\bar{\varphi}_1)} \tag{3-35}$$

$$\left\langle\frac{c_1^*}{c_0^*}\right\rangle \approx \langle c_1^*\rangle\langle c_0^{*-1}\rangle = \frac{K\bar{c}_1 v_0}{1-K\bar{\varphi}_1} \tag{3-36}$$

The set (3-34) to (3-36) and the equation (3-27) enable us to eliminate the internal concentrations of the set (3-31) to (3-33). So we obtain

$$R_{11} = \frac{d}{A_m}\left(\frac{1-K\bar{\varphi}_1}{K\bar{c}_1 v_0} r_{10} + \frac{1}{K(1-\varphi_m^*)\bar{c}_1} f_{1m}\right), \tag{3-37}$$

$$R_{10} = -\frac{d}{A_m} r_{10}, \tag{3-32}$$

$$R_{00} = \frac{d}{A_m}\left(\frac{K\bar{c}_1 v_0}{1-K\bar{\varphi}_1} r_{10} + \frac{v_0}{(1-\varphi_m^*)(1-K\bar{\varphi}_1)} f_{0m}\right). \tag{3-38}$$

We note that the resistance coefficients in the left-hand sides of (3-32), (3-37) and (3-38) can be expressed in terms of the experimental quantities σ, L_P and ω, as has already been done in the equations (2-50) to (2-52) within the framework of the discontinuous theory. With this a direct connection is made between the friction coefficients on the one hand and the experimental quantities on the other. Moreover, the equations so obtained can be solved for the friction coefficients by straight-forward algebraic operations. We omit the somewhat ponderous derivations here, but give immediately the results, reading

$$\frac{r_{10}}{v_1 v_0} = \frac{A_m}{d}\left[\frac{(1-\sigma)\{1-(1-\sigma)\bar{\varphi}_1\}}{\omega v_1} - \frac{1}{L_P}\right], \tag{3-39}$$

$$\frac{f_{1m}}{v_1(1-\varphi_m^*)} = \frac{A_m}{d}\left[\frac{1}{L_P} + \frac{\{1-(1-\sigma)\bar{\varphi}_1\}(\sigma-1+K)}{\omega v_1}\right], \tag{3-40}$$

$$\frac{f_{0m}}{v_0(1-\varphi_m^*)} = \frac{A_m}{d}\left[\frac{1}{L_P} - \frac{(1-\sigma)(\sigma-1+K)\bar{\varphi}_1}{\omega v_1}\right]. \tag{3-41}$$

With these equations we have formed the basis of the determination of the friction coefficients. The friction coefficient r_{10} can be calculated directly from (3-39) containing only well measurable quantities, not involving K. From this calculation it will also appear whether r_{10} is constant or not. When K is measured by a separate experiment f_{1m} and f_{0m} are easily evaluated from (3-40) and (3-41). But that is not necessary. The reason is that we can eliminate K in an elegant way from (3-40) and (3-41). Multiplication of (3-40) with the factor $(1-\sigma)$ and (3-41) with the factor $1-(1-\sigma)\bar{\varphi}_1$, followed by a summing up of the results yields after some arrangement

$$\frac{A_m}{d}\frac{1}{L_P} = \frac{f_{0m}}{v_0(1-\varphi_m^*)} + (1-\sigma)\left(\frac{f_{1m}}{v_1(1-\varphi_m^*)} - \frac{f_{0m}}{v_0(1-\varphi_m^*)}\right)\bar{\varphi}_1. \tag{3-42}$$

By plotting the left-hand side of (3-42) versus $(1-\sigma)\bar{\varphi}_1$ we obtain a straight line provided, that f_{0m} and f_{1m} are constant, as we have assumed. From slope and intercept both f_{0m} and f_{1m} can be calculated. By confronting (3-42) with (3-41) it immediately follows that

$$\frac{A_m}{d}\frac{(\sigma-1+K)}{\omega v_1} = \frac{f_{1m}}{v_1(1-\varphi_m^*)} - \frac{f_{0m}}{v_0(1-\varphi_m^*)}, \tag{3-43}$$

which enables us to calculate K. This somewhat indirect determination of K must be preferred to direct measurement of this quantity for practical reasons, to which we shall return later. Obviously, by utilizing the dependence on concentration of $1/L_P$ it is possible to evaluate four unknown quantities: r_{10}, f_{1m}, f_{0m} and K from three equations viz. (3-39), (3-40) and (3-41).

Several conclusions can be drawn from the equations (3-39) to (3-41).

1. Let us consider the case where equal volumina of the permeants are retarded by the membrane to the same degree. This means that the right-hand side of (3-43) must be equalized to zero. Consequently we find from the left-hand side of (3-43) that $\sigma = 1-K$, indicating that the membrane may reflect some component more than the other because of a different chemical interaction. Moreover, the slope in (3-42) will vanish and L_P will be independent of the composition of the liquid. The case may be of interest when small, or even negative values of σ are observed. The selectivity, if any, of the membrane may be described in such cases for the greater part to preferential adsorption of some component.
2. If the friction exerted by the membrane upon the solute is much larger than the friction upon the solvent, the right-hand side of (3-43) will differ considerably from zero. As a consequence of this $1/L_P$ will depend strongly on $(1-\sigma)\bar{\varphi}_1$. This effect becomes stronger according as the solute molecules are larger than the solvent molecules.

In order to obtain a better insight into the physical meaning of σ and ω it is worthwhile expressing them also in friction coefficients as has been done for L_P. Division of the sum of (3-39) and (3-41) by the sum of (3-39) and (3-41) yields, after some arrangement, for σ

$$\frac{(1-\sigma)}{1-(1-\sigma)\bar{\varphi}_1} = \left(\frac{K}{1-\bar{\varphi}_1 K}\right)\frac{(1-\varphi_m^*)r_{10}+f_{0m}v_1}{(1-\varphi_m^*)r_{10}+f_{1m}v_0}. \tag{3-44}$$

Similary we have for ω by adding (3-39) and (3-40) followed by some arrangement

$$\frac{\omega}{1-(1-\sigma)\bar{\varphi}_1} = \left(\frac{A_m}{d}\right) K \frac{(1-\varphi_m^*)v_0}{(1-\varphi_m^*)r_{10}+f_{1m}v_0}. \tag{3-45}$$

For very dilute solutions (3-44) and (3-45) may be further simplified by taking in a good approximation $1-(1-\sigma)\bar{\varphi}_1$ and $1-K\bar{\varphi}_1$ equal to unity.

Let us point out the influence of the various friction coefficients and the partition coefficient on L_P, σ and ω with the aid of (3-42), (3-44) and (3-45).

The friction between the solvent and the membrane (f_{0m}) has little significance for ω, because it appears in the immaterial factor $1-(1-\sigma)\bar{\varphi}_1$. However, it contributes more to σ and most of all to L_P.

The friction between the solute and the membrane (f_{1m}) influences σ and ω considerably and L_P only as far as its dependence on concentration is concerned.

The friction between the solute and the solvent (r_{10}) affects mostly ω and to a lesser degree σ, because it appears in both numerator and denominator of the right-hand side of (3-44). L_P is determined only to a certain degree by r_{10} via the factor $(1-\sigma)$.

The partition coefficient K is involved in all the experimental quantities. Never-

theless, one may devise expressions of these quantities in which K does not occur or may be ignored. An example of an expression which does not contain K is already given by (3-42). Further the ratio $(1-\sigma)/\omega$ involves K only in the insignificant factor $1-K\bar{\varphi}_1$. These sort of relationships of which K forms no part, or only a negligible one, are suitable starting points for the calculation of friction coefficients and for a check on their constancy.

We shall conclude this section by making some remarks about the dependence on concentration of the several quantities involved. The friction coefficients which have been assumed constant throughout the membrane actually depend on the average concentration $\bar{c}_1$. Mostly, especially when Fick's first law is obeyed perfectly, at least in free solution, r_{10} depends only slightly on concentration. Concerning f_{0m} determined mainly by the mechanical interaction of the membrane with the solvent, we expect that generally it will not vary more with concentration than the viscosity. The partition coefficient K may be strongly dependent on concentration. Evidently these concentration effects have influence on L_P, σ and ω. In some cases a conclusion may be drawn. When, for instance, σ and ω depend strongly on concentration, whereas $(1-\sigma)/\omega$ does not do so, f_{1m} or K must be a function of concentration. Then a further test can be made by inspecting the plot of $1/L_P$ versus $(1-\sigma)\bar{\varphi}_1$. A curved line will indicate that f_{1m} does indeed depend on concentration, but a straight line will prove its constancy. Another test can be made by plotting R_{00} versus $\bar{c}_1$ according to (3-38), which yields a straight line if K is constant and $K\bar{\varphi}_1$ is much smaller than unity. In the particular case that the friction coefficients as well as the partition coefficient are constant, we expect from (3-42), (3-44) and (3-45) that σ and ω are reasonably constant and that L_P decreases with increasing concentration. With regard to the resistance coefficients it follows from (3-37), (3-32) and (3-38) that R_{10} and the product $R_{11}\bar{c}_1$ turn out to be constant, whereas R_{00} increases with concentration. However, it must be noted that these considerations are only true if $K\bar{\varphi}_1$ may be neglected with respect to unity.

§ 5. *Classification of Membrane Systems*

Friction coefficients have already been used frequently in connection with the description of transport processes by many authors especially in the field of free diffusion. After Onsager [32] had introduced them, many papers have been devoted to their relation to diffusion coefficients [25, 7] and their foundation on statistical mechanics [2]. From the literature cited above it becomes clear that a simple transport process like an isothermal mutual diffusion in free solution of two components is characterized by a single friction coefficient r_{10}^f accounting for the friction between the solute and the solvent, and related to the mutual diffusion coefficient $\mathscr{D}$ according to

$$r_{10}^f = \frac{RTv_0\left(1+\dfrac{\partial \ln f_1}{\partial \ln c_1}\right)}{\mathscr{D}}. \tag{3-46}$$

Now it is worth drawing r_{10}^f of free solution into our considerations and comparing it with r_{10} in the membrane. In doing so we do indeed have a way of eliminating the chemical as well as the geometrical and mechanical effect of the membrane on the permeating components. The mechanical influence of the membrane, originating from its fixed situation in space, is expressed mainly by f_{1m} and f_{0m}. The chemical influence of the membrane on the permeants is accounted for by the partition coefficient K. As we have seen, $K \neq 1$ agrees with a chemically active membrane, whereas $K = 1$ corresponds to a chemically inert membrane. The geometrical influence of the membrane originates from the fact that the permeating molecules are forced to follow outlined pathways which are usually longer than the thickness of the membrane because of their tortuosity. Obviously the value of r_{10}^f/r_{10} is determined by these geometrical and chemical influences. A possible ambiguity concerning the average concentration to be chosen for the friction coefficients in this ratio may be avoided by extrapolating them to zero solute concentrations.

With respect to the influence of the membrane on permeation two extreme situations can be distinguished. If the membrane pores have dimensions much larger than the mean free path of the permeating molecules the membrane participates only marginally in the transport process. If, however, the membrane pores are of the same order of magnitude as the mean free path of the permeating molecules, wall effects have more grip on the permeation process and consequently chemical and other interactions will more strongly affect the value of r_{10}. In this case the membrane is involved completely in the transport process at a molecular level. Frequently one meets this distinction in two membrane models in literature, referred to as "pore model" and "solution model", concurring with respectively the former and latter case discussed above. Recently a similar view has been given by Mikulecky and Caplan [27]. Yet we object to such a distinction for several reasons. Our first objection is that it can only be a rather crude distinction for one can think of several intermediate cases. Our main objection is, however, that it is actually based on the pore dimensions, compared with the magnitude of the molecules, ignoring a possible specific interaction of the membrane with some component. Two examples may clarify this. Suppose we have a membrane possessing pore dimensions much larger than the molecular diameter but showing a preferential adsorption with respect to the solute ($K \neq 1$). On the grounds of the pore dimensions one would be inclined to think that the pore model must be adopted, but on the grounds of the specific interaction of the membrane one would decide on the solution model. Exactly the reverse situation is met if one is dealing with a membrane having pore dimensions in the order of magnitude of the molecules but chemically inert with respect to these molecules ($K = 1$). Here again it is not clear if either the pore model or the solution model covers this case. Therefore it is worth looking for more unambiguous bases for models of membrane systems. From the following it will be obvious that on the basis of two important characteristics of permeation viz. partition and friction, it is possible to arrive at a reasonable classification of membrane systems.

Let us suppose that we are dealing with a given membrane which is chemically indifferent ($K = 1$) to a number of solutes dissolved in the same solvent. Let us moreover assume that the different solutes follow the same diffusion pathways through the membrane and that none of them are excluded from the small pores because of their magnitude. With these suppositions we expect the ratio r_{10}^f/r_{10} to be purely geometrical and independent of the solute chosen. Now it is desirable to analyse this geometrical constant and to express it in measurable quantities. In this connection we recall that we have calculated r_{10} according to (3-12) or to (3-39) in which the factor A_m/d is involved, being the membrane surface divided by the membrane thickness. Indeed the choice of this factor was to some degree arbitrary, and had been suggested by the idea that it does not matter which value for A_m/d is taken as it enters in all three expressions for the friction coefficients. When, however one is interested in an absolute value of r_{10} a more realistic factor must be chosen which accounts fully for the tortuosity of the diffusion pathways. In fact the molecules permeating from one membrane face to the other do not cover a distance equal to d, but a much longer way, equal to d/ϑ where ϑ ($\leqslant 1$) represents the tortuosity factor. Instead of the total membrane surface a smaller effective membrane surface is only open for permeation. Debije and Cleland [3, 5] have shown this effective membrane surface to be $(1-\varphi_m^*)\vartheta A_m$. Hence the value of r_{10}, which is based on the factor A_m/d, must be multiplied by $(1-\varphi_m^*)\vartheta^2$ before being confronted with r_{10}^f. In the case considered here, we may write

$$\frac{r_{10}^f}{r_{10}} = (1-\varphi_m^*)\vartheta^2. \tag{3-47}$$

Thus the geometrical membrane properties determining the constant in the right-hand side of (3-47) are the porosity $(1-\varphi_m^*)$ and the tortuosity ϑ. Upon inspecting (3-47) it is clear that for merely geometrical reasons r_{10} will be larger than r_{10}^f. For instance, dealing with a membrane in which the pores have been distributed at random ($\vartheta = \frac{1}{2}$) [5] and have a pore volume fraction of $(1-\varphi_m^*)$ equal to $\frac{1}{2}$, we expect r_{10} eight times larger than r_{10}^f. However, the case may be that the interaction between solute and solvent is markedly affected by a chemical interaction of the membrane and the ratio r_{10}^f/r_{10} varies for a given membrane from solute to solute. In any case the partition coefficient K and the frictional ratio r_{10}^f/r_{10} are in our opinion the most appropriate quantities which may serve to classify the membranes by their behaviour with respect to a number of solutes. Along lines of formal reasoning we arrive at the following subdivision:

Class I

This class may be defined by $K = 1$ and the same value of r_{10}^f/r_{10} for a number of different solutes and represents in our terms the "pore model". An example is the glass filter of the diaphragm cell used for mutual and self-diffusion measurements.

The so-called calibration constant must then be a purely geometrical factor. The reflection coefficient is very small in these systems.

Class II

This class is defined by $K = 1$ and a ratio r_{10}^f/r_{10} variable with solute. The highly swollen membrane systems investigated by Ginzburg and Katchalsky [11] belong perhaps to this class. Indeed they find a non-constant value for r_{10}^f/r_{10} using aqueous solutions of sucrose, glucose, urea, tagged water and dialysis tubing and wet gel as membranes. However, they only assume that $K = 1$ for their systems, but do not prove or measure it. Therefore it may be quite possible that their systems belong rather to class IV than to class II. We note that another effect may cause a variable r_{10}^f/r_{10}. If the membrane possesses pores showing a broad distribution with respect to their diameters, some solutes may be excluded from the small pores which actually reduces r_{10}^f/r_{10}.

Class III

This class is defined by $K \neq 1$ and a constant ratio r_{10}^f/r_{10} for different solutes. We do not know of any examples of this class, which in fact is not very realistic.

Class IV

This class is defined by $K \neq 1$ and a frictional ratio r_{10}^f/r_{10} variable with solute. The membranes belonging to this class will show an obvious selectivity (easily measurable reflection coefficients) and the whole system may be regarded as a "solution model". In our opinion most membrane systems can be described by this very general model, because some molecular interaction between the membrane and the permeating components will always be present.

Yet, as will appear later as a result of our work, it is not a simple matter to distinguish on the basis of the magnitudes of K and r_{10}^f/r_{10} the purely geometrical effects from the purely chemical effects, unless the membrane is chemically inert. This means that the classification given above is perhaps too formal and is reduced mainly to two classes: "the pore model" and "the solution model". Nevertheless, these two models are best defined and distinguished by the two indicative quantities K and r_{10}^f/r_{10}.

CHAPTER 4

EXPERIMENTAL OUTLINE

§ 1. *The System: Membrane–Solute–Solvent*

The system which was the object of the experimental investigation consisted of a porous glass membrane (trade-mark Vycor) and the aqueous solutions of the following solutes, in sequence of increasing molecular weight: penta-erythritol, mannitol, sucrose and raffinose. The use of porous Vycor glass as a membrane shows favourable perspectives. In the first place, it has the great advantage of being tight and supporting itself even when exposed to pressures of up to 4 atmosphere. Moreover, it is easily purified by a simple treatment with nitric acid, while still retaining hereafter rather constant permeability properties. The choice of the solutes was suggested by the following considerations. All of them are available as commercial products in a high degree of purity. They form stable aqueous solutions with a sufficiently large refractive index increment (dn/dc) admitting, with the aid of interferometric methods, an accurate determination of their concentration. The fact that Talen and Staverman [42] have found an easily measurable reflection coefficient with a value of 0.2 for an aqueous sucrose solution with respect to a porous glass membrane indicates that solutes of this kind have interesting properties with respect to glass membranes. Because of their excellent transport properties in free solution they have been used many times in recent years for mutual and tracer diffusion measurements. Consequently, we can dispose of a great deal of auxiliary experimental data, such as the diffusion coefficients and the activity coefficients. The specifications of the different materials are mentioned below.

penta-erythritol formula: $C_5H_{12}O_4$; mwt: 136.15.
The commercial product (Fluka A.G., purum) was recrystallized from distilled water at 100 °C in a weight ratio 1:1. Thereupon it was dried over KOH in vacuo at room temperature till constant weight (16 hours). Melting point found: 257.0–257.7 °C in agreement with the literature value.

mannitol formula: $C_6H_{14}O_6$; mwt: 182.17.
The material used was the micro analytical reagens (organic analytical standard) from B.D.H. Its purity was very high; melting point found: 168.2–168.8 °C in agreement with the literature value. Before use it was dried in vacuo at room temperature.

sucrose formula: $C_{12}H_{22}O_{11}$; mwt: 342.30.
The commercial product (Baker Analyzed Reagent) was dried in vacuo at room temperature and found very pure (A.C.S. specification). Melting point found: 185.2–185.7 °C in agreement with the literature value.

raffinose formula: $C_{18}H_{32}O_{16}.5H_2O$; mwt: 504.44.
The hydrated product had a melting point 79.2–80.0 °C in agreement with the literature value. The anhydrous product was obtained by heating in vacuo at 70 °C for several days, and then heating in vacuo at 85 °C till constant weight. It was ensured that the anhydrous product was not exposed to the moist atmosphere, by means of special equipment allowing only air dried over concentrated H_2SO_4 and solid KOH to pass into the vacuum dry box.

The solutions were prepared by weighing both solvent and solutes. Volume concentrations and volume fractions were calculated with the help of auxiliary density data. The freshly prepared solutions were not longer tenable, for our purpose, than two days, and when not in use were kept cool.

The Glass Membrane

Porous Vycor Glass is a product of Corning Glass Works, N.Y., USA, and its fabrication is described fully in the literature [29]. The porous glass phase consists of about 96% silica glass with a pore radius which proved to be 20–30 Å for the specimen used by us. The membrane itself occupies the lower part (porous and open for permeation) of a finger-shaped glass cell. The membrane surface is about 25 cm^2, the membrane thickness about 0.14 cm. Closed at one side (the "fingertip"), the membrane ends on the other side via several impermeable glass transitions into an open Pyrex tube on which a group of glass joints may easily be melted. In the dry state the membrane must be handled carefully and may not be wetted suddenly, because swelling causes a tremendous internal tension in the glass, leading directly to cracking of the material. For good acclimatisation the membrane must be wrapped in moist Kleenex tissue and kept wetted for several hours. After this it can be acclimatised to water and further treated with nitric acid in order to remove remaining organic traces. For that purpose it is placed in a measuring glass filled with nitric acid. The membrane itself is also filled with the acid, so that there is contact on both sides. Then the whole is heated in a boiling water bath for several minutes, allowed to cool and thoroughly washed with distilled water. Finally, the membrane is boiled out with distilled water for several hours in order to drive out all traces of acid. Unfortunately this cleaning procedure, though efficient, affects the permeability properties of the membrane and makes it more permeable than before. However, by varying the strength of the acid and the time of cleaning, the change of permeability can be regulated to a desired degree. In our case the mechanical permeability for pure water changes about 3% after each cleaning procedure. A less drastic procedure using only water does not lead to constant permeabilities.

§ 2. *The Apparatus*

The whole osmotic assembly involves an osmometer (I), shown in Fig. 4.1 and in detail in Fig. 4.2, in which a constant temperature of 25 °C is maintained by a thermostating circuit (II), connected to the double wall of the outer vessel by means of the two spout-shaped glass joints on the right side. The plastic tube at the top connects the osmometer to a pressure system (III), enabling us to apply various overpressures. The two teflon tubes on the left side form part of a concentration-measuring circuit (IV) through which the solution of the outer vessel can be pumped and in which the concentration can be measured continuously during the experiments. The different parts of the whole assembly are discussed in more detail in the following.

I. The Osmometer

The inner or α compartment is represented by the finger-shaped tube of Vycor glass standing on the bottom of the outer or β compartment and ending at the top into two concentric glass joints. The pressure chamber fits onto the outer glass joint and the capillary onto the inner one. This construction is clearly seen in Fig. 4.3. Moreover, this picture shows that the glass joint connecting the pressure chamber to the α compartment is held tightly by a screwing device, assuring a solid enclosure when high pressures must be applied. That the osmometer can be dismounted into different parts facilitates the filling and cleaning procedure. Mounting or dismounting takes only a few minutes. The porous glass area reaches up to a distance of about 5 cm from the bottom. The transition from porous to non-porous glass is rather sharp and clearly visible. Leaks frequently met in placing mem-

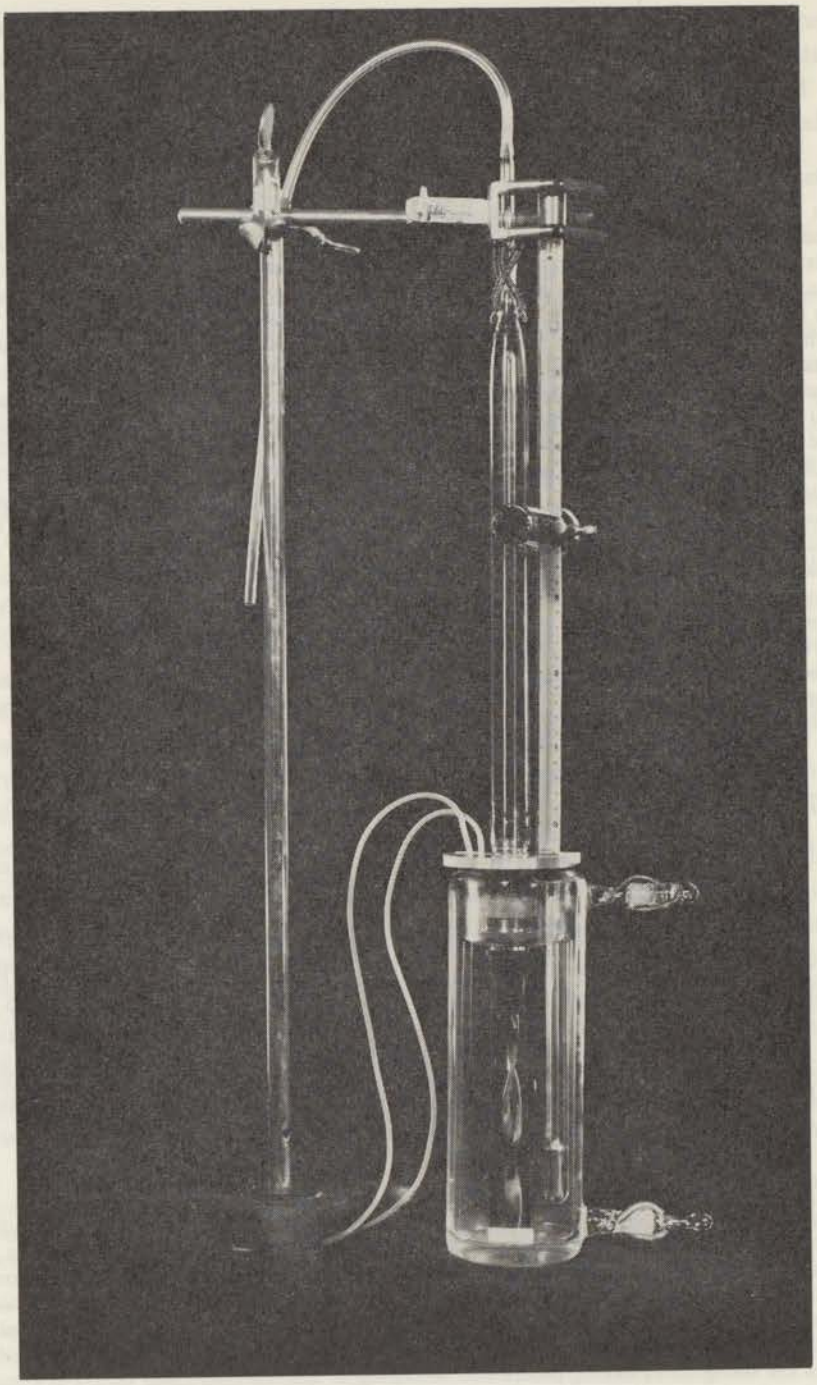

Fig. 4.1. Osmometer with Vycor glass membrane equipped with two stirrers and a pressure chamber.

branes in osmometers have been excluded here, as the membrane forms a whole with the α compartment. With the help of a calibrated burette the volume of the α compartment can be determined, and is found to be about 20 ml for the different osmometers used. The capillary standing on the α compartment is precision capillary (Verylia G.B.), of which the diameter was determined by measuring the length and weight of a small column of mercury brought in. The diameters used are 0.6 mm and 1.0 mm.

The β compartment of the osmometer is simply the doublewalled outer vessel which can contain 250 ml of the solution, in which the Beckmann thermometer is hanging. During the experiments the outer vessel was coated with an efficient isolating material.

The solutions in both compartments were stirred vigorously. In the α compartment this was realized by means of a spiral-formed stirrer of soft glass, filled with iron powder; in the β compartment the same was done by means of a small magnet coated in teflon. Both stirrers were driven by a rotating permanent magnet under the outer vessel.

The osmometer was filled in the following way. The α compartment was placed without capillary and pressure chamber in a measuring glass filled with the α solution. By means of an injection syringe the solution was brought into the α compartment up to the edge of the inner glass joint. The capillary was there fitted to it and the space between the inner and the outer glass joint filled up with mercury (mercury lock) in order to prevent the liquid head in the capillary from leaking through the inner glass joint. A very long needle was used to fill the capillary without including air bubbles. Finally, the sequence of assembling was carried out as shown in Fig. 4.3 and the whole mounted α compartment was placed in the outer vessel, partially filled beforehand with the β solution.

During the experiments the meniscus in the capillary was followed with the aid of a cathetometer (Wild M 10). The accuracy gained in the measurement of the osmotic height was 0.01 mm.

The osmometer discussed here may be considered as an improved version of the type described by Talen and Staverman [42].

II. The Thermostating Circuit

The thermostating circuit must satisfy the most severe requirements, for the α compartment with capillary acts itself as a perfect precision thermometer. In order to profit fully from the very accurate measurement of the osmotic height, we have to take care that the variation of temperature in the outer vessel is as small as possible. This problem was solved by applying a thermostating in three steps; the first step cools the second and the second step cools the final step, which actually forms the thermostating circuit for the outer vessel. The first step was formed by a cryomat (Lauda TK 30 D), yielding methanol of 10 ± 1 °C. The following step consisted of a pumping thermostat (Haake type F), producing water of 23 ± 0.1 °C. The final step was an ultra-thermostat (Haake TP 41) keeping the temperature in the outer vessel at 25 °C with a variation of 0.001–0.002 °C over a period of one hour, measured with the Beckmann thermometer. Measurements were carried out to observe the temperature in both the β compartment and the α compartment. It turned out that the temperature in the inner compartment follows the temperature in the outer compartment spontaneously. Because of the remaining small changes of temperature the measured osmotic heights were corrected.

III. The Pressure System

The pressure source was a cylinder of compressed nitrogen of extremely pure quality. By means of regulating manostats the pressure differences between the two osmometer compartments could be varied from 0 to 80 cm water or from 0 to 76 cm mercury. The manometers used were of the open U type and the difference in height between the menisci was measured with the cathetometer. With the mercury manostat constant pressures were obtained within 0.1 mm Hg. The heights of the mercury columns in the manometers were corrected for small variations of the room temperature. We had at our disposal a high mercury manostat without regulation outfit, yielding an overpressure of 2.5 atmosphere especially suited for ultrafiltration experiments. The whole system of manostats, manometers, conduits, valves and taps was devised by Talen, who has described it fully in his thesis [41].

IV. The Concentration-measuring Circuit

The outer or β concentration could be followed continuously during permeation. For that purpose

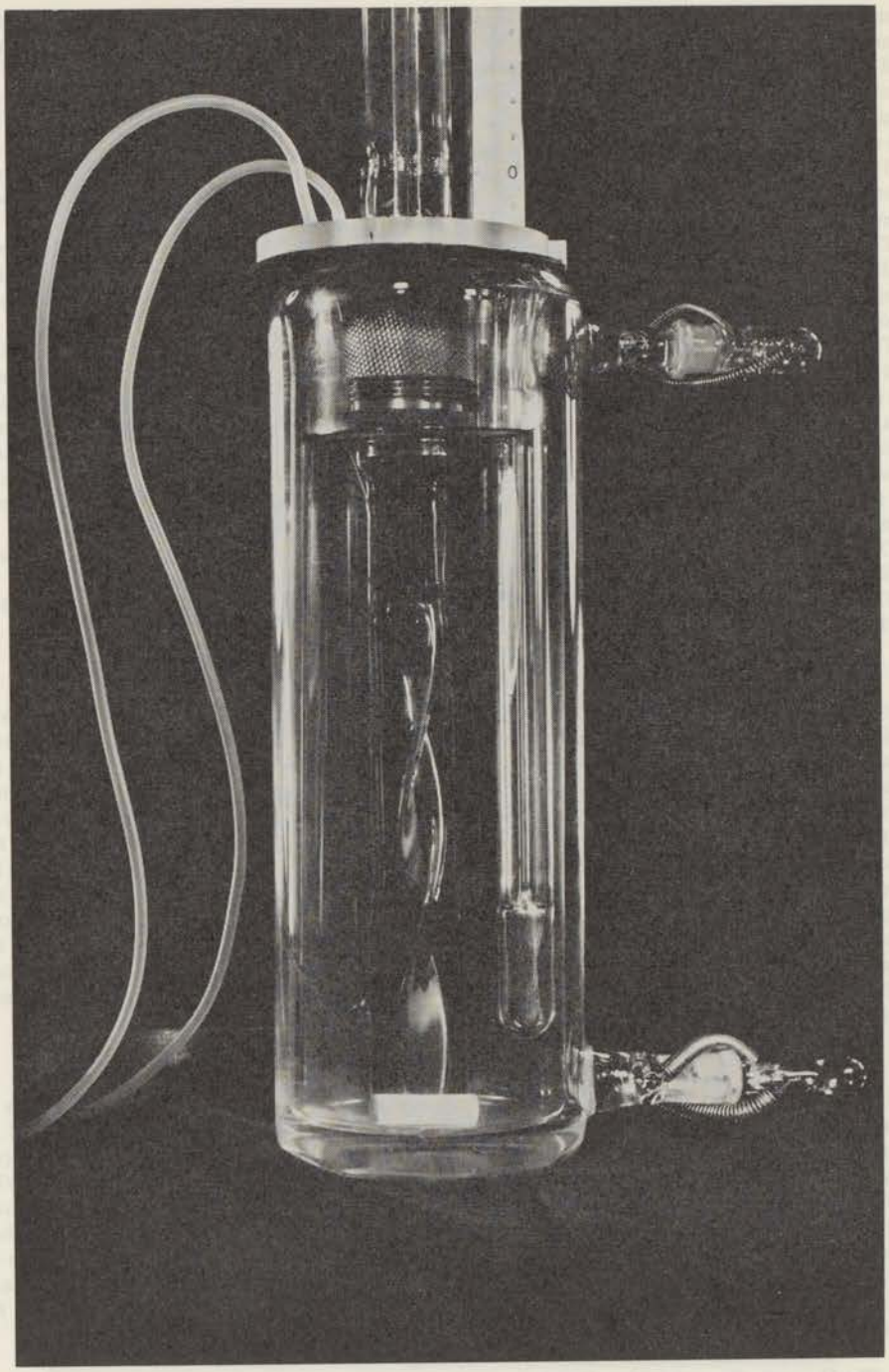

Fig. 4.2. The inner and outer compartment of the osmometer.

a peristaltic pump (L.K.B.) circulated the solution through a differential refractometer (Waters R 4) connected with the outer vessel, but also in a parallel way with a second identical outer vessel acting as dummy and containing the reference solution. At zero time the solutions in both vessels were equal and the recorder of the refractometer gave the usual base line. In the course of an experiment the solute concentration in the outer vessel, forming part of the osmometer, increased because of permeation contrary to the solute concentration in the dummy vessel. This phenomenon was observed on the recorder as a deflection from the base line which became larger in the course of time. The device of the dummy reference vessel was used to eliminate the disturbing effect of solvent evaporization assumed quite reasonably to be equal for both vessels.

Though this method of determining concentration differences appeared very sensitive, the accuracy was somewhat disappointing. Calibration with standard solutions showed that the deflections of the recorder were no more linear than about 3%, while the base line itself had a drift of about 2% over a period of 24 hours.

The flow rate in the circuit was 1 ml per minute, sufficiently small to assure a stable base line but on the other hand sufficiently large to follow the very slow change of concentration in the outer vessel. After the termination of each experiment a time lag of about 8 minutes was observed in accordance with the "dead volume" present in the pump, the refractometer and the conduits between them. This "dead volume", amounting to only 3% of the external liquid volume, had evidently been withdrawn from the influence of permeation.

The recorder data were strongly dependent on fluctuations of temperature. Also the base line drift must be ascribed mainly to temperature effects. By means of a pumping ultra-thermostat (Haake TP 41) the refractometer cell was kept as close as possible to a constant temperature.

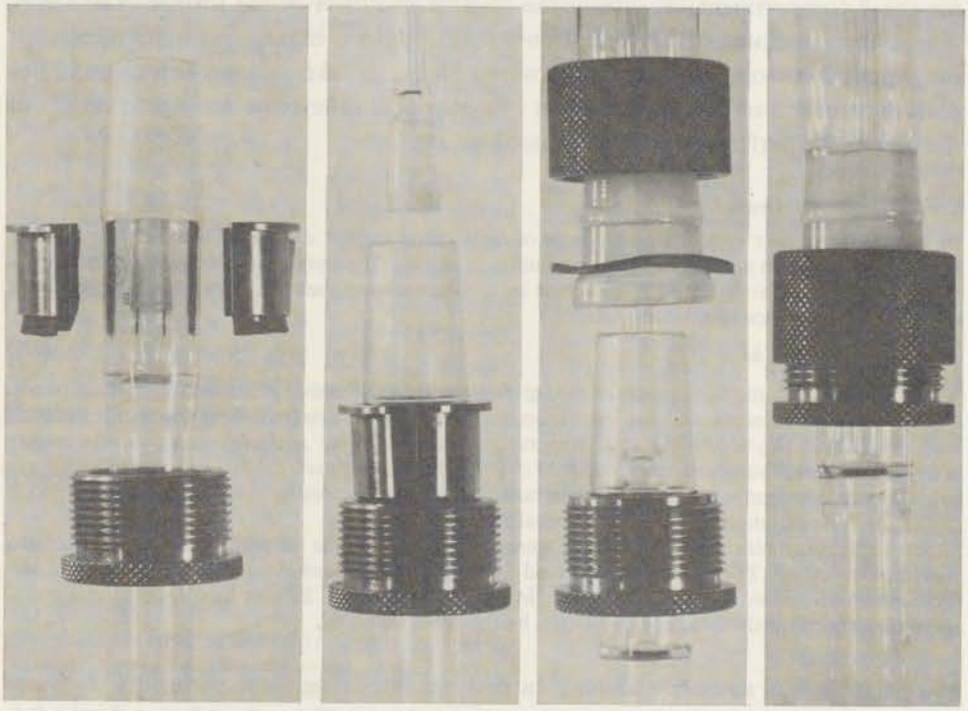

Fig. 4.3. The connection between the inner compartment and the pressure chamber of the osmometer.

The whole assembly outlined above works extremely well as a dynamic osmometer with a high accuracy. Its only drawback is perhaps the unfavourable combination of the laborious serving of the apparatus with the very slow progress of the permeation process. In fact, we can do nothing about this. The very fact that the system may not be far from equilibrium means that all processes, leading to its final state, take place very slowly or under quasi-stationary conditions. On the other hand, an automatic serving system such as has been achieved recently in some automatic high speed membrane osmometers might have been used, but only with loss of accuracy [1].

Some remarks must be made about the unequal volumina of the compartments of our osmometer, in which respect it differs from most osmometers. For several reasons the β compartment has been made much larger than the α compartment. Firstly, inherent in the construction of the osmometer, the larger volume of the β cell serves as a thermostating medium of the α compartment. Furthermore, during permeation processes the concentration in at least one compartment can be held as nearly constant as possible. This is important for ultrafiltration, where at the one hand the concentration difference must be kept at zero, but on the other hand a concentration difference, however small, is built up. Finally, in view of the "dead volume" present in the concentration measuring circuit, we have to deal with a relatively large β volume.

Evidently the change of concentration is much larger for the α compartment than for the β compartment because of the relative smallness of the former. Yet a continuous measurement of concentration seems in the α compartment quite impossible for practical reasons. Therefore, we were obliged to take samples before and after each experiment and to analyse them in a Rayleigh interferometer. Some details of the Rayleigh interferometer are discussed below.

The Rayleigh Interferometer

In the interferometer two coherent beams of light travel over a distance l through the solution and the solvent with respective refractive indices n and n_0. The optical path difference between the two beams equals $(n-n_0)l$ and is measured by a compensation method. It can be shown that the optical path difference satisfies the relation

$$(n-n_0)l = h\lambda_D, \tag{4-1}$$

where λ_D represents the wave length of the light used and h the number of shifted interference bands.

The relation between h and the interferometer readings was determined by us by a calibration with Na-D light ($\lambda_D = 5893$ Å) at a temperature of about 25 °C. A small correction was usually necessary to obtain values at exactly 25 °C ($\pm$ 1‰ per °C). For each solute used, the ratio h/c was proved to be constant in the concentration range considered, indicating that dn/dc is constant, as it should be. The variation observed in h was always less than 2‰.

Since in fact samples saturated with N_2 were to be measured, the influence of this gas in solution has been examined. The only thing observed by us was the somewhat inferior quality of the interference pattern caused by N_2 bubbles escaping from the solution. Besides this there was no quantitive disturbance in the interference pattern by the presence of N_2.

With the osmotic assembly we have carried out three types of experiments. They are the ultrafiltration, the osmotic experiment and the relaxation experiment. In the following we shall discuss them separately.

§ 3. *The Ultrafiltration Experiment*

In an ultrafiltration experiment the solution present in the α compartment was pressed through the membrane, under a constant overpressure of 2.5 atmosphere and equal concentrations on both sides of the membrane, at least at zero time. Since the solvent permeates faster than the solute across the membrane, the solute concentration in the α compartment will increase in the course of time, whereas the volume of the liquid present in the same compartment will decrease. A measurement of both effects gives us information about the reflection coefficient σ. This will be more clear after inspecting the expressions (2-70) and (2-71) which, applied to a two-component system, must coincide because $\sigma_n \equiv \sigma_w$. Remembering from equation (4-1) that h/c was found to be constant, σ can thus be determined with the use of

$$\sigma = -\frac{\mathrm{d} \ln h}{\mathrm{d} \ln V}. \tag{4-2}$$

In Fig. 4.4 we have plotted h versus V for the system sucrose–water. The negative slope represents σ in accordance with (4-2). Unfortunately we could not break off one individual experiment in order to take a sample out of the α compartment for analysis, and then continue the permeation, because this involves an inadmissible violation of the accuracy of the measurement. We have, therefore, performed several

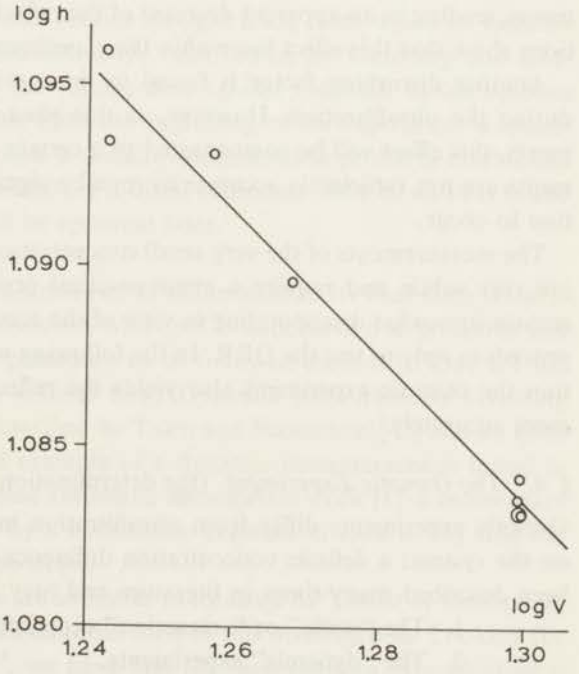

Fig. 4.4.
The change of concentration (h) and volume (V) of a solution of sucrose in water subjected to an ultrafiltration through a glass membrane. The negative slope represents the reflection coefficient σ.

experiments, starting in each case with the same initial concentration, but varying the time of filtration from 9, 18, 27 to 36 hours. These experiments were combined to one plot.

Before each experiment the α compartment was filled up to the edge of the glass joint and equipped with a very narrow capillary. The decrease in volume was determined by weighing the α cell before and after each experiment. From the initial volume known beforehand the final volume could be calculated. The liquid level in the α compartment was not allowed to fall too much, because otherwise the balance of the spiral stirrer was disturbed and it stopped working. This meant that the volume pressed through had to be restricted to 4 ml, about 20% of the content of the α compartment.

Before and after each experiment the α concentration was measured in the Rayleigh interferometer. The changes of the α concentration measured lay in the range of 2–3%; the change of the β concentration was completely negligible. The linearity of the plots was reasonable; probable errors in the slope calculated according to the method of least squares were always less than 5%.

Some remarks must be made about the contradiction between the measurement itself and the external condition under which it must be carried out. The external condition requires that the concentrations on both sides of the membrane are held strictly constant, but what one actually does is to measure a small change in concentration, thus admitting the presence of a concentration difference, however small. As a consequence of this a very small osmotic pressure is built up during the experiments, leading to an apparent decrease of the reflection coefficient. However, calculations show that this effect lies within the experimental error.

Another disturbing factor is found in the inevitable evaporation of the solvent during the ultrafiltration. However, as this phenomenon occurs in both compartments, this effect will be compensated to a certain degree. In any case, the measurements are not sufficiently accurate to reveal a significant indication for the evaporation to occur.

The measurements of the very small concentration effects involved in ultrafiltration are very subtle and require a great practical proficiency. Nevertheless, the results remain somewhat disappointing in view of the accuracy obtained. We have used this procedure only to test the ORR. In the following we shall see that besides ultrafiltration the osmotic experiment also yields the reflection coefficient, and in fact even more accurately.

§ 4. *The Osmotic Experiment* (the determination of σ and L_P)

Osmotic experiments differ from ultrafiltration in the external condition, imposed on the system: a definite concentration difference across the membrane. They have been described many times in literature and may be subdivided into two branches:

1. The "static" or "relaxation" experiments.
2. The "dynamic" experiments.

1. In the static experiments the system being in a state of non-equilibrium is left to itself and comes slowly to its final state. In an osmometer like ours the process is followed by observing the meniscus moving in the capillary. When the initial pressure difference (ΔP) is zero, or at least constant and smaller than the apparent osmotic pressure difference (ΔP^*), the meniscus runs through a maximum in the course of time. Exactly at this maximum the volume flow equals zero and ΔP^* is counterbalanced by ΔP. Before the maximum the volume flow is negative (rising meniscus); after the maximum the volume flow is positive (falling meniscus). This behaviour, typical for a solute permeable membrane, is easily explained from (2-44), which, however, is only true if a quasi-stationary regime is present. Laidler and Shuler [24] and also Vink [44, 45] have carried out relaxation experiments and have shown that much information can be obtained from the single curve relating the osmotic heights to the time. Kedem and Katchalsky [17] have pointed out how the experimental quantities σ, L_p and ω may be evaluated from these curves. However, we stress that their equations are only valid if from the beginning of the experiment a quasi-stationary state exists. Therefore, interpretations about relaxation curves must be taken with caution. At first sight one would think that from the maximum in any case ΔP^* can be evaluated, but this is only of interest when, at the time that the maximum occurs, Δc is known or measurable. Mostly one knows only the concentration difference at zero time exactly. This fact has been used by Cleland [3], and also by Ginzburg and Katchalsky [11]. They start their experiments with $\Delta P = 0$ and measure the volume flow as a function of time. Cleland plots the volume flow against the various concentration differences chosen and obtains straight lines, from which he deduces a quasi-steady state. Similar conclusions have been drawn by Ginzburg and Katchalsky from their linear plots of the volume flow against the time. In our opinion it is highly questionable if so soon after the beginning of an experiment a quasi-stationary regime has set in, in which a definite concentration profile is established across the membrane. The time needed for a quasi-stationary state to set in is found in our case to be 1–2 hours, as will be apparent later.

2. In dynamic measurements the normal run of the process to its final state is interrupted by intervention of the observer, who applies successive overpressures and measures the resulting flows. The procedure to be followed then, is to look for the overpressure belonging to a zero volume flow. Dynamic measurements involving solute permeable membranes are described by Talen and Staverman [42] and by Elias and Schlumpf [9]. A further good example of a dynamic measurement is found in the principle according to which some automatic osmometers work [1]: a momentary balancing of the osmotic pressure by a hydrostatic pressure in such a way that the volume flow through the membrane stops.

Thus, although many procedures are available to measure ΔP^*, most of them could not be applied to the Vycor glass membranes used in this investigation. Looking for the best method of measuring ΔP^*, we have first followed the idea of evaluating it

from a single relaxation curve. However, the curves found with glass membranes show rather flat maxima. Moreover, the whole measurement requires several days, and the waiting times for a quasi-stationary state are long. For these reasons we have ruled out the relaxation experiment for the determination of ΔP^*. Nevertheless, these experiments have taught us that we could maintain our system for many hours in a state in which $J_v \approx 0$, by applying an overpressure slightly lower than ΔP^*. As we shall see, we could make fruitful use of this principle for the measurement of ω.

From the above it is obvious that we were forced towards dynamic measurements. The tight thick glass membranes lend themselves excellently to this type of measurements and are able to resist overpressures of up to 1 atmosphere without showing any ballooning. Moreover, the concentration difference across the membrane has the favourable property of falling very slowly in the course of time, a few percent in four hours. On these grounds we arrived at a rather simple principle of measurement based on equation (2-44). Indeed, a plot of J_v against ΔP must yield a straight line with a slope equal to L_p and intersecting the ΔP axis exactly at ΔP^*, provided that the time needed to determine the measuring points turns out to be sufficiently short to make the assumption of a constant concentration difference across the membrane

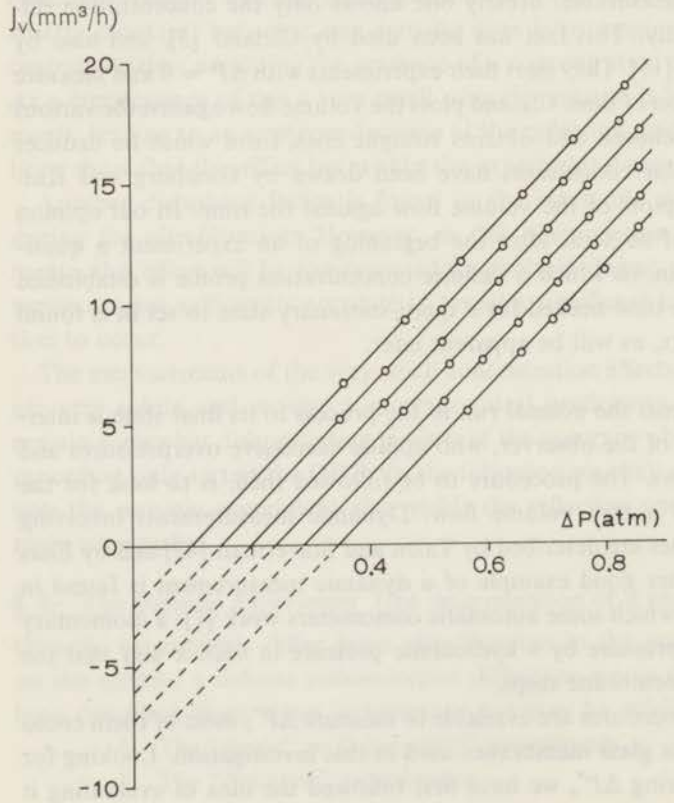

Fig. 4.5.
The dynamic measurement of the apparent osmotic pressure ΔP^* in an osmotic experiment with various solutions of mannitol in water and a glass membrane. The intersections with the ΔP axis represent the values of ΔP^*.

a good approximation. We have represented this for the system mannitol-water in Fig. 4.5. From left to right the curves refer to greater differences between the external concentrations. We have taken care to wait sufficiently long before starting measuring. Too short waiting times lead to non-linear plots. The reflection coefficient can be evaluated from ΔP^* and the osmotic pressure $\Delta\Pi$ calculated from the concentration difference.

The practical procedure was as follows. First, the α compartment was filled and equipped with a long capillary and the pressure chamber, as described above. During mounting, the α compartment was placed in an outer solution identical to the filling solution. After this, the α compartment was placed in the outer vessel filled with the β solution and put at a pressure high enough to keep the meniscus at a constant height in the capillary. This situation was maintained for 1–2 hours. The waiting times had to be made longer according as the molecular weight of the solute was larger, indicating evidently an effect resulting from non-stationarity. Then several overpressures were applied, starting with higher pressures and going down in steps, as can be seen in Fig. 4.5. The system was given about ten minutes to accustom itself to each new overpressure. The distance covered by the meniscus in each run was always chosen as about 10 mm. The volume flows were calculated by multiplication of the velocity of the descending meniscus with the diameter of the capillary, while a correction was made for a change of temperature, if any, during the measurement. The overpressures were calculated by summing up the manometer readings and the average liquid head during each run, corrected for temperature, density and capillary rise.

Our dynamic measurements differ from those cited above in that we have intentionally chosen an unidirectional movement of the meniscus by applying overpressures always higher than ΔP^*, in order to avoid complications with the draining of the capillary wall, deformation of the meniscus and a rapid change of the concentration profile within the membrane. We feel that the good agreement found between the reflection coefficients resulting from this method and those originating from the ultrafiltration, as should be by virtue of the ORR, has proved the correctness of the procedure outlined above.

§ 5. *The relaxation experiment* (the determination of ω)

As we have seen, the tardy glass membranes enable us to hold the system for long times in a state where little or no convection occurs ($J_v \approx 0$). Each relaxation experiment was started with the same concentration difference as used in the osmotic experiment, and with a hydrostatic overpressure equal to about 95% of ΔP^* previously measured. In this manner we succeeded in obtaining a minimal movement of the meniscus in the capillary, whereas the osmotic height ran very slowly through its maximum. The value of the maximum itself was immaterial, but it was precisely the state belonging to it which was important. Under the condition of sufficiently small

J_v, the last term of the right-hand side of (2-45) is negligible with respect to the first term (1% at most), and consequently we may write

$$J_1(t) = \omega \Delta \Pi(t). \tag{4-3}$$

When the permeation process proceeds very slowly, in the course of time an at least quasi-stationary regime is present, in which the solute flow J_1 and the osmotic pressure difference $\Delta\Pi$ are slightly dependent on the time (t). In these circumstances we may use equations strictly valid under stationary conditions. As a consequence of (4-3) we may apply (2-72) specified to two components. Moreover, we assume the solute permeability ω to be constant during an experiment. (This assumption is justified by the fact that the average concentration $\bar{c}_1$ on which ω depends does not change much during a measurement.) Hence we integrate (2-72) yielding

$$\Delta c(t) = \Delta c(0) e^{-\lambda t}, \tag{4-4}$$

where λ is given by

$$\lambda = RT \frac{V^\alpha + V^\beta}{V^\alpha V^\beta} \omega. \tag{4-5}$$

The osmotic non-ideality can be expressed by the ratio $\Delta\Pi/\Delta c$. When the osmotic coefficients for the system concerned are known, this ratio can be calculated in a straight forward way. Since in our experiments only relatively small variations of Δc are involved, $\Delta\Pi/\Delta c$ can be considered constant from the beginning to the end of each experiment. Therefore, we have besides (4-4) as an alternative expression:

$$\Delta \Pi(t) = \Delta \Pi(0) e^{-\lambda t}. \tag{4-6}$$

The quantity λ may be understood as a reciprocal relaxation time. From (4-4) and (4-6) it is obvious that λ may be evaluated from an analysis of concentrations in both compartments at the beginning and the end of each experiment. These measurements have been carried out by us with the help of a Rayleigh interferometer. Good constant values of λ have been obtained as shown in Table VI. The permeation half-times for the different solutes turn out to be 70 hours (penta-erythritol), 100 hours (mannitol), 150 hours (sucrose) and 250 hours (raffinose). These long times also determine the logarithmic decay of the solute flow, for from (4-6) and (4-3) it follows immediately that:

$$J_1(t) = J_1(0) e^{-\lambda t} \tag{4-7}$$

which falls only very slowly in the course of time. When once λ has been determined, ω can be calculated on the basis of (4-5).

Apart from the discontinuous measurements of concentration we were able to follow the β concentration continuously during the relaxation experiment by means of the concentration-measuring circuit already described. This extra equipment was used especially for the relaxation experiments. A typical example (mannitol/water) is seen in Fig. 4.6, where the change of the β concentration relative to its original value has been plotted against the time. The lines show hardly any curvature, which

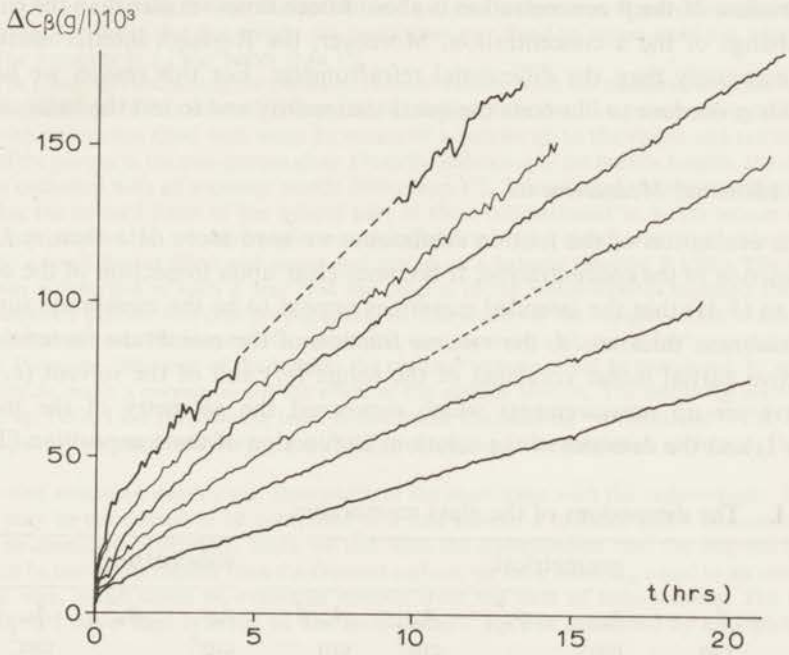

Fig. 4.6. The continuous increase of the concentration in the outer compartment of the osmometer in the course of time during a relaxation experiment with various solutions of mannitol in water and a glass membrane.

indeed indicates that a quasi-stationary state is present. At zero time a definite difference of concentration remains, due to a spontaneous release of solute by the membrane at the beginning. After a period of about one hour a quasi-stationary state has been established. These acclimation times are longer according as the molecular weight of the permeating solute increases. However, a quantitative approach to these curves is also of interest. Applying (4-7) and (4-3) to the β compartment we find

$$V^{\beta}\frac{\mathrm{d}c_{\beta}}{\mathrm{d}t} = \omega\Delta\Pi(0)e^{-\lambda t}. \tag{4-8}$$

Integration of (4-8) leads to

$$\Delta c_{\beta} = c_{\beta}(t) - c_{\beta}(0) = \frac{\omega\Delta\Pi(0)}{\lambda V^{\beta}}(1-e^{-\lambda t}). \tag{4-9}$$

Thus, a plot of $c_\beta(t)$ versus $e^{-\lambda t}$ must give a straight line. From the slope of the line ω can be evaluated. This value of ω must be in agreement with the value obtained from the discontinuous measurements if the solute flow entering the membrane equals the flow leaving it.

Yet the accuracy obtained in the continuous procedure must be estimated to be much smaller than that found in the discontinuous measurements. In the first place, the variation of the β concentration is about fifteen times smaller than the corresponding change of the α concentration. Moreover, the Rayleigh interferometer works more accurately than the differential refractometer. For this reason we have only used this procedure to illustrate the quasi-stationarity and to test the balance of flow.

§ 6. *Additional Measurements*

For the evaluation of the friction coefficients we need more data than σ, L_P and ω as a function of the concentration. It becomes clear upon inspection of the equations (3-39) to (3-41) that the intended quantities appear to be the membrane surface A_m, the membrane thickness d, the volume fraction of the membrane material φ_m^*, the respective partial molar volumina of the solute (v_1) and of the solvent (v_0). Hence we have set up measurements which concerned the geometry of the membrane (Table I) and the densities of the solutions as function of the composition (Table II).

Table I. The dimensions of the glass membranes

		geometrical				volumetrical			
	d cm	v_m cm^3	φ_m^*	A_m cm^2	A_m/d cm	v_m cm^3	φ_m^*	A_m cm^2	A_m/d cm
M 4.	0.133	3.34	0.680	25.13	188.9				
M 5.	0.132	3.23	0.693	24.47	185.4	3.22	0.691	24.39	184.8
M 6.	0.136	3.38	0.710	24.83	182.6	3.39	0.712	24.93	183.3
M 7.	0.138	3.40	0.721	24.63	178.5	3.41	0.723	24.71	179.1
M 8.	0.135	3.17	0.694	23.46	173.8	3.20	0.701	23.70	175.6

Table II. The partial molar volumina of the solvent (water) and the solutes at 25 °C calculated from density data. $\varrho = \varrho_0 + Ac$ (c in g/ml)

Solute	M	$\partial\varrho/\partial c$	v_1 cm^3/mole	v_0 cm^3/mole
Penta-erythritol	136.15	0.2515	101.94	18.069
Mannitol	182.17	0.3447	119.74	18.069
Sucrose	342.30	0.384	211.47	18.069
Raffinose	504.44	0.3927	307.24	18.069

The Geometry of the Membrane

The geometrical quantities of the membrane to be measured were the thickness (d), the volume of the pores (v_p) and the volume of the membrane material including the pores (v_m).

In order to measure d on different places of the membrane we let a drop of mercury move over the internal surface. In this way we obtained a good contrast and were able to measure the distance between the internal and external surface of the membrane with the aid of the cathetometer.

From the water content of the membrane, which could be measured by weighing the membrane in the wet state as well as in the dry state, v_p was calculated. For the membrane to be weighed in the wet state, the water adhering to both the internal and external surface was wiped off cautiously with Kleenex tissue. To obtain the dry weight the membrane was dried in vacuo until the weight was constant. The accuracy in v_p was better than 1%.

v_m could be found by subtracting the measured internal volume from the measured external volume. For the determination of the internal volume, the α compartment (with its membrane part already saturated with water) was filled with water by means of a burette up to the visible and rather sharp transition of the porous to the non-porous glass. From the difference of the burette heights, the internal volume was evaluated with an accuracy mostly better than 1%. The external volume was determined by measuring the upward force of the porous part of the α compartment in a submersion experiment. For that purpose the α compartment was clamped firmly to a stand, with its membrane part hanging into a small beaker filled with water and placed on a balance (Mettler P 1200). The α compartment was submerged in such a way that the heights of the water exactly matched the sharp boundary between porous and non-porous glass. In this situation the weight of the beaker with content was determined. Thereupon the membrane was removed and the weight was determined once again. From the difference of the weights the external volume could be calculated, by which it was necessary to make a correction for the effect of the surface tension. The estimated accuracy in v_m was 3%. In Table I the results have been shown under the heading "volumetrical". The volume fraction of the membrane material (φ_m*) is equal to $1-v_p/v_m$; the membrane surface A_m is equal to v_m/d.

We have also measured directly the dimensions of the membrane with the cathetometer. Yet the membrane may be considered to be composed of a half sphere, a cylinder and a truncated cone, which can be measured separately. Since we met with the complication that the internal surface turned out to be somewhat smaller than the external surface, we have taken A_m equal to an imaginary surface half way, which could be evaluated directly from the data of measurement. The results found in Table I have been referred to as "geometrical". v_m was calculated by multiplying A_m with d.

The Density Measurements

The densities of the sucrose [12] and raffinose [6] solutions were taken from literature data. The densities of the penta-erythritol and mannitol solutions were measured with the use of different types of pycnometers at 25 °C. The concentration range was always so chosen that the density ϱ was linear in the concentration according to $\varrho = \varrho_0 + Ac$ (c in g/ml). The values of A ($= \partial\varrho/\partial c$) have been mentioned in Table II. The partial molar volumina were calculated according to

$$v_1 = \frac{M_1\left(1 - \frac{\partial \varrho}{\partial c}\right)}{\varrho - c\frac{\partial \varrho}{\partial c}}, \tag{4-10}$$

$$v_0 = \frac{M_0}{\varrho - c\frac{\partial \varrho}{\partial c}}. \tag{4-11}$$

Dunlop [8] gives for the partial molar volume of mannitol 119.42 cm³/mole at 25 °C; Kelly, Mills and Stokes [20] report a partial molar volume for penta-erythritol being 101.7 cm³/mole at 25 °C. Our results (Table II) confirm these data.

CHAPTER 5

RESULTS AND THEIR INTERPRETATION

§ 1. *The Test of the Onsager Reciprocal Relation*

In our opinion the test of the ORR is the first way to set about measurements in the field of solute permeable membranes [36]. Yet, for these fundamental relations to be valid some essential conditions concerning the system must be fulfilled.

First, the system is not allowed to be too far from equilibrium so that the forces remain linear functions of the fluxes. In practice it means that the concentration difference across the membrane must be chosen as small as is possible in osmotic experiments ($c_1^{\alpha}/\bar{c}_1$ may not deviate too much from unity), and that only moderate pressures are permitted in ultrafiltration.

Moreover, the membrane must be homogeneous throughout. In this connection we recall the attention to the treatment of composite membranes by Kedem and Katchalsky [19]. They have pointed out that the ORR may break down in the case of heterogeneity of the membrane.

Finally, the validity of the ORR is based on the implied condition that for the membrane the state pertaining to ultrafiltration does not differ from the state pertaining to an osmotic experiment. Let us illustrate this with an example. Suppose we compare the reflection coefficient of a system measured by ultrafiltration with the one obtained from an osmotic experiment. Suppose, however, that the membrane shows a stronger adsorption with respect to the solute during ultrafiltration than during the osmotic experiment. It may then be expected that the reflection coefficient resulting from the former method is greater than that originating from the latter, leading to an apparent failure of the ORR. In fact one has measured not only in two different states but also with two different membranes. The question is of importance when one measures, for instance, σ and L_P by ultrafiltration and ω by an osmotic experiment. In doing this one risks obtaining a non-consistent set of experimental quantities.

From these considerations it is clear that the presence of disturbing factors, such as the non-linearity of the flow equations, the heterogeneity of the membrane and the occurrance of adsorption can cause deviations in the ORR. If, on the other hand no deviations are observed in the equalities which, as a consequence of the ORR ought to exist between some distinct experimental quantities, it inspires confidence in the ORR themselves as well as in the procedure of measurement followed.

A number of ultrafiltration experiments was set up by us in which for several systems σ was measured ($-L_{CP}/L_P$ in Table III). On both sides of the membrane the solute concentration was taken equal to 5 g/l; the overpressures applied amounted to 2.5 atm. The membranes, though different, all had a filtration coefficient L_P of about 30 mm^3/h atm.

Table III. Test of the Onsager reciprocal relation in Vycor glass membranes for different aqueous sugar solutions.
From ultrafiltration: $\sigma = -L_{CP}/L_P$; from an osmotic experiment and known $\Delta\Pi$: $\Delta P^*/\Delta\Pi = -L_{PC}/L_P$.

Membrane	Solute	$-L_{PC}/L_P$	$-L_{CP}/L_P$
M 2.	Sucrose	0.198	0.204
M 1.	Mannitol	0.124	0.130
M 3.	Mannitol	0.112	0.106
M 1.	Raffinose	0.28	0.30
M 3.	Raffinose	0.25	0.24

Estimated limits of error $-L_{PC}/L_P$: 1–3%; $-L_{CP}/L_P$: 3–5%.

Table IV. The average concentrations during the osmotic experiments (g/l)

	c_1^{α}	c_1^{β}	$\bar{c}_1$	$(c_1^{\alpha}/\bar{c}_1 - 1)$
Sucrose	15.71	0.81	5.03	2.12
	11.57	1.58	5.02	1.30
Mannitol	10.00	2.03	5.00	1.00
	9.64	2.17	5.01	0.92
	8.74	2.58	5.00	0.73
	8.21	2.76	5.05	0.64
Raffinose	10.03	2.02	5.00	1.01
	10.02	2.02	5.00	1.00
	9.24	2.31	5.00	0.85
	8.76	2.51	5.00	0.75

As well as ultrafiltration we have also carried out several osmotic experiments, of which the corresponding concentrations are mentioned in Table IV. The average concentration $\bar{c}_1$ is the logarithmic mean defined in Appendix I and equals as closely as possible the concentration used in ultrafiltration. The last column of Table IV indicates how far the system was from equilibrium. The reflection coefficients were found to be rather independent of concentration. Their average values are shown in Table III ($-L_{PC}/L_P$).

It is seen from Table III that the agreement between the quantities measured in different states is reasonable and that the relation of Staverman (2-40) holds true for our systems. The experimental evidence for the validity of the ORR in the case of a simple membrane transport process involving two permeating non-electrolytes is also confined in the work of Talen and Staverman [42], Cleland [3] and Krämer and Sauer [23].

Table V. The experimental data of the osmotic experiments.

	c_α^0 g/l	c_β^0 g/l	c_α^e g/l	c_β^e g/l	L_P mm³/h atm	ΔP^* atm
Penta-erythritol – Membrane 4						
0.	0.000	0.000	0.000	0.000	35.60	0.000
1.	9.993	3.489	9.560	3.523	34.55	0.094[9]
2.	15.014	5.304	14.631	5.353	33.85	0.141
3.	19.990	7.272	19.435	7.351	33.61	0.177
4.	25.003	9.129	24.331	9.206	33.08	0.227
5.	30.011	10.941	29.280	11.046	32.72	0.275
6.	34.967	12.848	34.157	12.968	32.02	0.319
Mannitol – Membrane 5						
0.	0.000	0.000	0.000	0.000	26.32	0.000
1.	9.996	4.046	9.714	4.071	25.37	0.094[1]
2.	15.002	5.995	14.677	6.047	25.54	0.146
3.	20.021	7.969	19.737	8.028	25.67	0.198
4.	25.000	9.947	24.606	9.997	25.06	0.238
5.	29.701	11.766	29.207	11.823	25.01	0.290
6.	35.048	13.879	34.525	13.949	25.23	0.347
Sucrose – Membrane 5						
0.	0.000	0.000	0.000	0.000	28.97	0.000
1.	10.01	4.00	9.92	4.01	28.16	0.079[1]
2.	20.01	10.96	19.77	10.97	27.53	0.123
3.	30.02	17.87	29.80	17.90	27.07	0.167
4.	39.51	24.54	39.19	24.61	25.85	0.206
5.	49.99	31.63	49.69	31.70	25.39	0.259
6.	60.03	38.72	59.43	38.82	24.70	0.303
Raffinose – Membrane 6						
0.	0.000	0.000	0.000	0.000	27.51	0.000
1.	9.971	3.605	9.780	3.612	27.27	0.078[4]
2.	14.939	5.494	14.798	5.511	26.88	0.117
3.	19.895	7.406	19.653	7.425	26.41	0.151
4.	24.853	9.361	24.546	9.385	25.91	0.185
5.	29.818	11.209	29.476	11.235	24.89	0.224
6.	34.756	12.719	34.430	12.750	25.22	0.267

§ 2. *The Evaluation of the Experimental Quantities*

Our main practical purpose was to determine a consistent set of σ, L_P and ω as a function of the solute concentration $\bar{c}_1$. The validity of the ORR for our systems opens up two possible ways for measuring σ: directly by an ultrafiltration, and indirectly by measuring the apparent osmotic pressure ΔP^* and using the relation of Staverman (2-40). For the latter method $\Delta\Pi$ must be known. L_P, too, can be measured by the same two procedures on the basis of (2-34) and (2-44). Yet we have given preference to measuring L_P and σ by an osmotic experiment ($\Delta c \neq 0$), whereas for ω there was no alternative but to use the relaxation experiment. There were several reasons for doing this. Firstly, we considered it important to keep the membrane under the most equal conditions possible. In view of the fact that ω only could be determined by a relaxation experiment this condition must be $\Delta c \neq 0$. If σ or L_P had been measured by ultrafiltration ($\Delta c = 0$) and ω by an osmotic experiment ($\Delta c \neq 0$), it would have led to indesirable discrepancies. In this connection we should point out the fact that although the ORR are valid there always remains a difference between the reflection coefficients found in different ways, as is apparent in Table III. Moreover, the values for L_P resulting from ultrafiltration turned out to be about 1% lower than the corresponding values obtained from osmotic experiments. Evidently it makes some difference whether the membrane is in a state $\Delta c = 0$ or $\Delta c \neq 0$.

In the Tables V and VI the outside concentrations are shown for both the osmotic and the relaxation experiments. The superscripts 0 and e refer to the concentration at the beginning and at the end of the experiment concerned.

In the relatively short ΔP^* measurements (Table V) the concentrations do not vary much during the measurements. Here two effects counteract each other: the permeation of solute from the α to the β compartment causes a decrease of the concentration difference across the membrane, whereas the net transport of the solvent, induced by the dynamical application of overpressures, produces the reverse effect. In the rather long ω measurements (Table VI) the variations of the concentrations are much larger, while, moreover, the static overpressure, being nearly equal to ΔP^* hardly gives rise to the occurence of a convective flow across the membrane. From both Tables V and VI it is clearly seen that the concentrations remain the more constant according as the molecular weight of the permeating solute is higher. The average concentration during an experiment was calculated as follows. First the logarithmic mean values of the initial concentration $\bar{c}_1^{\,0}$ and of the final concentration $\bar{c}_1^{\,e}$ were calculated according to (3-25), after which the arithmetical mean was taken of $\bar{c}_1^{\,0}$ and $\bar{c}_1^{\,e}$.

The measured values for L_P and ΔP^* have been collected in Table V. The limits of errors found (standard deviations) were 0.5–1.0% for L_P and 1–3% for ΔP^*. Obviously L_P decreases systematically with increasing $\bar{c}_1$. For each system ΔP^* turns out to be nearly proportional to the concentration difference across the membrane.

In Table VI we have placed in the last columns the times of measuring (t_e) and the

Table VI. The experimental data of the relaxation experiments.

	c_α^0 g/l	c_β^0 g/l	c_α^e g/l	c_β^e g/l	t_e h	λ h^{-1}
Penta-erythritol – Membrane 4						
1.	9.988	3.488	8.714	3.631	24.00	10.24×10^{-3}
2.	15.028	5.306	13.359	5.482	21.00	10.02
3.	20.004	7.275	18.377	7.446	15.00	10.15
4.	25.008	9.131	23.400	9.311	12.00	9.96
5.	30.033	10.952	28.378	11.132	10.00	10.18
6.	34.963	12.836	33.518	13.034	8.00	9.65
Mannitol – Membrane 5						
1.	10.003	4.049	9.287	4.124	20.60	6.94×10^{-3}
2.	15.021	5.995	13.967	6.097	19.00	7.25
3.	20.010	7.974	18.447	8.119	21.10	7.30
4.	25.017	9.958	22.868	10.151	23.50	7.25
5.	29.738	11.772	28.057	11.924	15.60	6.97
6.	35.024	13.870	33.330	14.041	13.00	7.18
Sucrose – Membrane 5						
1.	10.008	3.992	9.434	4.058	23.90	4.72×10^{-3}
2.	20.003	10.955	19.147	11.040	24.10	4.58
3.	30.03	17.86	28.65	18.00	29.10	4.62
4.	39.51	24.54	37.91	24.68	27.00	4.58
5.	50.08	31.63	48.70	31.77	19.00	4.60
6.	60.04	38.74	57.75	38.95	27.50	4.61
Raffinose – Membrane 6						
1.	9.978	3.607	9.391	3.664	35.50	3.00×10^{-3}
2.	14.959	5.496	14.076	5.582	36.40	2.97
3.	19.895	7.406	18.735	7.512	36.20	2.95
4.	24.878	9.363	23.499	9.492	34.30	2.98
5.	29.858	11.209	28.703	11.294	21.50	3.20
6.	34.875	12.728	33.935	12.804	14.90	3.15

reciprocal relaxation times (λ). The small values of the latter quantities reflect the very slow progress of the permeation processes. It must be noted that λ is found to be rather independent of the magnitude of the concentration difference and the average solute concentration.

In Table VII the experimental quantities have been compiled as a function of the average volume fraction of the solute. The volume fractions were obtained by multiplication of $\bar{c}_1$ (calculated from the osmotic data of Table VI) with v_1 the partial molar volume of the solute. The reflection coefficients (σ) were calculated by dividing ΔP^* by $\Delta\Pi$ previously evaluated from the measured concentration data and, in the case of mannitol and sucrose, even with the use of the osmotic coefficients [33, 34]. The solute permeabilities (ω) were calculated according to (4-5). Moreover, using (4-9) we have calculated solute permeabilities from the increase of the external concentration during the relaxation experiment (the values for ω in parentheses). With respect to L_p and ω the brackets [ ] mean that the relevant quantity has been multiplied with the factor d/A_m in order to obtain a specific quantity for the glass membrane. Concerning Table VII we make the following statements:

1. For the different systems considered the reflection coefficient σ proves to be constant in the measured range of concentration. In the case of sucrose this constancy could only be gained if the non-ideality was taken into account in the calculation of $\Delta\Pi$. Neglect of non-ideality generally leads to slowly decreasing values of σ with increasing concentration. The accuracy gained was better than 3% for all systems.
2. The filtration coefficient L_p decreases with increasing concentration, as already stated. The discrepancies between the value for the pure solvent found in different membranes must be explained by the difference in pore radius and pore volume. The accuracy was 0.5–1.0%.
3. The solute permeability ω is inclined to decrease slightly with increasing concentration, but this trend does not emerge clearly because it probably falls within the accuracy of measurement (5%). The balance of the solute flow entering and leaving the membrane is given by the two values for ω. Since this balance has been found reasonably fulfilled, the obtainable accuracy considered, it may be concluded that a quasi-stationary state was indeed present. Actually $\bar{\varphi}_1$ averaged over the relaxation experiment was somewhat smaller than the corresponding $\bar{\varphi}_1$ averaged over the osmotic experiment. Because of the weak dependence on concentration of ω observed we have ignored this fact completely, since it cannot be handled accurately and is not, in any case, important.

We note that the observed concentration dependence of σ, L_p and ω can be explained completely by assuming constant friction coefficients and a constant partition coefficient, as we have argued at the end of § 4, Chapter 3. The consequent dependence on concentration of the resistance coefficients to be expected on these grounds means a constancy of R_{10} and $R_{11}\bar{c}_1$, and an increase with concentration for R_{00}. Indeed

Table VII. The experimental quantities as a function of the solute concentration in the glass membrane at 25 °C.

	$\bar{\varphi}_1$	σ	$[L_P]$ cm^4/dyne sec	$[\omega]$ mole cm/dyne sec
Penta-erythritol – Membrane 4				
0.	0.000×10^{-3}		0.5163×10^{-13}	
1.	4.584	0.0839	0.5010	1.17 (1.25) $\times 10^{-17}$
2.	6.948	0.0825	0.4909	1.15 (1.18)
3.	9.361	0.0795	0.4875	1.17 (1.11)
4.	11.724	0.0816	0.4798	1.15 (1.25)
5.	14.080	0.0821	0.4746	1.16 (1.19)
6.	16.485	0.0820	0.4644	1.11 (1.14)
Mannitol – Membrane 5				
0.	0.000×10^{-3}		0.3902×10^{-13}	
1.	4.316	0.120	0.3761	0.716 (0.81) $\times 10^{-17}$
2.	6.476	0.121	0.3786	0.749 (0.77)
3.	8.665	0.122	0.3806	0.740 (0.73)
4.	10.838	0.117	0.3715	0.740 (0.73)
5.	12.881	0.119	0.3708	0.708 (0.72)
6.	15.247	0.120	0.3740	0.724 (0.73)
Sucrose – Membrane 5				
0.	0.000×10^{-3}		0.4295×10^{-13}	
1.	4.071	0.184	0.4175	0.494 $\times 10^{-17}$
2.	9.415	0.188	0.4081	0.475 (0.49)
3.	14.815	0.187	0.4013	0.470 (0.47)
4.	20.072	0.185	0.3832	0.461 (0.46)
5.	25.861	0.186	0.3764	0.453 (0.47)
6.	31.582	0.186	0.3662	0.448 (0.43)
Raffinose – Membrane 6				
0.	0.000×10^{-3}		0.4118×10^{-13}	
1.	3.788	0.258	0.4076	0.330 $\times 10^{-17}$
2.	5.738	0.257	0.4018	0.344
3.	7.674	0.255	0.3947	0.340
4.	9.636	0.251	0.3873	0.344
5.	11.548	0.250	0.3720	0.370
6.	13.321	0.252	0.3770	0.364

this behaviour is recognized in the values shown in Table VIII, which indicate that the assumption of a constant partition coefficient and of constant friction coefficients is consistent with our results.

§ 3. *The Evaluation of the Friction Coefficients and the Partition Coefficient*

In Chapter 3 we have already discussed how the friction coefficients r_{10}, f_{1m}, f_{0m} and the partition coefficient K can be evaluated when σ, L_p and ω are known as a function of the concentration. In this section we shall be concerned in particular with the calculation of the quantities involved, and shall try to interprete the results.

r_{10} was calculated in the following way. First the resistance coefficient R_{10} was calculated according to (2-50) and then multiplied with the factor A_m/d yielding the more convenient specific quantity $[R_{10}]$. These values have been tabulated in the second column of Table VIII. According to (3-11) the simple relation $r_{10} = -[R_{10}]$ is valid. So the quoted values in Table VIII do represent r_{10} as function of the concentration. The case of sucrose excepted, r_{10} proves to be almost constant. Regarding the results with sucrose, we note that the friction coefficient in free solution r_{10}^f has an analogous behaviour in the rather extended concentration range considered. Probably the concentration ranges of the other solutes were not large enough for conclusive evidence on this point. In any case, our previous assumption about the constancy of r_{10} is justified after all, at least in a limited concentration range, by the practical results.

The performance of a duplo experiment with raffinose and a membrane more permeable than M 6 has led us to another striking property of r_{10}. Although L_p of the membrane used was about 1% higher and consequently σ was somewhat smaller and ω at the same time somewhat larger, the values of r_{10} found were exactly the same as those measured in the less permeable membrane M6. This result may be understood better upon closer inspection of (2-50). In fact we were dealing with membranes for which ωv_1 turned out to be much smaller than L_p. As a consequence of this the first term of the right-hand side of (2-50) contributes only to about 3% of the whole member, and r_{10} is determined mainly by the ratio $(1-\sigma)/\omega v_1$. Now the more permeable the membrane, the greater $(1-\sigma)$ and the greater ωv_1, but the ratio of these quantities is affected to a much less degree by a slightly increased permeability of the membrane, resulting in the mentioned insensitivity of r_{10}.

Whereas the constancy of r_{10} can easily be checked experimentally, this is more difficult in the case of f_{0m} and f_{1m}. On the grounds of (3-44) and (3-45) one finds in dilute solution that $(1-\sigma)/\omega$ is only a function of r_{10} and f_{0m}. This function must be constant – and is indeed found to be so – when neither r_{10} nor f_{0m} depend on concentration. Yet such a test of the constancy of f_{0m} is only meaningful provided $f_{0m}/\{v_0(1-\varphi_m^*)\}$ is at least of the same order as $r_{10}/(v_1 v_0)$. In the case of our membranes where, as we have seen, $\omega v_1 \ll L_p$, this procedure cannot be used. However, when both f_{0m} and f_{1m} are assumed to be constant there must exist a linear relation-

Table VIII. The resistance coefficients as a function of the solute concentration in the glass membrane at 25 °C.

	$\bar{c}_1$ mole/cm³	$[-R_{10}]$ dyne sec cm²/mole²	$[R_{11}]$ dyne sec cm²/mole²	$[R_{00}]$ dyne sec cm²/mole²	$[R_{11}]\bar{c}_1$ dyne sec/mole cm
Penta-erythritol – Membrane 4					
0.	0.000×10^{-5}			6.32×10^{15}	
1.	4.497	1.37×10^{18}	1.88×10^{21}	7.57	0.085×10^{18}
2.	6.816	1.39	1.26	8.28	0.086
3.	9.183	1.37	0.91	8.87	0.084
4.	11.501	1.39	0.74	9.56	0.085
5.	13.812	1.37	0.61	10.15	0.084
6.	16.172	1.43	0.54	11.04	0.088
Mannitol – Membrane 5					
0.	0.000×10^{-5}			8.37×10^{15}	
1.	3.605	2.16×10^{18}	3.85×10^{21}	9.95	0.139×10^{18}
2.	5.409	2.05	2.44	10.44	0.132
3.	7.237	2.07	1.84	11.04	0.133
4.	9.052	2.08	1.46	11.90	0.133
5.	10.758	2.16	1.30	12.65	0.140
6.	12.734	2.11	1.06	13.17	0.134
Sucrose – Membrane 5					
0.	0.000×10^{-5}			7.60×10^{15}	
1.	1.925	2.88×10^{18}	10.51×10^{21}	8.67	0.202×10^{18}
2.	4.452	2.97	4.66	10.02	0.211
3.	7.006	2.99	2.96	11.35	0.212
4.	9.491	3.04	2.21	12.98	0.213
5.	12.229	3.08	1.73	14.52	0.215
6.	14.934	3.09	1.42	16.13	0.215
Raffinose – Membrane 6					
0.	0.000×10^{-5}			7.94×10^{15}	
1.	1.238	3.72×10^{18}	23.26×10^{21}	8.65	0.287×10^{18}
2.	1.868	3.75	15.44	9.11	0.288
3.	2.497	3.79	11.63	9.60	0.290
4.	3.136	3.76	9.14	10.10	0.286
5.	3.759	3.48	7.07	10.64	0.266
6.	4.336	3.53	6.21	10.84	0.269

ship between $1/L_P$ and $(1-\sigma)\bar{\varphi}_1$ according to (3-42). We have expressed this in still more detail at the head of Table IX. The constants C and D have been calculated with the use of the method of least squares. The values in parentheses represent the standard deviations. In the case of mannitol only, the linearity found is poor. The values of f_{1m} and f_{0m} calculated from C and D are shown in Table XII.

Still better linear relationships are found between $[R_{00}]$ and $\bar{c}_1/\bar{c}_0$ as shown by the constants A and B, and their standard deviations in Table IX. The relation $[R_{00}] = A(\bar{c}_1/\bar{c}_0)+B$ is suggested by (3-38) under the assumption that when K does not differ much from unity, $(1-\bar{\varphi}_1 K)$ equals approximately $\bar{\varphi}_0$ and that both r_{10} and f_{0m} are constant. The expressions for A and B stand at the head of Table IX. Upon inspecting them it will be clear that provided r_{10} is known, K may be calculated from A and B. The values of K obtained can be seen from Table X, which also shows the average values of r_{10} used in the calculation. Another way to evaluate K is to start from calculated values of f_{1m} and f_{0m} and insert them into (3-43). This procedure yields somewhat smaller values of K than those mentioned in Table X in the order of 1–2%. For the system sucrose–water we had at our disposal data measured under the condition of equal external concentrations [41]. The value of K calculated from these data agrees completely with ours, which indicates that no experimental evidence is present for possible deviations caused by the fact that we have used (3-28) instead of (3-26). Nevertheless, we have measured K in experiments involving finite concentration differences obtaining so exactly the same conditions as those under which σ and L_P were measured.

The fact that in the case of mannitol, sucrose and raffinose the values of K turn out to be about unity, indicates that the membrane acts as chemically indifferent. Contrary to this, some adsorption occurs in the case of penta-erythritol, where K is significantly greater than unity. However, this anomalous behaviour of penta-erythritol is also clearly seen in Table XI. In the first column of Table XI we have collected the mutual diffusion coefficients of the different solutes extrapolated to zero concentration. The second column of this table shows the values of the corresponding friction coefficients in free solution, which have been calculated according to (3-46). In the last column we have presented the ratio $r_{10}^f/\{r_{10}(1-\varphi_m^*)\}$, which does not depend on the solute as far as mannitol, sucrose and raffinose are concerned. The exception mentioned is formed by penta-erythritol. This may be interpreted as follows. Equation (3-47) has been derived from purely geometrical considerations and consequently ϑ^2 is supposed to depend on the geometry of the membrane only. This is apparent in the fact that ϑ^2 assumes the same value for mannitol, sucrose and raffinose. However the fact that for penta-erythritol we find a different value, combined with the fact that for penta-erythritol K differs from unity, shows that within our present theoretical insight purely geometrical and purely chemical effects cannot be separated, except in membranes which are chemical inert. The physical meaning of this state of affairs may be described by saying that, as soon as the membrane shows preferential adsorption of a component, some molecules of this component behave

Table IX. The linear dependence on concentration of R_{00} and $1/L_P$ according to

$$[R_{00}] = A(\bar{c}_1/\bar{c}_0)+B \quad \text{and} \quad 1/[L_P] = C(1-\sigma)\bar{\varphi}_1+D$$

$$A = K\left\{r_{10} + \frac{f_{0m}v_1}{(1-\varphi_m^*)}\right\} \qquad C = \frac{f_{1m}}{v_1(1-\varphi_m^*)} - \frac{f_{0m}}{v_0(1-\varphi_m^*)}$$

$$B = \frac{f_{0m}v_0}{(1-\varphi_m^*)} \qquad D = \frac{f_{0m}}{v_0(1-\varphi_m^*)}$$

Solute/ membrane	A dyne sec cm^2 / mole^2	B dyne sec cm^2 / mole^2	C dyne sec / cm^4	D dyne sec / cm^4
Penta-erythritol M4	1.58×10^{18} ($\pm$0.03)	6.29×10^{15} ($\pm$0.06)	13.7×10^{13} ($\pm$0.5)	1.94×10^{13} ($\pm$0.01)
Mannitol M5	2.09 ($\pm$0.08)	8.42 ($\pm$0.12)	8.2 ($\pm$2.6)	2.59 ($\pm$0.02)
Sucrose M5	3.06 ($\pm$0.03)	7.56 ($\pm$0.05)	15.6 ($\pm$0.7)	2.33 ($\pm$0.01)
Raffinose M6	3.85 ($\pm$0.13)	7.87 ($\pm$0.07)	27.0 ($\pm$4.2)	2.40 ($\pm$0.03)

Table X. The friction coefficient r_{10} and the partition coefficient K in the glass membrane at 25 °C

Solute	r_{10} dyne sec cm^2/mole^2	K
Penta-erythritol M4	1.39×10^{18} ($\pm$0.02)	1.10 ($\pm$0.03)
Mannitol M5	2.11 ($\pm$0.08)	0.96 ($\pm$0.05)
Sucrose M5	3.01 ($\pm$0.08)	0.99 ($\pm$0.03)
Raffinose M6	3.67 ($\pm$0.16)	1.01 ($\pm$0.06)

Table XI. The friction between the solute and water in free solution and in the glass membrane at 25 °C.

Solute	$\mathscr{D}$ cm^2/sec	r_{10}^f dyne sec cm^2 / mole^2	$(1-\varphi_m^*)$	r_{10} dyne sec cm^2 / mole^2	$\frac{r_{10}^f}{(1-\varphi_m^*)r_{10}}$
Penta-erythritol [20]	7.61×10^{-6}	5.886×10^{16}	0.352	1.39×10^{18}	0.12
Mannitol [8]	6.664	6.721	0.309	2.11	0.10
Sucrose [12]	5.226	8.571	0.324	3.01	0.09
Raffinose [6]	4.359	10.276	0.288	3.67	0.10

differently from those moving in the "pore liquid" and both types of molecules contribute in a different way to the overall friction coefficients. In our case this evidently reflects an increased apparent tortuosity for the penta-erythritol molecules. Obviously the "pore model" fits the cases of mannitol, sucrose and raffinose rather well, whereas a more general model, "the solution model", must be adopted in the case of penta-erythritol.

A general view of the frictions present in the system has been given in Table XII. The friction coefficient f_{ik} indicates the friction exerted on one mole i by all moles present of species k. Thus $f_{10} = r_{10}c_0^*$ and $f_{01} = r_{01}\bar{c}_1^*$. From Table XII it is seen that:

1. $f_{10} > f_{1m}$: one mole of the solute undergoes more friction from the solvent than from the membrane material during permeation. The effect is the stronger according as the molecular weight of the permeating solute is larger.
2. $f_{1m} \gg f_{0m}$: the membrane exerts more friction on one mole of the solute than on one mole of the solvent during permeation. In the sequence of mannitol, sucrose and raffinose this effect is stronger according as the molecular weight increases. The relatively large value of f_{1m} in the case of penta-erythritol may be explained by the occurrence of adsorption of this solute.
3. f_{0m} is of the order of f_{01}: in the concentration range of 0 till 1×10^{-4} mole/cm^3 one mole of the solvent undergoes friction from the membrane which is of the same order as the friction from the solute. The influence of the solute becomes larger according as its molecular weight and its concentration increase.
4. The remaining discrepancies between the different f_{0m} of the membranes used must be explained on the grounds of the differences in c_m and the average pore radius.

Table XII. The friction coefficients of the different components in dynesec/molecm in the glass membrane at 25 °C.

Solute/ membrane	$(1-\varphi_m^*)$	f_{10}	f_{1m}	f_{0m}	f_{01} ($\bar{c}_1$ in mole/cm^3)		
					1×10^{-5}	0.5×10^{-4}	1×10^{-4}
Penta-erythritol M4	0.352	7.69×10^{16}	0.56×10^{16}	1.23×10^{14}	1.39×10^{13}	0.70×10^{14}	1.39×10^{14}
Mannitol M5	0.309	11.68	0.40	1.44	2.11	1.06	2.11
Sucrose M5	0.324	16.66	1.23	1.36	3.01	1.51	3.01
Raffinose M6	0.288	20.31	2.60	1.25	3.67	1.85	...

§ 4. *Summarizing Conclusions*

The mechanism of an isotherm transport process through a membrane involving two non-electrolytic permeants can be characterized by a purely phenomenological description in terms of friction and partition, as we have shown theoretically in Chapter 3.

Experimentally we have shown this by analysing the permeation of the successive solutes: penta-erythritol, mannitol, sucrose and raffinose, and of the solvent water, through a Vycor glass membrane. In these systems states of nearly stationary flow can be established and maintained for long periods of time (Fig. 4.5 and 4.6), as is necessary for determining the experimental quantities σ, L_P and ω (Chapter 2).

The course of the permeation process was characterized by means of two types of coefficients:

1. The partition coefficient K, relating the internal and external concentrations of both permeants, and indicating whether or not there was adsorption of any component within the membrane.
2. The friction coefficient r_{10} accounting for the friction exerted by one mole of the solvent on one mole of the solute, and the friction coefficients f_{1m} and f_{0m} accounting for the friction exerted by the membrane respectively on one mole of the solute and one mole of the solvent.

All these coefficients were calculated from values of σ, L_P and ω measured as a function of the composition. The evaluation of r_{10} from the experimental quantities involves a minimum of assumptions; not even the solute concentration within the membrane nor the partition coefficient needs be known. For the evaluation of f_{1m} and f_{0m} more assumptions must be made. r_{10} was experimentally found to be constant in the concentration ranges considered. The assumed constancy of K, f_{0m} and f_{1m} could subsequently be confirmed, as it was consistent with the observed slight change of the experimental quantities with the concentration.

From the description as a whole two relevant characteristics emerge:

1. The partition coefficient K, which gives a primary indication of the chemical interaction of the membrane with one of the components.
2. The frictional ratio r_{10}^f/r_{10}, being the quotient of the friction coefficients in free solution (f) and within the membrane. The frictional ratio gives, at least in a chemically indifferent membrane, information about the geometrical influence of the membrane, and in particular about its porosity and the tortuosity of the diffusion paths within it (3-47).

We have found that the permeation of mannitol, sucrose and raffinose is not accompanied by adsorption of these solutes by the membrane, and that the friction between these solutes and the solvent water is not essentially affected by the presence of the

membrane. These two facts are recognized in Table X where K is about unity, and in Table XI where $r_{10}^f/\{r_{10}(1-\varphi_m^*)\}$ has the same value for these solutes and equals the purely geometrical tortuosity ϑ^2 (3-47).

On the other hand, we have found that in the case of penta-erythritol some adsorption of this solute occurs, as is evident in Table X where K is significantly larger than unity. In complete agreement with this we see in Table XII that f_{1m} is relative large for penta-erythritol compared to the corresponding values of the other solutes.

Now this adsorption has an important corollary. The penta-erythritol molecules will be in two different states within the membrane: "free" in the pore liquid or "bound" in the adsorbed layers. Consequently r_{10} can only refer to the "overall behaviour" of the solute with respect to the solvent, leading, as is seen in Table XI, to an apparently increased value of ϑ^2 which so loses its purely geometrical character.

It must be noted that an adsorption phenomenon as above would have been obscured in a conventional description in terms of σ, L_p and ω, and that for this reason we have given preference to an analysis based on friction and partition. However, the case of penta-erythritol has taught us that r_{10} is essentially different from r_{10}^f if adsorption occurs, and that it is impossible in such cases to distinguish between the purely geometrical properties of the membrane (r_{10}^f/r_{10} if $K = 1$) and the chemical properties (K). Nevertheless, we have shown in Chapter 3 § 5 that for a satisfactory and unambiguous distinction between the "pore model" and the "solution model" both K and r_{10}^f/r_{10} should be taken into consideration.

APPENDIX I

ON THE EFFECTIVE SOLUTE CONCENTRATION OUTSIDE THE MEMBRANE

By means of (2-8) and (2-9) we have introduced average concentrations which are of particular interest when we meet with finite concentration differences across the membrane. Applying these equations to the case where two components are present ($n = 1$), we write for the average volume fraction quite generally

$$\bar{\varphi}_1 = \bar{c}_1 v_1 = \frac{1}{1 - \dfrac{\Delta\mu_1 v_0}{\Delta\mu_0 v_1}}. \tag{I-1}$$

$\Delta\mu_1$ and $\Delta\mu_0$ can be expressed in terms of the solute concentrations present in the α and the β cell of the osmometer. We shall perform this for the special case of ideal solutions, which are so dilute that in a good approximation

$$\bar{c}_1 = -\frac{\Delta\mu_0}{v_0 \Delta\mu_1}. \tag{I-2}$$

Using the familiar relations

$$-\frac{\Delta\mu_0}{v_0} = \Delta\Pi = RT(c_1^\alpha - c_1^\beta)$$

and

$$\Delta\mu_1 = RT \ln(c_1^\alpha / c_1^\beta),$$

where R and T stand respectively for the gas constant and the absolute temperature, we arrive at

$$\bar{c}_1 = \frac{c_1^\alpha - c_1^\beta}{\ln(c_1^\alpha / c_1^\beta)}. \tag{I-3}$$

For the case of a dilute multi-component system we proceed as follows. We integrate the Gibbs-Duhem relation

$$\sum_i c_i \mathrm{d}\mu_i = 0$$

across the membrane according to

$$\int_\beta^\alpha \sum_i c_i \mathrm{d}\mu_i = 0,$$

which by defining

$$\bar{c}_i = \int_{\beta}^{\alpha} \frac{c_i \mathrm{d}\mu_i}{\Delta\mu_i} \qquad (i = 0, 1, 2, \ldots, n) \tag{I-4}$$

is in accordance with (2-8). For ideal solutions

$$\mathrm{d}\mu_i = RT\,\mathrm{d}\ln c_i$$

and

$$\Delta\mu_i = RT \ln (c_i^{\alpha}/c_i^{\beta}), \qquad (i = 1, 2, \ldots, n)$$

which combined with (I-4) yields

$$\bar{c}_i = \frac{c_i^{\alpha} - c_i^{\beta}}{\ln (c_i^{\alpha}/c_i^{\beta})}. \qquad (i = 1, 2, \ldots, n) \tag{I-5}$$

The logarithm may be developed in the series

$$\ln (c_i^{\alpha}/c_i^{\beta}) = 2\left\{\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_i^{\alpha} + c_i^{\beta}}\right) + \tfrac{1}{3}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_i^{\alpha} + c_i^{\beta}}\right)^3 + \tfrac{1}{5}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_i^{\alpha} + c_i^{\beta}}\right)^5 + \ldots\right\},$$

which can be substituted into (I-5), resulting in

$$\bar{c}_i = \frac{\tfrac{1}{2}(c_i^{\alpha} + c_i^{\beta})}{\left\{1 + \tfrac{1}{3}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_i^{\alpha} + c_i^{\beta}}\right)^2 + \tfrac{1}{5}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_i^{\alpha} + c_i^{\beta}}\right)^4 + \ldots\right\}}. \qquad (i = 1, 2, \ldots, n) \tag{I-6}$$

By replacing in (I-6) the index i by 1 also an expansion of (I-3) is obtained. It is clearly seen from (I-6) that only in the limit $c_i^{\alpha} = c_i^{\beta}$ the average concentration $\bar{c}_i$ becomes an arithmetical mean and that in all other cases negative deviations from this value occur. It is easy to show that for very dilute solutions $\bar{c}_0 \approx 1/v_0$ in accordance with (2-9).

A particular situation arises when c_i^{β} equals zero, for instance, at the very beginning of an osmotic experiment where pure solvent is present on the β side of the membrane. Then the average concentration $\bar{c}_i$ becomes equal to zero and looses its operational value in transformations involving (2-8). Thus the flow equations resulting from these transformations are strictly valid when finite concentrations are present on both sides of the membrane. Such, however was the case in our experiments. Moreover, it must be noted that when c_i^{β} vanishes the force $\Delta\mu_i$ in (2-1) tends to infinity.

APPENDIX II

ON THE EVALUATION OF THE REFLECTION COEFFICIENTS AND THE SOLUTE PERMEABILITIES

We wish to derive here the equations (2-70) to (2-73), which indicate how σ_n, σ_w, $(\omega_s)_n$ and $(\omega_s')_n$ can be expressed in terms of volumes and concentrations. The definitions of σ_w and σ_n are

$$\sigma_w = \left(1 - \frac{\sum_{k=1}^{n} J_k v_k}{\bar{\varphi}_s J_v} \right)_{\Delta\Pi = 0}, \tag{II-1}$$

$$\sigma_n = \left(1 - \frac{J_s}{\bar{c}_s J_v} \right)_{\Delta\Pi = 0}. \tag{II-2}$$

Recalling that

V^α is the volume of the bulk liquid present in the α compartment,

$c_s^\alpha V^\alpha$ is the number of moles of the whole solute present in the α compartment,

$\varphi_s^\alpha V^\alpha$ is the volume of the whole solute present in the α compartment,

we can formulate the flows ($\Delta\Pi = 0$) as time derivatives of these quantities according to

$$J_v = -\frac{\mathrm{d}V^\alpha}{\mathrm{d}t}, \tag{II-3}$$

$$\sum_{k=1}^{n} J_k v_k = -\frac{\mathrm{d}(\varphi_s^\alpha V^\alpha)}{\mathrm{d}t} = -\varphi_s^\alpha \frac{\mathrm{d}V^\alpha}{\mathrm{d}t} - V^\alpha \frac{\mathrm{d}\varphi_s^\alpha}{\mathrm{d}t}, \tag{II-4}$$

$$J_s = -\frac{\mathrm{d}(c_s^\alpha V^\alpha)}{\mathrm{d}t} = -c_s^\alpha \frac{\mathrm{d}V^\alpha}{\mathrm{d}t} - V^\alpha \frac{\mathrm{d}c_s^\alpha}{\mathrm{d}t}. \tag{II-5}$$

Introduction of the explicit expressions of the flows from (II-3) to (II-5) into (II-1) and (II-2) yields

$$\sigma_w = -\left(\frac{\mathrm{d} \ln \varphi_s^\alpha}{\mathrm{d} \ln V^\alpha} \right)_{\Delta\Pi = 0}, \tag{II-6}$$

$$\sigma_n = -\left(\frac{\mathrm{d} \ln c_s^\alpha}{\mathrm{d} \ln V^\alpha} \right)_{\Delta\Pi = 0}. \tag{II-7}$$

The solute permeabilities are defined by

$$(\omega_s)_n = \left(\frac{J_s}{\Delta\Pi} \right)_{J_v = 0}. \tag{II-8}$$

and

$$(\omega_s')_n = \left(\frac{\sum_{k=1}^{n} J_k v_k}{\Delta \Pi} \right)_{J_v = 0}. \tag{II-9}$$

For ideal solutions

$$\Delta \Pi = RT \Delta c_s \tag{II-10}$$

and when, moreover, in both the α and the β compartment the same distribution exists within the whole solute,

$$\Delta \Pi = \frac{RT \Delta \varphi_s}{v_n}, \tag{II-11}$$

where v_n is defined by (2-65).

Assuming that the number of moles of solute escaping per unit time from the α compartment equals the number of moles of solute entering the β compartment per unit time, we write for the solute flow ($\mathrm{d}V^{\alpha}/\mathrm{d}t = 0$)

$$J_s = -V^{\alpha} \frac{\mathrm{d}c_s^{\alpha}}{\mathrm{d}t} = V^{\beta} \frac{\mathrm{d}c_s^{\beta}}{\mathrm{d}t}$$

or

$$J_s = -\frac{V^{\alpha} V^{\beta}}{V^{\alpha} + V^{\beta}} \left(\frac{\mathrm{d} \Delta c_s}{\mathrm{d}t} \right). \tag{II-12}$$

Along the same lines of reasoning we find that

$$\sum_{k=1}^{n} J_k v_k = -\frac{V^{\alpha} V^{\beta}}{V^{\alpha} + V^{\beta}} \frac{\mathrm{d} \Delta \varphi_s}{\mathrm{d}t}. \tag{II-13}$$

Insertion of (II-10) and (II-12) into (II-8) and of (II-11) and (II-13) into (II-9) leads to respectively

$$(\omega_s)_n = -\frac{V^{\alpha} V^{\beta}}{RT(V^{\alpha} + V^{\beta})} \left(\frac{\mathrm{d} \ln \Delta c_s}{\mathrm{d}t} \right)_{J_v = 0} \tag{II-14}$$

and

$$(\omega_s')_n = -\frac{v_n V^{\alpha} V^{\beta}}{RT(V^{\alpha} + V^{\beta})} \left(\frac{\mathrm{d} \ln \Delta \varphi_s}{\mathrm{d}t} \right)_{J_v = 0}. \tag{II-15}$$

APPENDIX III

ON THE PRESSURE TERM IN THE CHEMICAL POTENTIAL OF THE SOLUTE

In those cases where only moderate pressures are applied, the pressure term in the chemical potential, $v_1 \Delta P$, may be ignored with respect to the concentration term $\Delta \mu_1$. If $J_v = 0$, we obtain on the one side with the help of (2-40),

$$v_1 \Delta P^* = v_1 \sigma \Delta \Pi. \tag{III-1}$$

From (I-1) it follows on the other hand, with the help of (2-20), and after some rearrangement, that

$$\Delta \mu_1 = \frac{(1-\bar{\varphi}_1) v_1 \Delta \Pi}{\bar{\varphi}_1}. \tag{III-2}$$

Combining (III-1) and (III-2) yields

$$\frac{v_1 \Delta P^*}{\Delta \mu_1} = \frac{\sigma \bar{\varphi}_1}{(1-\bar{\varphi}_1)}. \tag{III-3}$$

The right-hand side of (III-3) is in our cases of the order of 10^{-3}. Thus, even when pressures are applied of several times ΔP^*, the pressure term remains small compared with the concentration term.

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SAMENVATTING

Het mechanisme van een isotherm transportproces door een membraan, waarbij twee permeërende niet-elektrolyten betrokken zijn, kan gekarakteriseerd worden door een zuiver fenomenologische beschrijving uitgedrukt in frictie en partitie zoals we het theoretisch hebben laten zien in hoofdstuk 3.

We hebben dit experimenteel laten zien door de permeatie te analyseren van de volgende opgeloste stoffen: penta-erythritol, mannitol, sucrose en raffinose en van het oplosmiddel water door een Vycor glasmembraan. In deze systemen kunnen toestanden ingesteld en gedurende lange tijd gehandhaafd worden, waarbij de stromen nagenoeg stationair blijven (fig. 4.5 en 4.6), hetgeen noodzakelijk is om de experimentele grootheden σ, L_p en ω te bepalen.

Het verloop van het permeatie-proces werd gekarakteriseerd door twee soorten coëfficiënten:

1. De partitie-coëfficiënt K, die de interne en externe concentraties van beide permeërende componenten met elkaar in verband brengt en aangeeft of er al dan niet een component wordt geadsorbeerd.
2. De frictie-coëfficiënt r_{10}, die rekenschap geeft van de frictie die door één mol oplosmiddel wordt uitgeoefend op één mol opgeloste stof en de frictie-coëfficiënten f_{0m} en f_{1m}, die rekenschap geven van de frictie uitgeoefend door het membraan respectievelijk op één mol oplosmiddel en één mol opgeloste stof.

Al deze coëfficiënten werden berekend uit waarden van σ, L_p en ω, gemeten als functie van de samenstelling. De berekening van r_{10} uit de experimentele grootheden brengt een minimum aan onderstellingen met zich mee; zelfs de concentratie van de opgeloste stof in het membraan of de partitie-coëfficiënt behoeft niet bekend te zijn. Om f_{1m} en f_{0m} te berekenen moeten meer onderstellingen worden gemaakt. Experimenteel werd gevonden, dat r_{10} constant was in het beschouwde concentratiegebied. De onderstelde constantheid van K, f_{0m} en f_{1m} kon achteraf bevestigd worden, daar dit consistent was met de waargenomen geringe verandering van de experimentele grootheden met de concentratie.

Uit de totale beschrijving komen twee ter zake dienende karakteristieken duidelijk naar voren:

1. De partitie-coëfficiënt K, die een eerste aanduiding geeft voor de chemische interactie van het membraan met een van de componenten.
2. De frictieverhouding r_{10}^f/r_{10}, het quotiënt van de frictie-coëfficiënten in vrije oplossing (f) en in het membraan. De frictieverhouding geeft, althans in een

chemisch indifferent membraan, informatie over de geometrische invloed van het membraan en wel in het bijzonder over zijn poreusheid en de tortueusheid van de diffusie-wegen daarbinnen (3-47).

We hebben gevonden, dat de permeatie van mannitol, sucrose en raffinose niet gepaard gaat met adsorptie van deze opgeloste stoffen door het membraam en dat de frictie tussen deze stoffen en het oplosmiddel niet wezenlijk beïnvloed wordt door de aanwezigheid van het membraan. Deze beide feiten worden teruggevonden in Tabel X, waar K ongeveer één is en in Tabel XI, waar $r_{10}^f/\{r_{10}(1-\varphi_m^*)\}$ dezelfde waarde heeft voor deze opgeloste stoffen en gelijk is aan de zuiver geometrische ϑ^2 (3-47).

Daarentegen hebben we gevonden, dat in het geval van penta-erythritol enige adsorptie optreedt, zoals duidelijk te zien is in Tabel X, waar K significant groter is dan één. In volledige overeenstemming hiermee, zien we in Tabel XII, dat f_{1m} relatief groter is voor penta-erythritol in vergelijking met de overeenkomstige waarden voor de andere opgeloste stoffen.

Deze adsorptie nu heeft een belangrijk nevengevolg. De penta-erythritol-moleculen zullen in twee verschillende toestanden verkeren in het membraan: „vrij" in de poriënvloeistof of „gebonden" in de geadsorbeerde lagen. Dientengevolge kan r_{10} slechts betrekking hebben op het „totaalgedrag" van de opgeloste stof ten opzichte van het oplosmiddel, hetgeen leidt, zoals men ziet in Tabel XI, tot een schijnbaar toegenomen waarde van ϑ^2, die zo zijn zuiver geometrisch karakter verliest.

Het is juist dit adsorptieverschijnsel, dat verdoezeld zou zijn in een conventionele beschrijving uitgedrukt in σ, L_P en ω, en juist om die reden hebben wij de voorkeur gegeven aan een analyse gebaseerd op frictie en partitie. Het geval van penta-erythritol heeft ons echter geleerd, dat r_{10} essentieel verschilt van r_{10}^f, als er adsorptie optreedt en dat het onmogelijk is in dergelijke gevallen een onderscheid te maken tussen de zuiver geometrische eigenschappen van het membraan (r_{10}^f/r_{10}, als $K = 1$) en de chemische eigenschappen (K). We hebben evenwel in hoofdstuk 3, § 5 duidelijk laten zien, dat voor een bevredigend en ondubbelzinnig onderscheid tussen het „poriënmodel" en het „oplossingmodel" zowel K als r_{10}^f/r_{10} in overweging zouden moeten worden genomen.