A STUDY OF BI-IONIC MEMBRANE
POTENTIALS

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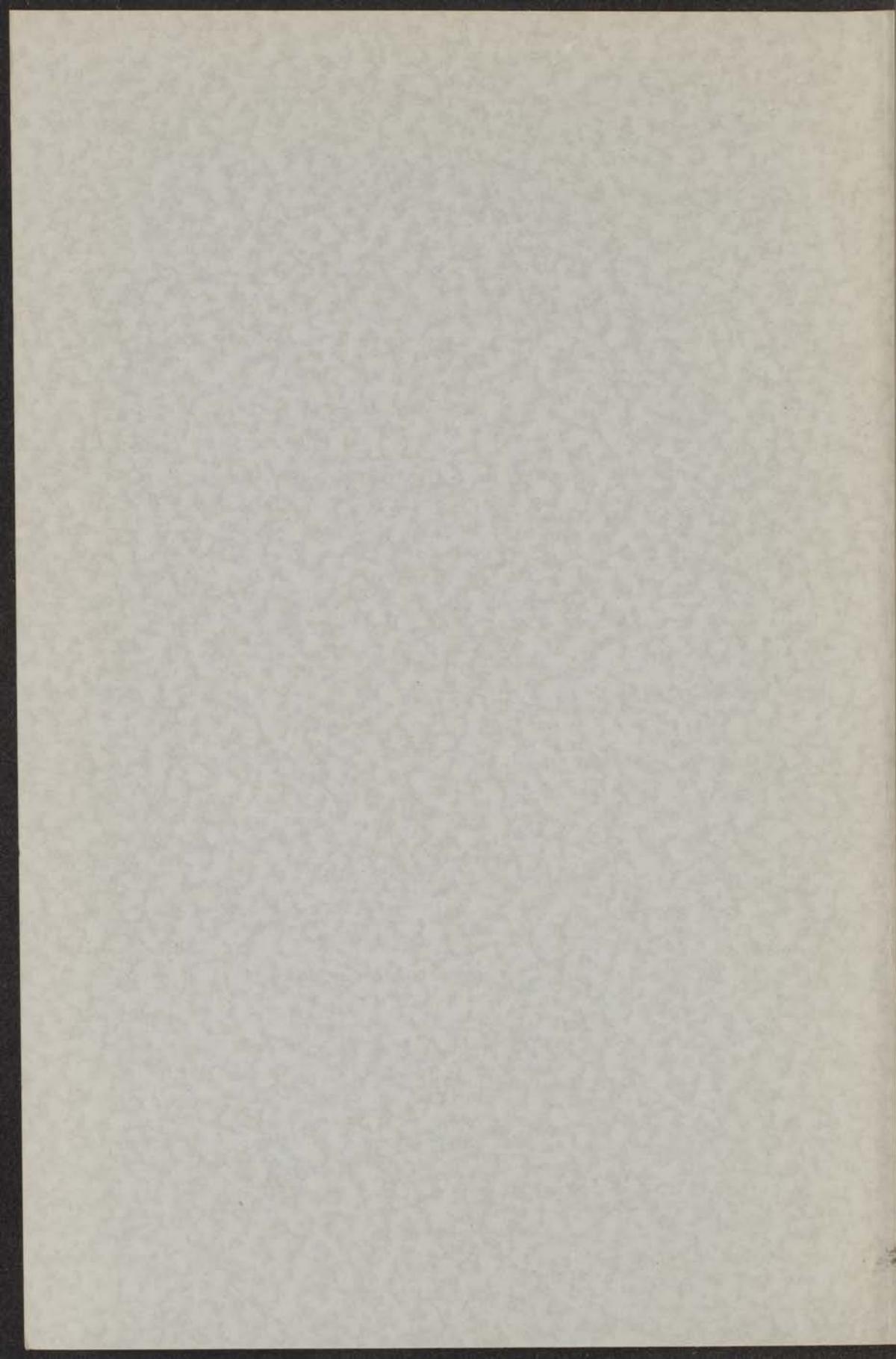
A STUDY OF BI-IONIC MEMBRANE POTENTIALS

PROEFSCHRIFT

FEIKE BERGSMA
GEBOREN TE OLDENZAAL IN 1920

Promotor: Prof. Dr. J. J. Hermans

Aan mijn ouders
Aan mijn vrouw

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INTRODUCTION

When a membrane is placed between two solutions of different composition a potential difference is, as a rule, established. If the two solutions contain the same electrolyte, but that in different concentrations, this potential is called concentration potential or dialysis potential. Its value is a measure for the selectivity of the membrane for ions of different sign. A membrane is called selective if the ratio of the transference numbers of cations and anions *in* the membrane has a value differing from that in the solution. A membrane is called anion selective if the transference number of the anions in the membrane is greater than that in the free solution. In the reverse case it is called cation selective.

According to current theories the selectivity is caused by the presence of charged groups fixed on the membrane skeleton. The charge of these groups is compensated by the counter-ions which are able to move freely in the imbibed solvent. If a selective membrane separates two solutions with different "critical" ions, the corresponding potential is called a bi-ionic potential (B.I.P.). "Critical" ions are ions that have the same sign of charge as the counter-ions and can exchange against them. When we have on one or on both sides of the membrane an electrolyte solution containing a mixture of "critical" ions, the corresponding potential is called multi-ionic potential. The B.I.P.'s are a measure for the selectivity of a membrane for ions of the same sign.

Investigations into this phenomenon are of great importance as these systems are frequently found in living organisms (red blood cell, frog skin, plant root cells, etc.). In the technical sector the interest is increasing too. In recent years membranes were successfully made on a semi-technical scale with a very high selectivity even in concentrated solutions. These membranes can be applied in electrolytic processes (desalting of seawater and brackish water, concentration of electrolytes, etc.).

Besides, researchwork is being done on the development of membranes with specific selectivity for definite ions or groups of ions, they show selectivity for ions of the same sign. Various investigators have measured B.I.P.'s for this kind of membrane in order to determine its selective properties. In particular the ratio of transference numbers has been derived from these B.I.P.'s in a wide concentration range. The basis of the relation between this ratio and the B.I.P. however, is not yet well established.

In this thesis an attempt will be made to give a critical survey of the existing formulae for the B.I.P. and to connect the B.I.P.'s with the ratio of transference numbers in such a way as is theoretically justified.

Another object is to examine in how far corrective terms in the
B.I.P. formulae affect the result. A special study was made of
the water transport. Attention is paid to the disturbing factors in
the measurements, particularly boundary-layer phenomena. The
research will be restricted to univalent ions.

I. LITERATURE ON ION SELECTIVE MEMBRANES

B. I. P. measurements are of great importance for the study of membranes with a specific selectivity. Hence it seems worthwhile to give in this thesis a brief review of the development of selective membranes and ion exchange resins which can be used as base for these membranes.

Though the interest in selective membranes dates from the beginning of this century, serviceable types were not successfully made until some years ago. The membranes, which were made earlier were less selective, especially with higher salt concentrations, besides they were often mechanically bad and frequently chemically less resistant. As negative membranes were used a.o. porcelain plates, asbestos, sintered glass, or collodion and cellophane films. The choice of positive membranes especially was very limited. Examples are: woollen fabrics impregnated with gelatine, films dyed with basic dyes, animal membranes such as hog's bladder and leather. The disadvantage of gelatine and other animal membranes is that they are amphoteric; they can be used as positive membranes only in the pH region below their iso-electric points. As for dyed membranes, the dye is sometimes dissolved too easily from the film.

The application of ion exchange resins as base for the membranes meant an important progress. An ion exchange resin consists of a macromolecular skeleton, to which dissociable groups are attached. It swells in water, giving rise to a charged network, whereas the counterions dissolve in the imbibed water. The active groups usually are $-SO_3H$ or $-COOH$ groups in the case of cation exchange resins, and quaternary ammoniumgroups or secundary or tertiary aminogroups in the case of anion exchange resins. Only the counterions can move freely in the water of the gel. A membrane based on a cation exchanger thus has a negatively charged network and in the ideal case is permeable only for positive ions.

In the case of an anion exchange membrane the network is positively charged and the membrane is only permeable for negative ions. If such a membrane is placed in a salt solution some salt diffuses into the imbibed water. A Donnan-equilibrium is obtained and in the membrane as well some ions with the same sign of charge as the fixed groups (co-ions) occur. These participate in the electrical transport. Consequently the membrane is less selective with higher salt concentrations. The theory for this kind of membranes was given by Meyer (1936), Sievers (1936) and Teorell (1935).

For a high selectivity the membrane must have a high selec-

tivity constant, i.e. a high concentration of charged groups in the membrane. For the new types of membranes the leakage caused by the co-ions is small, even in concentrated solutions, hence it is possible to measure B.I.P.'s in rather concentrated solutions.

It is possible to make membranes on the basis of ion exchange resins in various ways:

a. Mixing powdered ion exchange resin with a thermoplast and moulding at higher temperatures. This method was applied for the first time by M.R.J.Wyllie and H.W.Patnode (1950). By so doing heterogeneous membranes are obtained.

b. With a great number of ion exchangers a homogeneous gel occurs during the preparation. When the necessary precautions are taken, it is often possible to get this gel in the required shape. This method was first published by T.R.E. Kressman (1950). Afterwards W.Juda (1949) turned out to have been the first to apply and patent the method.

Various other techniques have been described. We may mention cellophane membranes for instance in which selective groups have been introduced by a chemical procedure, with the aid of the methylolderivatives of organic acid amides, e.g. betain amide (P. 1955).

Another promising method is the introduction of active groups in a hydrophobic film. In this direction much work has been done by T.N.O. As an example may be mentioned the introduction of $-SO_3H$ groups in a polyethylene film with the aid of chlorosulphonic acid (P.1954). The resulting membranes imbibe but little water, so that a high selectivity constant is obtained.

The selective membranes have been improved recently to such an extent that their technical application in the near future can be anticipated. The common types of selective membranes are permeable either to positive ions, or to negative ions. The affinity of a cation exchanger, however, is not equally high for the different cations. The same holds for the affinity of an anion exchanger for anions. The following rules can be given (see E.C.Nachod (1949)):

1. At low concentrations and room temperature the affinity increases with increasing charge of the ion. ($Na^+ < Ca^{++} < Al^{+++} < Th^{++++}$).

2. In dilute solutions the affinity changes in accordance with the Hofmeister or lyotrophic series: $Li^+ < Na^+ < K^+ < Rb^+ < CS^+$. $F^- < Cl^- < Br^- < J^-$.

3. The affinity for H^+ respectively OH^- ions depends on the strength of the acid respectively basic groups.

In some cases small changes in the sequences can occur. Boyd et al (1954) for instance found that for Dowex 50 (a strongly acid ion exchanger with $-SO_3H$ on polystyrene base) the selectivity for Na^+ decreases with respect to H^+ with decreasing capacity of the exchanger. Below a certain capacity H^+ ions are preferred to Na^+ Besides the authors observed an influence of the ratio Na^+/H^+ in the solution and of the number of crosslinks. Consequently membranes made from common types of cation (or anion) exchange resins also show differences in selectivity for different cations (or anions).

However, a much higher selectivity for a definite ion or a group of ions can be achieved if we start from special ion exchangers, with a specific preference for the ion or group of ions concerned. These specific ion exchangers have been greatly improved in recent years. They can be made according to different principles:

a) By preparing polymers with active groups having a specific affinity for the ion or group of ions concerned.
b) When synthesizing an ion exchange resin, by performing the polymerisation or polycondensation in the presence of reagents that are specific for certain ions. The resulting ion exchanger has an increased selectivity for these ions.
c) By making use of an ion-sieve effect. Reducing the pore size of an exchanger, increases its selectivity for small ions.

Membranes based on these particular ion exchangers are called specific selective membranes.

Ad a. Skogseid (1948) introduced in polystyrene, among other things, hexanitrodiphenylamino groups (reagent for K). The cation exchange resin obtained showed an increased selectivity for K^+-ions. The selectivity factor, defined as

$$K_{Na}^K = \frac{m_K^r}{m_{Na}^r} \cdot \frac{m_{Na}^s}{m_K^s} \tag{1-1}$$

(r = resin; s = solution; m = molality) reached values ranging from 2 to 5, depending on the molal ratio of Na^+ and K^+ in the solution.

H. P. Gregor, M. Taifer, L. Citarel and E. I. Becker (1952) synthetized ion-exchange resins in which organic reagents for different metals were introduced. They made for instance resins based on m. phenylene-diglycine, $(C_6H_4)(NHCH_2COOH)_2$, anthranilic acid, o. aminophenol. Polycondensation was achieved with formaldehyde. The resins showed increased affinity for Fe, Cu Co, Ni, Zn, Mg. Also chelating groups of the ethylene-diamine tetra-acetic acid type were introduced. These exchangers are selective for Ca^{++}, Mg^{++} and heavy metal ions.

J. P. Cornaz and H. Deuel (1954) obtained a specific ion exchange resin for ferri ions by introducing hydroxamic acid groups. E. Jenckel and H. von Lillin (1954, 1956), synthetized an ion exchange resin with selectivity for heavy metals by introducing anthranilic acid groups and 8-oxy-quinoline groups. The ion exchange resin with anthranilic acid groups is selective for Zn in particular. The degree of dissociation for both the acid and the heavy metal salt is $\alpha \simeq 3.10^{-3}$. For the Ba^{++} and the Ca^{++} salt the same values are found. The conductivity of the heavy metal salt is $1/1000$ of that in the Na^+ form. In free solutions this ratio is of the same order.

H. P. Gregor, D. Doler and G. K. Hoeschele (1955) describe an exchanger consisting of polythiolstyrene. The resin is very selective with respect to metals, forming mercaptides. J. R. Parrish (1956) prepared various selective cation-exchange resins on

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the basis of polystyrene. He observed a strong absorption of Hg by polythiol-methylstyrene. In general the resin had an affinity for metals forming mercaptides. An ion exchanger containing arsonic acid groups showed no absorption of Zn, Mg, and Ca, whereas Th was taken up in small amounts. Cu, Ni, and Co were absorbed strongly in the pH region 2-3 on a polystyrene (4-azo-5) 8-hydroxyquinoline resin. Zn, Mn, Al, Mg, and Ca were not absorbed below pH 1.5, 2.0, 2.8, 4.0, and 4.8 respectively.

Ad b. V. N. Lenskaya and M. F. Garanina (1955) condensed p-phenol sulfonic acid with formaldehyde in the presence of oxalic acid, citric acid or quercetrine. The first two acids gave a resin with a high affinity for Fe and Al. V. A. Klyachko (1951) added Na ethylene-diamine tetra-acetate in the preparation of a cation exchange resin from phenolsulphonic acid and formaldehyde. The resin obtained was selective for Ca^{++}.

Ad c. The increase in selectivity for small ions by reducing the pore size has been mentioned in the literature on several occasions. A well-known example is the collodion membrane. By drying intensively, its selectivity for small ions increases. The pore size of ion exchange resins can be decreased by introducing more crosslinks.

BI-IONIC POTENTIALS

The oldest B.I.P. measurements are due to L. Michaelis (1925a, 1925b, 1925c, 1926, 1928, 1933), who investigated dried collodion membranes and used the formula:

$$E = 58 \log u_1/u_2 \text{ mV} \tag{1-2}$$

(maintaining the same concentrations on both sides of the membrane) where u_1 and u_2 are the ionic mobilities. In Table 1 his results are given. The ratio u_x/u_K in the membrane is compared with that in the solution.

Table 1

Ratios u_x/u_K in a dried collodion membrane and in free solution.

	Li	Na	K	Rb	H
u_x/u_K (in membrane)	0.048	0.14	1	2.8	42.5
u_x/u_K (in free solution)	0.52	0.65	1	1.04	4.9

In reality Michaelis compared the ratios $\frac{u_i/\gamma_i}{u_K/\gamma_K}$, where γ_i and γ_K are the ionic activity coefficients. So it is not clear whether the large changes of the ratios in the membrane are due to changes in mobility u or to changes in activity coefficient γ or to both. Probably the change in mobility has the greater influence (sieve effect).

R. Mond and F. Hoffmann (1928) performed measurements on collodion membranes dyed with a basic dye, viz. Rhodamine B. For the sequence of permeability of the anions they found the Hofmeister or lyotropic series:

$$SCN > NO_3 > J > Br > Cl > acetate > SO_4,$$
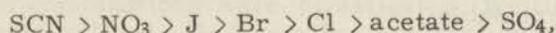
whereas the sequence of the mobilities in free solution is:

$$SO_4 > Br > J > Cl > NO_3 > SCN > acetate.$$
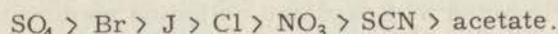
R. Höber (1936) also investigated collodion- and rhodamine collodion membranes. Regarding the inorganic anions his results agree with those of Mond and Hoffmann. In addition he found an irregular behaviour of the organic anions. The permeability of these ions is large as compared with that of the inorganic anions of the same volume.
He attributes this phenomenon to a higher adsorbability of these ions, due to some kind of van der Waals affinity. Moreover he observed that the anion permeability of the red blood cells is in many respects consistent with the permeability of the selective anion permeable collodion membrane.

K. H. Meyer and P. Bernfeld (1945a, 1945b, 1946) measured B. I. P.'s on frog skin and on different kinds of dyed films, such as an acetyl cellulose film dyed with the acid dye chloranthin-lichtrot or with the basic dye Victoria blue. They used the formula:

$$E = \frac{RT}{F} \ln \frac{u_1 l_2}{u_2 l_1} \tag{1-3}$$

maintaining the same concentrations of the cations M_1 and M_2 respectively on the left and right side of the membrane. l_1 and l_2 are the partition coefficients (or the ratios of the activity coefficients) of the ions M_1^+ and M_2^+ in the solutions and in the surface-layers in the membrane. The ratio u_1/u_2 was obtained from selectivity measurements at different concentrations of solutions of M_1^+ respectively M_2^+ salts. In table 2 their results are given for a chloranthin-lichtrot-acetyl cellulose membrane.

Table 2

Ratios of mobilities and of partitioncoefficients for a chloranthin-lichtrot-acetyl cellulose membrane

Me^+	$\dfrac{u_{Me^+}}{u_{K^+}} \dfrac{l_{Me^+}}{l_{K^+}}$	$\dfrac{u_{Me^+}}{u_{K^+}}$	$\dfrac{l_{Me^+}}{l_{K^+}}$
K^+	1	1	1
NH_4^+	1.55	1.6	1
Na^+	0.7	0.8	0.9
Li^+	0.45	0.65	0.7

The permeability of the frog skin depended strongly on the p_H of the solution. Placing a Ringer solution on one side of the frog skin and a KCl solution on the either side, they found that at p_H = 6.8 the membrane was anion permeable, whereas at p_H = 7.8 it was cation permeable.

K.Sollner and co-workers (1946a, 1946b, 1949a, 1949b, 1950, 1954, 1955) made a thorough study of bi-ionic potentials. They chiefly experimented with oxydized collodion membranes as negative and protamine-collodion membranes as positive membranes. They used the formula:

$$E = \frac{RT}{F} \ln \frac{t_1}{t_2} \tag{1-4}$$

in which t_1 and t_2 are the transference numbers of the ions 1 and 2 in the membrane. As the sequence of permeabilities for the above-mentioned membranes the Hofmeister series was again found for univalent inorganic ions.

In the theoretical part of his papers Sollner considers the influence of: 1) steric hindrance, 2) difference in absorption, 3) difference in mobility, 4) incomplete dissociation of the active groups, 5) heteroporosity, 6) degree of dissociation of the salts in the solution, 7) shape of the ions. Sollner supposes that an ion with a higher affinity has a greater part in the transport.

S. Dray and K. Sollner (1955) mention measurements on a sulphonated polystyrene-collodion membrane, an oxydized collodion membrane, a polyacrylic acid collodion membrane and a protamine collodion membrane. For inorganic ions in all cases the Hofmeister series was found as the sequence of permeabilities. Moreover they established the fact that the non-critical ion had no influence on the membrane potential for the membranes investigated. At low salt concentrations they found lower values for the B.I.P.'s than predicted by theory. The discrepancies were considerable especially for membranes with a low resistance, showing a high diffusion-rate. The authors attribute this phenomenon to diffusion layers near the membranes. The effect sets in at concentration below 0.05 N, it does not vanish entirely by vigorous stirring.

M.R.J.Wyllie and S.L.Kanaan (1954) verified experimentally the correctness of the B.I.P. formula derived by Wyllie (1954).

$$E = \frac{RT}{F} \ln \frac{a_M}{a_P} \cdot \frac{\bar{u}_M}{\bar{u}_P} \tag{1-5}$$

in which a_M and a_P are the activities of the ions M respectively P in the two salt solutions. Wyllie calls $\bar{u}_M$ and $\bar{u}_P$ the apparent mobilities of the ions M and P. This is one of the few examples in the literature, where a B.I.P. formula was experimentally tested. Wyllie and Kanaan remark that if $\bar{u}_M/\bar{u}_P$ is constant, a plot of E against ln a_M, keeping a_P constant must give a straight line, having a slope corresponding with a change in B.I.P. = 2.3026 RT/F (= 59.16 mV at 25°C) for each tenfold change in a_M.

For the single ion activities they substituted mean activities of the salt solutions. In most cases they actually found straight lines with the correct slope for their membranes. These belonged to the heterogenous type, consisting of an ion exchanger and a binder. Different combinations were investigated. Wyllie and Kanaan determined the ratio $\bar{u}_M/\bar{u}_P$ from the intersection of the straight line with the abscissa. In this point: $\bar{u}_M/\bar{u}_P = a_P/a_M$. The authors found a deviating slope in the case of a sulphonated polystyrene of 17% nominal divinylbenzene crosslinking. For the system:

| KCl solu. | Membr. 17% dvb. | LiCl solu. |
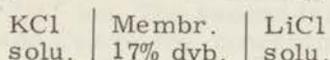
at constant a_{KCl} and varying a_{LiCl} they found a change of only 50 mV in B.I.P. for a tenfold change in a_{LiCl}. They ascribed this discrepancy to the approximate nature of the equations and to the fact that these equations ignore B.I.P. effects resulting from volume changes in the membrane.

Wyllie and Kanaan substituted the ratio $\bar{u}_M/\bar{u}_P$, obtained as mentioned above in their formula:

$$\frac{\bar{k}_M}{\bar{k}_P} \simeq \frac{\bar{u}_M/\bar{u}_P}{K_P^M}, \tag{1-6}$$

in which $\bar{k}_M$ and $\bar{k}_P$ are the mobilities of the ions M and P in the membrane and K_P^M is the selectivity constant. defined as

$$K_P^M = \frac{M_M}{M_P} \frac{a_P'}{a_M'} \tag{1-7}$$

M_M/M_P is the ratio of the concentrations of the ions M and P in the membrane when this is equilibrated with a solution in which the mean activities of the ions M and P are a_M' and a_P' respectively. Values for K_P^M were taken from the literature. The ratios $\bar{k}_M/\bar{k}_P$ calculated in this way were compared with the ratios of the mobilities obtained from conductivity measurements of the membrane in the M^+ respectively P^+ form. Different combinations of univalent cations were taken. On the whole the agreement was satisfactory. The $H^+ - Ag^+$ values are an exception. In this case the measured $\bar{k}_H/\bar{k}_{Ag}$ values exceed by far those calculated. From the data gained by Wyllie and Kanaan may be concluded that if an ion is absorbed selectively by the membrane, its mobility is lowered. As for its contribution to the transport however, the first factor predominates, so that a higher affinity yields a relatively higher transference number.

D. Woermann, K. F. Bonhoeffer and F. Helfferich (1956) investigated a membrane consisting of Skogseid's K-selective ion exchange resin and polyethylene. The self-diffusion coefficient of the Na^+ ions ($\bar{D}_{Na}$) appeared to be 1.2 times that of the K^+ ions

($\bar{D}_K$). The selectivity coefficient $K_{c_{Na}}^K$ (defined as $\dfrac{C_K c_{Na}}{C_{Na} c_K}$ in which

C_K and C_{Na} are the concentrations of the K^+ respectively Na^+ ions in the membrane and c_{Na} and c_K are the corresponding values in the solution) varied from 3.2 to 2.3, depending on the mole fraction of the K^+ ions, at a total concentration of $10^{-2} N$. (mean value 2.7). The authors also measured B.I.P.'s. For the scheme:
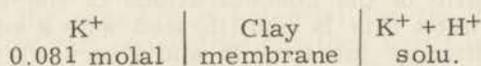
$$\text{Ag} \ \left| \ \text{AgCl} \ \right| \ \begin{matrix} \text{KCl} \\ a'_K \end{matrix} \ \left| \ \text{Membr.} \ \right| \ \begin{matrix} \text{KCl} & a''_K \\ \text{NaCl} & a''_{Na} \end{matrix} \ \left| \ \text{AgCl} \ \right| \ \text{Ag}$$
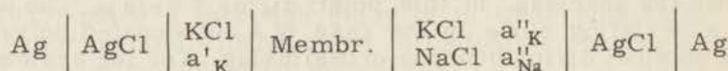
they used the formula:

$$E_{B.I.P.} = \frac{RT}{F} \ln \frac{a'_K}{a''_K + \dfrac{\overline{D}_{Na}}{\overline{D}_K} \cdot \dfrac{\gamma_K}{\gamma_{Na}} \cdot a''_{Na}} \tag{1-8}$$

when for γ_K/γ_{Na} they substituted $K^{Na}_{c_K}$. For a series of measurements at   h $c'_K = 5.10^{-2} N$ and $c''_K + c''_{Na} = 0.5.10^{-2} N$ the agreement between the experimental B.I.P. values and those calculated according the formula (1-8) was satisfactory, if they substituted $\overline{D}_{Na}/\overline{D}_K = 1.2$ and $\gamma_K/\gamma_{Na} = 1/2.7$.

B.I.P. measurements are also used to determine transport ratios in clay membranes. These investigations are of great importance in agricultural research. C.E. Marshall and W.E. Bergman (1942a) tried to measure K ion activities in colloidal clays. They prepared films from electrodialyzed bentonite according to the following scheme:

$$\begin{matrix} K^+ \\ 0.081 \text{ molal} \end{matrix} \ \left| \ \begin{matrix} \text{Clay} \\ \text{membrane} \end{matrix} \ \right| \ \begin{matrix} K^+ + H^+ \\ \text{solu.} \end{matrix}$$

and used the (incorrect) formula

$$E = \frac{RT}{F} \ln \frac{(0.0810)}{(K^+) + (H^+)} \tag{1-9}$$

in which (M^+) is the molality of the M^+ ion. They estimated a_{H^+} with the aid of a glass electrode; a_{K^+} was calculated from E and a_{H^+}. In two subsequent papers C.E. Marshall and W.E. Bergman (1942b, 1942c) repeated the experiments with NH_4^+ instead of K^+. They found that high acidities were not tolerated by the membranes which gave erratic results at pH values below 4. It may be remarked that besides a part of the error was due to the incorrect B.I.P. formula used.

C.E. Marshall (1948) considered for various clay membranes the relation between the differences in differential heats of absorption of M^+ or N^+ ions and the ratio u_{M^+}/u_{N^+}, where u_{M^+} and u_{N^+} are the mobilities of the ions M^+ or N^+ in the membrane. He estimated the potential of the cell:

$$\text{NaCl} \quad \Big| \quad \text{Membr.} \quad \Big| \quad \text{KCl}$$
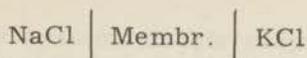
by calculating the heat effects which occur when a small amount of charge flows through the cell.

$$E_{membr.} = \frac{4.185}{F} (H_{K^+} - H_{Na^+}) + \frac{RT}{F} \ln \frac{\alpha_1 C_1}{\alpha_2 C_2} \qquad (1\text{-}10)$$

in which H_{K^+} and H_{Na^+} are the differential heats of absorption for the K^+ respectively Na^+ ion. The second term originates from the osmotic work. C_1 and C_2 are the concentrations of KCl or NaCl on either side of the membrane; α_1 and α_2 are the corresponding mean activity coefficients.

For the B.I.P. Marshall used the formula:

$$E = \frac{RT}{F} \ln \frac{a_{K^+}}{a_{Na^+}} \cdot \frac{u_{K^+}}{u_{Na^+}} \qquad (1\text{-}11)$$

where, for dilute solutions, he set $\alpha_1 C_1 / \alpha_2 C_2$ equal to a_{K^+}/a_{Na^+}, thus:

$$\frac{RT}{F} \ln \frac{u_{K^+}}{u_{Na^+}} = \frac{4.185}{F} (H_{K^+} - H_{Na^+}) \qquad (1\text{-}12)$$

Marshall's theory was revised by Coleman (1952) (see below).

Marshall also studied the possibility of using clay membranes for the determination of the activities of mono- and divalent cations in solution (K^+, NH_4^+, Na^+, Ca^{++}, Mg^{++}). In a later paper E.O. McLean, S.A. Barber and C.E. Marshall (1951) described a method to determine the separate activities in a solution of two univalent cations. They also performed B.I.P. measurements with the same salt solutions, but with two membranes, which had different values for u_1/u_2. For the system

$$\overset{I}{\text{Na}^+} \quad \Big| \quad \text{Membr.} \quad \Big| \quad \overset{II}{\text{Na}^+ + \text{K}^+}$$
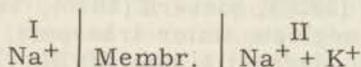
they used the formula:

$$E = \frac{RT}{F} \ln \frac{\overset{I}{a_{Na^+}}}{\overset{II}{a_{Na^+}} + \frac{u_{K^+}}{u_{Na^+}} \cdot \overset{II}{a_{K^+}}} \qquad (1\text{-}13)$$

$\overset{II}{a_{Na^+}}$ and $\overset{II}{a_{K^+}}$ can be estimated in this way. The authors succeeded in preparing clay membranes with u_K/u_{Na} values varying from 2.5 to 11.7, depending on the preparation. Especially the temperature to which the membranes were heated is very important. In reality the authors did not estimate u_K/u_{Na}, but $u_K/u_{Na} \times \gamma_{Na}/\gamma_K$.

N.T. Coleman (1952) remarked that in the thermodynamic derivation of the B.I.P. it was not the difference in heat of absorption, but the difference in free energy that should be substituted.

He used the formulae:

$$\Delta F = -FE \tag{1-14}$$

and

$$\Delta F = -RT \ln K \tag{1-15}$$

in which K is the equilibrium constant for the exchange of two ions in a solution with the membrane.

Coleman studied membranes of the heterogeneous type, consisting of a cation exchange resin (Amberlite I. R. 100, I. R. 105, and I. R. 120) or clay ("Volclay" bentonite) and polystyrene in a weight ratio of 6 : 4. With different combinations of univalent cations such as LiCl-KCl; NaCl-KCl; NH$_4$Cl-KCl he found agreement between the ΔF values calculated from equilibrium experiments and those from B. I. P. measurements. However, he remarks that theoretically this agreement can be expected only when the mobilities of the two ions in the membrane are equal.

S. K. Bose (1955) studied the Na$^+$/K$^+$ reversibility on clay membranes. He investigated a montmorillonite membrane and used Marshall's formula:

$$E = \frac{RT}{F} \ln \frac{a_{K^+}}{a_{Na^+}} \cdot \frac{u_{K^+}}{u_{Na^+}} \tag{1-11}$$

In some cases u_{K^+}/u_{Na^+} amounted to about 6.

Water transport through membranes

In deriving their formulae for the dialysis potential and bi-ionic potential most investigators did not take into account the transport of uncharged particles, e. g. water molecules. The well-known M.S.T. theory (Meyer (1936), Sievers (1936), Teorell (1935)) for the dialysis potential neglects water transport, the B. I. P. formulae of Sollner (1949), Marshall (1944), Wyllie (1954) and Helfferich (1956) are derived without considering water transport.

The application of the theory of non-equilibrium thermodynamics emphasized the importance of transport of uncharged particles for the potential. For electro kinetic effects this theory has been elaborated by P. Mazur and J. Th. G. Overbeek (1951). For osmosis by A. J. Staverman (1951a), for the diffusion potential by E. H. Wiebenga (1946). Staverman (1951b, 1952, 1954) has given a general survey of the theories applied to membrane processes.

In the theoretical part it will be shown that the effect of uncharged molecules on the membrane potential is given by the formula:

$$E_{solv.} = -\frac{RT}{F} \int_\alpha^\omega t_W \, d\mu_W \tag{1-16}$$

Staverman's work caused G. Schmid (1950, 1951a, 1951b, 1951c, 1952a, 1952b) to revise his studies on the electrochemistry of

small pore capillary systems in this respect. It is a well-known fact, that the theories of Helmholtz (1879) and Smoluchowski (1921) hold only for capillaries having a diameter large in comparison with the thickness of the double layer.

G. Schmid, on the contrary, examined the case that the double layer fills the whole pore, assuming an equal concentration of active groups throughout the pore, corresponding with the M. S. T. theory. Drag effects were accounted for only to a certain extent in the formulae of Helmholtz and Smoluchowski. Schmid in his initial work neglected solvent transport entirely and later on (1952b) he examined in how far it had influenced his results. It appeared that the formula for electro osmotic permeability, like that for the streaming-current, was not affected. In the formulae for the electro osmotic pressure per unit of voltage and for the streaming-potential the corrections turned out to cancel exactly, only in the formula for the electro osmotic pressure per unit of current a correction had to be made. This brought Schmid's formulae in full accord with the relations derived from irreversible thermodynamics.

Deriving his formula for the B. I. P. Scatchard (1953) did take account of water transport. For the calculation of the dialysis potential the influence of water transport has been considered also by J. W. Lorimer, E. I. Boterenbrood and J. J. Hermans (1956).

There is a more practical reason as well for water transport through membranes to arouse interest. In the electro-dialytical water desalting, transport of water takes place from the dialysate to the concentrate. In desalting sea-water, this can cause a loss amounting to 20% of the original volume of water, resulting in a considerable economical come down.

The electro-osmosis has been studied for a long time. The phenomenon was discovered by F. F. Reuss (1809). Later on investigations were made by G. Wiedeman (1852) and G. Quincke (1859, 1861). A. Bethe and T. Toropoff (1915) studied the phenomenon on different types of membranes. For the chromegelatine membrane they found that the direction and the extent of water transport depended on the pH of the solution. At a low pH the water was transported in the direction of the anode, at a higher pH in the direction of the cathode.

The authors placed the membrane between two half-cells provided with capillaries. The solvent transport was derived from the displacement of the meniscus in either capillary. H. Remy and H. Reisner (1926) did measurements on a parchment membrane at a high salt concentration. They also used the capillary method. The transport of water not bound to the ions can be neglected in this case. The water displacement observed depends on the hydration water of the ions and their transference numbers. Similarly, E. Manegold and K. Solf (1931) carried out experiments on collodion membranes with the aid of the capillary method. Especially the connection between watertransport and pore-diameter was examined. Their experimental results did not agree with the Helmholtz-Smoluchowski formulae. However, G. Schmid (1951a) showed that these results could be explained by his theory.

In a review paper on ion exchange by W. Juda, J. A. Marinsky, and N. W. Rosenberg (1953), Rosenberg's measurements of water transport through a Nepton CR-51 membrane are reproduced. (Presented at Gordon Research Conf. on ion-exchange, New London, N. H. July 16-20, 1951). This membrane is a homogeneous gel (supported by a saran screen) of a cation exchange resin with sulphonic acid groups. The water transport was measured according to the capillary method. For the Nepton CR 51-NaCl system the transference numbers of the Na^+ ions and of water were measured. The "dynamic" transference numbers

$$t_+ = \frac{d\ meq.\ Na}{d\ meq.\ el} = \frac{d\ NV}{d\ meq.\ el} = V\frac{d\ N}{d\ meq.\ el} + N\frac{d\ V}{d\ meq.\ el}\ (1\text{-}17)$$

were compared with the transference numbers from e. m. f. measurements.

N = normality of NaCl in the external solution.

V = volume of solution in the cell.

The author states that the agreement between the "dynamic" transference numbers and those calculated from e. m. f. measurements was good. However, it may be remarked that the transference numbers he obtained from e. m. f. measurements are Hittorf transference numbers, whereas the "dynamic" ones correspond to true transference numbers. Consequently the influence of the water transport on the e. m. f. must have been small. In 0.1 N NaCl and 0.03 N NaCl the water transport amounted to 17 mole H_2O/Far.

W. F. Graydon and R. J. Stewart (1955) calculated the water transport from membrane potential measurements. The membranes investigated were prepared by the copolymerization of the propylester of p-styrene sulphonic acid with styrene and divinylbenzene and subsequent hydrolysis of the polymer. The deviations from the ideal membrane potential are due to transport of co-ions and of water. The transport number of the co-ions was calculated with the aid of the M. S. T. theory. The rest of the deviation gives the water transport. For their membranes the authors found:

$$t_w = K\ (W_D/X_L) \tag{1-18}$$

W_D = grams of water per gram of dry membrane.

X_L = nominal cross-linking in mole % divinylbenzene.

A. G. Winger, R. Ferguson and R. Kunin (1956) applied an other technique for measuring the water transport. They estimated the total change in the number of ions and the quantity of water on both sides of the membrane during the electrolysis by transmitting the contents of a cell in a "vacuum line trap" which had been weighed before. An accuracy of ± 3% is given. The Amberplex C 1 membrane was investigated. It is a heterogeneous membrane, consisting of a cation exchange resin with polyethylene as a binder. The relation between the extent of the water transport and the number of crosslinks was examined. The water transport did not

prove to be proportional to the water content of the membrane.
There was an approximate proportionality between the mobility of
the ion and the reciprocal of the water transport of the ion for
univalent cations, however. Ions with the highest "true" hydra-
tion numbers gave the highest values of the water transport num-
bers.

A. Despić and G. J. Hills (1956) made water transport measure-
ments on a membrane composed of crosslinked polymethacrylic
acid. Their apparatus consisted of two half-cells, either of which
contained about one liter, with two vertical capillaries. They used
two non-reversible electrodes. The gas bubbles forming during
the experiment escaped up the capillaries. The authors estimated
the mobility of the Na^+ ion from conductivity measurements and
also from self-diffusion experiments. The latter values are smal-
ler, the difference being caused by the movement of the water
during the conductivity measurements. The authors devided the
water transport in a part originating from the "free" water mole-
cules, and a part originating from the hydration water of the Na^+
ion. A primary solvation number of 9 for the Na^+ ions in the
membrane phase was found.

II. THEORY

The oldest formula for the bi-ionic potential was derived by Michaelis (1926, 1929).

Michaelis looked upon his membrane as a pore system in which the mobility of one kind of ions (positive or negative) was zero. This hindrance he attributed to a sieve effect, or to the influence of charges fixed on the pore walls. His cell consisted of a membrane separating two simple uni-univalent salt solutions of equal concentration with different "critical" ions. He started from the quasi-thermodynamic rule that in the steady state the change in free energy equals the electrical work, when an infinitely small displacement of electrical charge takes place. Michaelis considered ideal solutions and neglected transport of water. He assumed constant mobilities of the two "critical" ions in the membrane. Though his calculation was not quite correct, Michaelis obtained for his model the right formula, viz.

$$E_{B.I.P.} = (RT/F \ln u_1/u_2) \tag{1-2}$$

in which u_1 and u_2 are the mobilities of the two "critical" ions 1 and 2 in the membrane, R is the gas constant, T the absolute temperature and F the faraday. His formula only holds if the sum of the concentrations of the "critical" ions is constant across the membrane: $C_1 + C_2 = C$.

K. Sollner (1949a, 1949b) essentially used the same model as Michaelis, However, Sollner replaces the ratio of the mobilities by the ratio of the transference numbers, without proving that this is permissible.

$$E_{B.I.P.} = (RT/F) \ln t_1/t_2 \tag{1-4}$$

t_1 and t_2 are the transference numbers of the "critical" ions 1 and 2 in the membrane. Sollner supposes that the membrane contains a mixture of the two solutions.

C. E. Marshall (1944), who in the main investigated clay membranes, does not give a clear model of these membranes. He looked upon the B.I.P. as a liquid junction potential and applied Henderson's (1907, 1908) formula in a straight-forward manner. This implies ideal solutions and constant mobilities of the ions in the membrane and the neglect of solvent transport. Marshall supposes that the mobility of the negative ions in the membrane is zero. He incorrectly substitutes activities for concentrations in the Henderson diffusion potential formula. In the case of simple uni-univalent salt solutions separated by the membrane, his result is:

$$E = (RT/F) \ln \frac{a_1{}'}{a_2{}'} \cdot \frac{u_1}{u_2} \qquad (2-1)$$

$a_1{}'$ and $a_2{}'$ are the activities of the ions 1 and 2 in the solutions 1 and 2, separated by the membrane, u_1 and u_2 are the mobilities of the ions 1 and 2 in the membrane.

M. R. J. Wyllie (1954a, 1954b) derived a B. I. P. formula for a perfectly selective ion exchange membrane. The model used by him is a macromolecular network to which fixed charges are attached, imbibed with water. A constant concentration of these active groups is assumed. The mobility of the co-ions in the membrane (ions with the same kind of charge as the active groups) is supposed to be zero. This model corresponds to that of Meyer (1936), Sievers (1936) and Teorell (1935). Like Meyer, Sievers and Teorell in their derivation of the concentration potential formula, Wyllie split up the membrane potential in two phase boundary or Donnan potentials, situated in the membrane surfaces, and a liquid junction potential within the membrane itself. Calculating the liquid junction potential he used the Henderson formula, in which he incorrectly substituted activities for concentrations. He obtained:

$$E_{B.I.P.} = \frac{RT}{F} \left[\ln \frac{a_1{}'}{a_1} - \ln \frac{a_2{}'}{a_2} + \ln \frac{a_1 u_1}{a_2 u_2} \right] \qquad (2-2)$$

in which $a_1{}'$ and $a_2{}'$ are the activities of the "critical" ions in the solutions, separated by the membrane, while a_1 and a_2 are the activities of these ions in the membrane surfaces in contact with the respective solutions. Thus:

$$E_{B.I.P.} = \frac{RT}{F} \ln \frac{a_1{}' u_1}{a_2{}' u_2} \qquad (2-3)$$

The rest of Wyllie's argument is not very exact. He states that as a result of preferent adsorption of one ion the distribution of ions in the liquid junction may be very different from that assumed in the derivation of the Henderson equation. Therefore Wyllie calls u_1 and u_2 "apparent" mobilities, and replaces the ratio u_1/u_2 by t_1/t_2, the ratio of the transference numbers in the membrane. For t_1/t_2 he writes: $\frac{m_1}{m_2} \times \frac{k_1}{k_2}$. m_1/m_2 he calls the steady state equilibrium concentration ratio of the ions 1 and 2 in the junction zone (the meaning of this statement is not clear), and k_1/k_2 is the ratio of the conductivities of the membrane when fully in the 1 or 2 form. For m_1/m_2 Wyllie substitutes K_2^1, the selectivity constant, defined as:

$$K_2^1 = \frac{M_1}{M_2} \cdot \frac{a_2{}'}{a_1{}'}, \qquad (1-7)$$

in which M_1/M_2 is the ratio of the concentrations of the ions 1 and 2 in the membrane when this is equilibrated with a solution

in which the mean activities of the ions 1 and 2 are a_1' and $a_2'+$ respectively. His ultimate result is:

$$E_{B.I.P.} = (RT/F) \ln \frac{a_1'}{a_2'} \cdot K_2^{\frac{1}{2}} \cdot k_1/k_2 \qquad (2-4)$$

Much of the intricacy of Wyllie's paper is caused by the incorrect substitution in the Henderson formula. Correct use of this formula gives, instead of (2-4):

$$E_{B.I.P.} = (RT/F) \left[\ln \frac{a_1'}{a_1} - \ln \frac{a_2'}{a_2} + \ln \frac{C_1 u_1}{C_2 u_2} \right] \qquad (2-5)$$

in which C_1 and C_2 are the concentrations of the ions 1 and 2 in the membrane surfaces in contact with the respective solutions. Now $C_1 = a_1/\gamma_1^{\alpha}$ and $C_2 = a_2/\gamma_2^{\omega}$. γ_1^{α} is the activity coefficient of the ions 1 in the membrane face in contact with solution 1; γ_2^{ω} is the activity coefficient of the ions 2 in the membrane face in contact with solution 2. Thus:

$$E_{B.I.P.} = (RT/F) \ln \frac{a_1' u_1 \gamma_2^{\omega}}{a_2' u_2 \gamma_1^{\alpha}} \qquad (2-6)$$

Application of the Henderson's diffusion potential formula implies the assumption that u_1 and u_2 are constant across the membrane. Below it will be shown that under some additional assumptions formula (2-6) is identical with that of Wyllie. We must remark that also in Wyllie's calculations the transport of water has been neglected.

G. Scatchard (1953) in this study on B.I.P.'s also used the ion exchange membrane model. He started from the quasi-thermodynamic equation

$$E = RT/F \int_{\alpha}^{\omega} \Sigma_i t_i \, d \ln a_i \qquad (2-7)$$

t_i = transference number of ion i, i.e. the number of moles of species i transferred when one faraday of electricity goes through the membrane.

a_i = activity of ion i.

For a cation exchange membrane, separating two solutions with different "critical" ions, but with one common anion, he derived the formula:

$$E_{B.I.P.} = \frac{RT}{F} \left[\ln \frac{a_2' u_2^{\omega} \gamma_1^{\alpha}}{a_1' u_1^{\alpha} \gamma_2^{\omega}} - \int_{\alpha}^{\omega} \frac{\Sigma_i^+ m_i u_i \, d \ln u_i/\gamma_i}{\Sigma_i^+ m_i u_i} + \right.$$

$$\left. + \int_{\alpha}^{\omega} t_x \frac{\Sigma_i^+ m_i u_i \, d \ln a_i a_x}{\Sigma_i^+ m_i u_i} + \int_{\alpha}^{\omega} t_w d \ln a_w \right] \qquad (2-8)$$

a_1', a_2', u_1, u_2, γ_i, m_i, u_i have the usual meaning. γ_1^{α} is the

activity coefficient of the ions 1 in the membrane face near solution 1; γ_2^ω is the corresponding value for the ions 2; t_x = transference number of the common negative ion in the membrane; t_w = transference number of water in the membrane; a_w = activity of water in the membrane; Σ_i^+ indicates summation over positive ions.

The first term in Scatchard's formula is the main term, the others are correction terms. The first of these is a correction for the change in mobilities and activity coefficients in the membrane, the second accounts for the transport by the negative ion and the third is a correction for the water transport. As Scatchard gives little more than the final result of his calculation, the derivation of his formula will be given in appendix 1.

Neglecting the first correction term means that u_1/γ_1 and u_2/γ_2 are assumed constant across the whole membrane. Then, instead of $u_1^\alpha/\gamma_1^\alpha$ and $u_2^\omega/\gamma_2^\omega$ we may write u_1/γ_1 and u_2/γ_2. This is of interest for the comparison of B.I.P.'s and transport ratios. These conditions also make the formulae (2-6) and (2-4) identical to each other. Though essentially the same result is obtained as in splitting up the potential in two Donnan potentials and a diffusion potential, Scatchard's approach gives a good idea of the importance of the correction terms.

F. Helfferich (1956) also started from the ion exchange membrane model. He split up the B.I.P. in two Donnan potentials and a diffusion potential. For the calculation of the latter he used the Nernst-Planck flux equation:

$$\Phi_i = -D_i \left(\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_i}{\partial x} + C_i Z_i \frac{F}{RT} \frac{\partial E}{\partial x} \right) \qquad (2-9)$$

Φ_i = flux of ion i.
D_i = diffusion coefficient of ion i in the membrane.
E = electrical potential.

He assumes the membrane non-permeable for anions, thus the flux of the common anion $\Phi_x = 0$. On account of electroneutrality $\Sigma_i \Phi_i = 0$ (only univalent ions are present). Assuming, that the total cation concentration is constant throughout the membrane, i.e. $C_1 + C_2 = C$, and also that D_1/D_2 is constant, Helfferich finds for the diffusion potential, considering the steady state:

$$E_{diff.} = RT/F \left[\ln D_2/D_1 - \int_\alpha^\omega (t_1 \, d \ln \gamma_1 + t_2 \, d \ln \gamma_2). \right] (2-10)$$

t_1 and t_2 are the transference numbers of the ions 1 and 2 in the membrane. The first term equals the Henderson diffusion potential. Adding the two Donnan potentials, he gets:

$$E_{B.I.P.} = RT/F \left[\ln \frac{a_2' \, D_2 \, \gamma_1^\alpha}{a_1' \, D_1 \, \gamma_2^\omega} - \int_\alpha^\omega (t_1 \, d \ln \gamma_1 + t_2 \, d \ln \gamma_2) \right] (2-11)$$

in which the symbols have their usual meaning.

Helfferich's assumption that D_1/D_2 is constant was introduced

to simplify the calculation. Though there is some evidence from the literature that this is approximately correct in some instances this simplification need not be introduced a priori. Therefore we have given in appendix 2 another calculation, avoiding this assumption. As a result the same formula as Scatchard's is obtained, except for correction for water transport and transport by the negative ion.

Summarizing we may say that Scatchard has given the most accurate derivation, but the approaches of Sollner, Wyllie and Helfferich, except for correction terms, give about the same result.

It is possible to introduce a further improvement of the theory. Scatchard's starting point was the quasi-thermodynamical formula for the membrane potential.

$$E = RT/F \int_\alpha^\omega \Sigma_i \, t_i \, d \ln a_i \qquad (2-7)$$

in which t_i is the number of moles of ion i transported from α to ω as a result of the passage of one Faraday of charge. Deriving this formula, one supposes that at current passage the work done on the cell equals the increase in free energy caused by the transport of matter due to this passage of current. This supposition is disputable. Application of non-equilibrium thermodynamics (see P. Mazur and J. Th. G. Overbeek (1951), A. J. Staverman (1951a, 1951b, 1952)), however, has given a more solid base to this formula.

In this theory a system of forces X_i working on the ions, and the corresponding currents J_i is introduced in such a way, that the entropy production per unit of time can be written:

$$dS/dt = \Sigma_i \, X_i \, J_i \qquad (2-12)$$

Choosing for the currents $\dot{n}_i$ (i.e. dn/dt, the number of molecules of the ith component passing per second through the membrane), we get for the corresponding forces:

$$X_i = z_i \, E + v_i P + \Delta\mu_i \qquad (2-13)$$

z_i = charge of ion i.
E = electrical potential difference.
P = pressure difference.
v_i = partial volume of ion i.
μ_i = chemical potential of ion i.

It is assumed that the occurring streams are proportional to the forces (linear region), thus:

$$\dot{n}_i = \Sigma_k \, L_{ik} \, X_k$$

$$\dot{n}_i = \Sigma_k \, L_{ik} \, (z_k E + v_k P + \Delta\mu_k) \qquad (2-14)$$

According to Onsager's fundamental law:

$$L_{ik} = L_{ki} \qquad (2-15)$$

To describe the membrane processes the phenomenological constants are used. They are functions of the L_{ik}'s.

For example, the electrical conductivity is:

$$L_E = (I/E)_{P=0, \ \Delta\mu=0} \qquad (2-16)$$

$$= 1/E \ \Sigma \ z_i \ \dot{n}_i \ (P=0, \ \Delta\mu=0)$$

$$= \Sigma_i \ \Sigma_k \ L_{ik} \ z_i \ z_k \qquad (2-17)$$

The electrical transport number is:

$$T_i = \left(\frac{z_i \ \dot{n}_i}{\Sigma z_i \ \dot{n}_i}\right)_{\Delta\mu=0, \ P=0} = \frac{z_i \ \Sigma_k \ L_{ik} \ z_k}{L_E} \qquad (2-18)$$

The reduced transport number or transference number is:

$$t_i = T_i/z_i = 1/L_E \ . \ \Sigma_k L_{ik} \ z_k$$

In another type of experiment we measure the potential difference when $P = 0$ while the $\Delta\mu_k$'s are different from zero, so that

$$I = \Sigma_i z_i \ \dot{n}_i = \Sigma_i \ \Sigma_k \ L_{ik} \ z_i \ z_k E + \Sigma_i \ \Sigma_k \ L_{ik} \ z_i \ \Delta\mu_k$$

In the absence of an electric current, i.e. when $I = 0$, this gives:

$$E = -\frac{\Sigma_i \ \Sigma_k \ L_{ik} \ z_i \ \Delta\mu_k}{\Sigma_i \ \Sigma_k \ L_{ik} \ z_i \ z_k}$$

$$= -\frac{L_E \ \Sigma_k t_k \ \Delta\mu_k}{L_E} = - \Sigma_k \ t_k \Delta\mu_k \qquad (2-19)$$

From this can be concluded that for the calculation of the membrane potential the summation has to include the uncharged components. Formula (2-19) cannot simply be applied to calculate the bi-ionic potential, since in this case two of the $\Delta\mu_k$'s are infinite. The reason is, that non-equilibrium thermodynamics may be applied only to systems with small deviations from the equilibrium state. Staverman (1956) has solved this difficulty by dividing the membrane in a great number of layers parallel to the membrane face, which are so thin that the change in thermodynamic potential is small when passing from one side of the layer to the other. However, it must then be assumed that the ion concentrations change gradually from one layer to the next. The B.I.P. is found by calculating the potential differences across the separate layers and integrating over the total membrane thickness. Staverman has remarked that this treatment is identical in practice with Scatchard's (1953).

Appendix I

Derivation of Scatchard's B.I.P. formula

Scatchard considers a perfectly cation selective membrane, separating two mixtures of uni-univalent ions with one common anion,

$$E = \frac{RT}{F} \int_\alpha^\omega \Sigma_i \, t_i \, d \ln a_i \qquad (2-7)$$

$$\Sigma_i \, t_i \, d \ln a_i = \Sigma_i^+ t_i^+ \, d \ln a_i + t_x \, d \ln a_x + t_w \, d \ln a_w$$

t_x = transference number of the common negative ion.
t_w = transference number of water.
Σ_i^+ = indicates summation over positive ions.

$$\Sigma_i \, t_i \, d \ln a_i = \frac{\Sigma_i^+ m_i \, u_i \, d \ln a_i}{\Sigma_i \, m_i \, u_i} + t_x \, d \ln a_x + t_w \, d \ln a_w$$

$$= (1 + t_x) \frac{\Sigma_i^+ m_i \, u_i \, d \ln a_i}{\Sigma_i^+ m_i \, u_i} + t_x \, d \ln a_x + t_w \, d \ln a_w$$

$$\left(\text{as} \quad \frac{\Sigma_i^+ m_i \, u_i}{\Sigma_i \, m_i \, u_i} - t_x = 1 \longrightarrow \frac{1}{\Sigma_i \, m_i \, u_i} = \frac{1 + t_x}{\Sigma_i^+ m_i \, u_i} \right)$$

$$= \frac{\Sigma_i^+ m_i \, u_i \, d \ln m_i}{\Sigma_i^+ m_i \, u_i} \gamma_i + t_x \frac{\Sigma_i^+ m_i \, u_i \, d \ln a_i \, a_x}{\Sigma_i^+ m_i \, u_i} + t_w \, d \ln a_w$$

$$= \frac{\Sigma_i^+ m_i \, u_i \, d \ln m_i \, u_i}{\Sigma_i^+ m_i \, u_i} - \frac{\Sigma_i^+ m_i \, u_i \, d \ln u_i / \gamma_i}{\Sigma_i^+ m_i \, u_i} +$$

$$+ t_x \frac{\Sigma_i^+ m_i \, u_i \, d \ln a_i \, a_x}{\Sigma_i^+ m_i \, u_i} + t_w \, d \ln a_w$$

$$= d \ln (\Sigma_i^+ m_i \, u_i) - \frac{\Sigma_i^+ m_i \, u_i \, d \ln u_i / \gamma_i}{\Sigma_i^+ m_i \, u_i} +$$

$$+ t_x \frac{\Sigma_i^+ m_i \, u_i \, d \ln a_i \, a_x}{\Sigma_i^+ m_i \, u_i} + t_w \, d \ln a_w$$

Introducing a standard ion s with mobility u_s and activity coefficient γ_s, one gets:

$$\frac{F}{RT} \cdot E_{B.I.P.} = d \ln \Sigma_i^+ a_i \frac{u_i}{u_s} \cdot \frac{\gamma_s}{\gamma_i} - \frac{\Sigma_i^+ m_i \, u_i \, d \ln u_i / u_s \cdot \gamma_s / \gamma_i}{\Sigma_i^+ m_i \, u_i} +$$

$$+ t_x \ \frac{\Sigma_i^+ m_i \ u_i \ d \ ln \ a_i \ a_x}{\Sigma_i^+ m_i \ u_i} + t_w \ d \ ln \ a_w \qquad (2\text{-}20)$$

Appendix 2

Calculation of the B.I.P. using the Nernst-Planck flux equation and avoiding the assumption D_1/D_2 is constant.

$$\Phi_1 = - \ D_1 \ \frac{\partial C_1}{\partial x} - D_1 C_1 \ \frac{\partial \ ln \ \gamma_1}{\partial x} - D_1 C_1 \ \frac{F}{RT} \ \frac{\partial E}{\partial x} \qquad (2\text{-}21)$$

$$\Phi_2 = - \ D_2 \ \frac{\partial C_2}{\partial x} - D_2 C_2 \ \frac{\partial \ ln \ \gamma_2}{\partial x} - D_2 C_2 \ \frac{F}{RT} \ \frac{\partial E}{\partial x}$$

$$\Phi_1 + \Phi_2 = 0$$

We introduce the new variables $D_1/\gamma_1 = p_1$ and $D_2/\gamma_2 = p_2$, which gives in the steady state:

$$\Phi_1 = - \ D_1 \ \frac{d \ C_1}{dx} - C_1 \ \frac{d \ D_1}{dx} + D_1 C_1 \ \frac{d \ ln \ p_1}{dx} - D_1 C_1 \ \frac{F}{RT} \frac{dE}{dx}$$

$$\Phi_2 = - \ D_2 \ \frac{d \ C_2}{dx} - C_2 \ \frac{d \ D_2}{dx} + D_2 C_2 \ \frac{d \ ln \ p_2}{dx} - D_2 C_2 \ \frac{F}{RT} \frac{dE}{dx}$$

$$F/RT \ dE = - \ \frac{d(C_1 D_1 + C_2 D_2)}{C_1 D_1 + C_2 D_2} + \frac{C_1 D_1 \ d \ ln \ p_1}{C_1 D_1 + C_2 D_2} + \frac{C_2 D_2 \ d \ ln \ p_2}{C_1 D_1 + C_2 D_2}$$

$$E = \frac{RT}{F} \ \left[- \ ln \ \frac{D_2^\omega C_2^\omega}{D_1^\alpha C_1^\alpha} + \int_\alpha^\omega t_1 \ d \ ln \ \frac{D_1}{\gamma_1} + \int_\alpha^\omega t_2 \ d \ ln \ \frac{D_2}{\gamma_2} \right]$$

Adding the two Donnan potentials results in:

$$E_{B.I.P.} = - \ \frac{RT}{F} \ \left[ln \ \frac{a_1' \ D_1^\alpha \ \gamma_2^\omega}{a_2^1 \ D_2^\omega \gamma_1^\alpha} + \int_\alpha^\omega t_1 \ d \ ln \ \frac{D_1}{\gamma_1} + \int_\alpha^\omega t_2 \ d \ ln \ \frac{D_2}{\gamma_2} \right] (2\text{-}22)$$

Apart from correction for water transport and transport by the negative ion this formula is identical with Scatchard's. This is not very surprising, as the flux equations in the steady state in this case are equivalent with the Nernst equation, for:

$$\left. \begin{aligned} \Phi_1 &= - \ D_1 \left[\ C_1 \ \frac{\partial \ ln \ a_1}{\partial x} + C_1 \ \frac{F}{RT} \cdot \frac{\partial E}{\partial x} \ \right] \\[2mm] \Phi_2 &= - \ D_2 \left[\ C_2 \ \frac{\partial \ ln \ a_2}{\partial x} + C_2 \ \frac{F}{RT} \cdot \frac{\partial E}{\partial x} \ \right] \\[2mm] \Phi_1 &+ \Phi_2 = 0 \end{aligned} \right\} \qquad (2\text{-}23)$$

In the steady state:

$$F^{'}/RT \frac{dE}{dx} = \frac{D_1 C_1}{D_1 C_1 + D_2 C_2} \frac{d \ln a_1}{dx} + \frac{D_2 C_2}{D_1 C_1 + D_2 C_2} \frac{d \ln a_2}{dx}$$

$$F/RT \frac{dE}{dx} = t_1 \frac{d \ln a_1}{dx} + t_2 \frac{d \ln a_2}{dx},$$

thus:

$$E = \frac{RT}{F} \int_{\alpha}^{\omega} t_i \, d \ln a_i$$

The equations (2-23) are a special case of the more general phenomenological equations of irreversible thermodynamics; this explains the formal equivalence between the equations (2-23) and that of Scatchard.

Checking the theory

In the case of a membrane separating two uni-univalent salt solutions we found for the B.I.P.

$$E_{B.I.P.} = \frac{RT}{F}\left[\ln \frac{a_2'}{a_1'} + \ln \frac{u_2^\omega \gamma_1^\alpha}{u_1^\alpha \gamma_2^\omega} + \right.$$
$$- \int_\alpha^\omega \frac{\Sigma_i^+ m_i\, u_i\, d \ln u_i/\gamma_i}{\Sigma_i^+ m_i\, u_i} +$$
$$\left. + \int_\alpha^\omega t_x \frac{\Sigma_i^+ m_i\, u_i\, d \ln a_i\, a_x}{\Sigma_i^+ m_i\, u_i} + \int_\alpha^\omega t_w\, d \ln a_w \right] \qquad (2-8)$$

Neglecting correction terms for the moment, Wyllie's technique (1954b) is the best way to check this formula. In his technique the concentration of one of the solutions is kept constant. Plotting the measured B.I.P. against the logarithm of the varying activity, in the first place the result should be a straight line with a slope corresponding to a change of B.I.P. of 58 mV for each tenfold change in activity. In the second place: at the intersection of the straight line with the abscissa we must have

$$\frac{u_2^\omega \cdot \gamma_1^\alpha}{u_1^\alpha \cdot \gamma_2^\omega} = \left(\frac{u_2\, \gamma_1}{u_1\, \gamma_2}\right) = \left(\frac{a_1'}{a_2'}\right) E = 0$$

$u_2 \gamma_1 / u_1 \gamma_2$ can be derived from transference number measurements. Here the membrane is placed in a solution of a mixture of the two salts. At current passage the ratio of the transference numbers of the ions 1 and 2 is:

$$\frac{t_1}{t_2} = \frac{u_1\, c_1}{u_2\, c_2}$$

u_i and c_i are the mobility and the concentration of the ion i in the membrane. Or also

$$\frac{t_1}{t_2} = \frac{u_1\, \gamma_2\, a_1}{u_2\, \gamma_1\, a_2}$$

Now, according to Donnan's law:

$$\frac{a_1}{a_2} = \frac{a_1'}{a_2'}$$

where a_1' and a_2' are the activities of the ions 1 and 2 in the solutions. Besides the ratio u_1/u_2 can be estimated from conductivity measurements and γ_2/γ_1 from selectivity measurements, provided we may assume u_1, u_2, γ_1 and γ_2 to be constant across the

whole membrane. This goes further than Scatchard's assumptions: $u_1/\gamma_1 = P_1$ and $u_2/\gamma_2 = P_2$.

The correction terms

Calculation of the first correction term is very difficult, as the concentrations, the mobilities and the activity coefficients of the separate ions have to be known throughout the whole membrane. The second correction term originating from transport by the negative ion can be neglected if the selectivity constant (defined according to the M.S.T. theory, i.e. the concentration of active groups in the membrane) of the membrane is high compared with the activities of the external solutions. The correction term for the water transport $\int_\alpha^\omega t_w \, d \ln a_w$ can be estimated by measuring water transport numbers. From the literature it can be learned that the water transport number depends only to a small extent on the current density and the external concentration. An estimate of this correction term can be made by taking $\bar{t}_w \ln a_w{}^\omega/a_w{}^\alpha$, where $\bar{t}_w$ is the mean value of the water transport number in the membrane, equilibrated with a solution of the ions 1 and 2 respectively.

III. EXPERIMENTS

1. Membranes

We tried to include in our investigation as many different types of membranes as possible. In general one can divide the membranes according to their structure into homogeneous and heterogeheous membranes, or according to the nature of their network into hydrophylic and hydrophobic membranes.

1. Hydrophilic type. In a permeable hydrophilic membrane active groups are introduced in a chemical way. The resistance of this type can be very low, but the selectivity in concentrated salt solutions is mostly poor.

2. Hydrophobic type. A hydrophobic sheet is treated chemically to introduce positive or negative groups. The resistance may be very low, especially if one starts from a thin film. Selectivity can be very high, even in concentrated salt solutions.

3. Homogeneous type. The membrane consists of a continuous gel of an ion exchange resin. The resistance of this type is mostly low, but the mechanical properties are often poor.

4. Heterogeneous type. The membrane consists of a powdered ion exchange resin and a binder. It has a somewhat higher resistance, but also a high selectivity in concentrated solutions.

Further one can distinguish the membranes according to their active groups. Our research included the $-SO_3H$, the $-OP(O)(OH_2)$ and the $-COOH$ groups. We will now give a brief description of the membranes used.

a. A 58. This is a cellophane-type membrane, obtained by treatment of a cellophane film with the dimethylol compound of adipamide- $\alpha \alpha'$ disulfonic acid (Brit. 733, 100). The properties of this membrane are as follows:

Capacity: 0.27 mgaeq/gram dry.
Resistance in 0.1 N NaCl solution 20 Ω cm^2.
Thickness 0.15 mm.
Watercontent 33% of dry weight.

b. A 71. Also a cellophane type membrane, containing however, phosphate groups. It is obtained by impregnating a cellophane film with a solution of urea and diammoniumphosphate, followed by curing. To decrease swelling in water, it can be cross-linked afterwards with dimethyloladipamide. The membrane has the following properties:

Capacity: 0.42 mgaeq/gram dry.
Resistance in 0.1 N NaCl solution 20 Ω cm^2.
Thickness 0.17 mm.
Watercontent 45% of dry weight.

c. Dowex 50-polyethylene membrane. A heterogeneous membrane, containing -SO3H groups, obtained by mixing powdered Dowex 50 with polyethylene in a weight ratio of 2 to 1, followed by moulding at a higher temperature (Brit. 719, 315). Properties:

Capacity: 2.0 mgaeq/gram dry.

Resistance in 0.1 N NaCl solution 19 Ω cm².

Thickness 0.57 mm.

Watercontent 37% of dry weight.

d. Amberlite IRC 50-polyethylene membrane. A heterogeneous membrane, containing -COOH groups, also made according to Brit. 719, 315. Properties:

Capacity: 3.3 mgaeq/gram dry.

Resistance in 0.1 N NaCl solution 2 Ω cm².

Thickness 0.47 mm.

Watercontent 24% of dry weight.

e. Stamex K. A hydrophobic-type membrane, containing -SO3H groups, obtained by sulphonating a polyethylene film with the aid of chlorsulphonic acid (Dutch Appl. 180, 986). Properties:

Capacity: 1.1 mgaeq/gram dry.

Resistance in 0.1 N NaCl solution 13 Ω cm².

Watercontent 14% of dry weight.

N. B. As the properties of the membranes vary somewhat from one case to another, the data given above have to be considered as average values.

2. Bi-ionic potential measurements

The technique of these measurements has been described already in the contribution of Bergsma and Staverman (1956) to the symposium of the Faraday Society on membrane phenomena in Nottingham. The membrane is clamped between the ground-in flanges of two glass cells, containing salt solutions with different cations. The cells form part of a circuit in which the solutions (volume 60 cm³) were circulated with a velocity of about 2 l/h. The potentials are measured with a lampvolt meter with compensator (accuracy 0.1 mV). For the chloride solutions calomel and silverchloride electrodes were used. The AgCl electrodes were prepared according to directions of A. S. Brown (1934).

Measurements with the two different kinds of electrodes were made to check the results. Often a difference of 1 à 2 mV was found between both measurements. We did not investigate whether this effect was caused by an incomplete reversible behaviour of the AgCl electrode or by the diffusion potential at the calomel electrode, but made separate plots of the two series of measurements. For the solutions with silvernitrate we used calomel electrodes provided with a saturated ammoniumnitrate bridge to prevent precipitation of Ag. The mutual differences of the electrodes were compensated by regularly changing them, taking the average of both potential values. The following combinations of electrolytes were used:

$$AgNO_3 - HNO_3.$$
$$AgNO_3 - NaNO_3.$$
$$NaCl \quad - HCl.$$
$$NaCl \quad - KCl.$$

The Ag^+-ion was chosen on account of its great affinity to many ion exchange resins. The H^+-ion has a great affinity to cation exchange resins with weak acid groups and a small affinity to cation exchange resins with strong acid groups. The used chemicals were p.a. qualities of Merck's (for the KCl) and of May and Baker's (for the other electrolytes).

The B.I.P.'s were plotted against the logarithm of the activity of one of the electrolytes, leaving constant the other solution, following a procedure of Wyllie's (1954) (see fig. 2 to 11). In all plots the arrows indicate the theoretical slope. From these plots the ratio of transference numbers in the membrane can be calculated. At the point of intersection of the straight lines with the abscissa

$$\frac{u_1 \; \gamma_2}{u_2 \; \gamma_1} = \frac{(a_2')}{(a_1')_\omega} \alpha$$

since at that point $E_{B.I.P.} = 0$.

The constant solution in most cases had a normality of 0.01. This low concentration was chosen to meet the requirement of complete selectivity of the membranes. As is shown in fig. 12, the cellophane-type membranes in particular lose their selectivity at higher salt concentrations. However, low concentrations have the disadvantage that diffusion layers near the membrane may influence the membrane potential (see the discussion remark by F. Helfferich at the Nottingham symposium on membrane phenomena (1956b)). Therefore a number of measurements were repeated with higher flow rates, namely 30 l/h (see fig. 13 to 18). For the higher selective membranes it is possible to measure with more concentrated solutions. For some of these membranes we made additional B.I.P. measurements, in which the constant concentration was kept at 0.1 N or 0.05 N. Also in these cases the B.I.P. measurements at flow rates of 2 l/h and 30 l/h were compared (see fig. 19 to 24).

Measuring B.I.P.'s, a stationary state has to be established across the membrane. To that end the membrane was previously shaken for some hours in the solution that is kept constant during a series of measurements. This solution was replaced several times. After that the membrane was mounted in the apparatus and the two solutions were circulated for several hours along the membrane. Both solutions were replaced several times. Potentials were then read every five minutes. Measurements were continued for about one hour. Also during this time the solutions were renewed occasionally. The membrane potential should not change systematically in the course of time, so that one can as-

sume that equilibrium has been established. Only when membranes come into equilibrium with solutions very slowly are incorrect results obtained (examples of that were given at the Nottingham symposium; see G. Scatchard and F. Helfferich (1956), D. Hutchings and R. J. P. Williams (1956)). A very slow establishment of equilibrium occurs for instance if a "strange" ion is present in the membrane, showing a great affinity to the active groups. Some examples of this occurring are given in the literature. Scatchard and Helfferich (1956) call: Wyllie (1952), Coleman (1953), Scatchard (1954, 1955). As an accompanying phenomenon a straight line with a slope, deviating from the theoretical one, occurs in that case. We could demonstrate this effect on a cellophane-type membrane, used previously in solutions containing Ag^+-ions. An A 58 membrane was first brought to equilibrium between a 0.01 N HNO_3 solution on one side and a 0.01 N $AgNO_3$ solution on the other side by circulating these solutions for several hours along the membrane. After that the membrane was rinsed with distilled water in the apparatus for some hours. Then a series of B.I.P. measurements were carried out in the usual way with the HCl/M/NaCl system in which the constant concentration was kept at 0.01 N. The results are given in fig. 19.

3. Transport number measurements

These experiments have also been described in our paper for the Nottingham symposium. Originally the measurements were carried out in a two-cell electrolysis apparatus with a Ag anode and a AgCl cathode. However, reproducibility was rather poor. For this two reasons can be given:
1. It is possible that the electrodes are not perfectly reversible.
2. Some absorption of electrolyte on the formed AgCl layer may occur.
Satisfactory results were obtained, using a multicell, schematically shown in fig. 1. The membrane (3:4) was the negative membrane to be tested. Membranes (2:3) and (4:5) were positive membranes with high selectivity, only permeable to anions. In the beginning, cells 2, 3, 4 and 5 were filled with solutions of identical composition, containing two kinds of cations in equal concentration and a total concentration of 0.1 N. The cells 3 and 4 each form part of a circuit of 60 cm^3 volume in which the solutions are circulated with a velocity of 2 l/h. Cells 2 and 5 are rinsed with the same solution as is present in the beginning in cells 3 and 4. The electrode cells are rinsed with 0.1 N $NaNO_3$ solution. Membranes (1:2) and (5:6) are negative membranes. However, using Ag^+ solutions, (5:6) is replaced by a positive membrane in order to prevent precipitation of Ag in the cathode cell. The effective area of each membrane was 40 cm^2. The current density was 0.5 mA/cm^2. After passage of a known amount of electricity, the contents of cells 3 and 4 were transferred separately and quantitatively into standard flasks. The total amount of either kind of cations was determined. In this way true trans-

ference numbers were determined. In order to check the results, a balance was made afterwards of the total amount of ions of either kind in cells 3 and 4 together. The membrane investigated had previously been equilibrated by shaking for some hours with the relevant salt solution. Nevertheless a small loss of cations was found in the first experiments. Apparently equilibrium had not been established completely.

The composition of the salt mixture was determined as follows: in the mixture $HNO_3 + AgNO_3$, the amounts of cations were determined directly. In the mixtures $HCl + KCl$ and $AgNO_3 + NaNO_3$, the first cation and the total amount of anion were determined and the second cation was calculated by subtraction. H^+, Ag^+ and Cl^- were determined by titration, NO_3^- by means of a column of Dowex 50 (see Samuelson (1954)). In the mixture $KCl + NaCl$ the concentrations of K^+ and Na^+ were determined spectrophotometrically. For checking, the sum was compared with total Cl^-, found by titration.

The tables 3 to 6 give the ratios $u_1 \gamma_2/u_2 \gamma_1$ obtained from B.I.P. measurements and from transport measurements. For purposes of comparison, the ratios of the equivalent conductivities at infinite dilution are also given.

$$\text{"Transport ratios"} \quad \frac{u_1 \, \gamma_2}{u_2 . \gamma_1}$$

Table 3

$$\frac{u_{Ag^+} \cdot \gamma_{H^+}}{u_{H^+} \, \gamma_{Ag^+}}$$

ratio of limiting equivalent conductivities is 0.18

membrane	transport measurement	B.I.P.
Dowex 50	0.57 ± 0.05	0.45 ± 0.04
Stamex K	0.53 ± 0.04	0.47 ± 0.04
A 58	0.34 ± 0.02	0.24 ± 0.02
A 71	0.31 ± 0.01	0.22 ± 0.02
IRC 50	0.17 ± 0.01	0.19 ± 0.01

Table 4

$$\frac{u_{Na^+} \cdot \gamma_{Ag^+}}{u_{Ag^+} \cdot \gamma_{Na^+}}$$

ratio of limiting equivalent conductivities is 0.81

membrane	transport measurement	B.I.P.
Dowex 50	0.62 ± 0.02	0.76 ± 0.04
Stamex K	0.40 ± 0.01	0.55 ± 0.03
A 58	0.65 ± 0.05	0.80 ± 0.02
A 71	0.66 ± 0.04	0.69 ± 0.02
IRC 50	0.53 ± 0.04	0.52 ± 0.02

Table 5

$$\frac{u_{Na^+} \cdot \gamma_{H^+}}{u_{H^+} \cdot \gamma_{Na^+}}$$

ratio of limiting equivalent conductivities is 0.14

membrane	transport measurement	B.I.P.
Dowex 50	0.36 ± 0.04	0.19 ± 0.01
Stamex K	0.25 ± 0.03	0.21 ± 0.01
A 58	0.27 ± 0.03	0.12 ± 0.01
A 71	0.18 ± 0.03	0.14 ± 0.02
IRC 50	0.17 ± 0.03	0.10 ± 0.01

Table 6

$$\frac{u_{Na^+} \cdot \gamma_{K^+}}{u_{K^+} \cdot \gamma_{Na^+}}$$

ratio of limiting equivalent conductivities is 0.68

membrane	transport measurement	B.I.P.
Dowex 50	0.73 ± 0.04	0.64 ± 0.05
Stamex K	0.63 ± 0.09	0.65 ± 0.04
A 58	0.65 ± 0.07	0.65 ± 0.08
A 71	0.72 ± 0.08	0.61 ± 0.08
IRC 50	0.48 ± 0.07	0.48 ± 0.04

Remarks:

1. In the series Ag^+/H^+ the Dowex 50 and Stamex K membrane were investigated at a constant concentration of 0.05 N. In all other cases the constant concentration amounted to 0.01 N.

2. Several of the above-mentioned data have already been presented at the Nottingham membrane conference. Later on, some of the series were repeated with a view to compare the B.I.P.'s at 2 l/h flow velocity with those of 30 l/h velocity. In most instances the agreement between the 2 l/h measurements was satisfactory; only for the A 58 and A 71 membrane in the Na^+/Ag^+ series were other values found, whereas the slopes of the straight lines in the later measurements were closer to the theoretical value. Possibly the membranes were not completely in equilibrium in the former experiments.

4. Water transport measurements

For the measurement of water transport numbers we had to make a choice from two methods.

a. *Balance method*. Before and after the experiment the total amount of ions and of water is estimated on both sides of the membrane. From these the water transport can be calculated. A variant of this method consists in measuring in a first experiment the change in the number of ions on both sides of the membrane during current passage and in estimating the change in concentrations in a duplicate experiment. From this the amount of solvent displaced can be calculated.

b. *Capillary method*. The water transport is measured by providing both cells with a capillary. The displacement of the menisci gives the quantity of the solvent transported.

Ad a. An advantage of the first method is that both cells can easily be stirred. For the capillary method this is nearly impossible.

A disadvantage of the balance method is the difficulty of transferring the solutions quantitatively from the cell to a measuring vessel. Therefore it is necessary to allow the passage of a large amount of charge through the cell to get a relatively large amount of solvent (order of magnitude about 1 ml). This results in large concentration changes in the two cells especially in the case of a low water transport number. For this reason the concentrations at the beginning are chosen in such a way that at the end of the experiment the concentrations are reversed. The influence of diffusion and osmosis is eliminated in this fashion. The long duration of the experiment gives rise to a noticeable evaporation of solvent. Therefore, checking the experiment by calculating the balances of both cells and comparing the results is impossible. One assumes the amount of evaporation in the two cells to be equal, and correct for this effect. A.G. Winger et al. (1956) claimed an experimental accuracy of about 3%. The content of the cell amounted to 75 ml. About 2 ml of water was transported. This means that transferring the solutions, the losses may not exceed

0.06 ml. If water transport is calculated from concentration changes during the experiment, the concentrations have to be measured with a very high accuracy. Besides, the electrodes should be perfectly reversible and the experimental results should be very reproducible.

Ad b. With the capillary method it is possible to measure small solvent displacements with a high accuracy. Care has to be taken that displacements of the membrane and changes in shape of it are prevented. A suitable support is therefore needed. This, however, has the disadvantage that the transport of matter near the membrane is hindered. Concentration polarization may occur and H^+ respectively OH^- ions may begin to participate in the transport of charge.

Our first measurements were carried out according to the above mentioned variant of the balance method. The apparatus consisted of two cylindrical perspex cells, between which the membrane was clamped. The active membrane area amounted to 38.5 cm^2. The inner thickness of each cell was 1 cm; the content of each cell 38.5 cm^3. The electrodes consisted of silver grids, electrolytically covered with a layer of AgCl. After each measurement these electrodes were exchanged against each other. The electrical current was very accurately determined by means of a precision resistance of 100 Ω. The voltage across this resistance was measured with a lampvoltmeter. The accuracy amounted to 1‰. The current was supplied by a 6 V accumulator. The influence of back-diffusion and osmosis was eliminated by taking care that during the experiment the time-averaged concentrations on either side were equal. The volume of the solution at the end of the experiment was determined from

$$V = c/n$$

V = volume of the solution
c = concentration
n = number of gaeq. electrolyte
V must be estimated with an accuracy better than 1‰.

Therefore c and n must be known to a very high accuracy. c was determined by the aid of a potentiometric titration (differential method), described by Mac Innes (1950). At the beginning of the experiment both cells were filled with an accurately measured volume of a salt solution of known concentration. Two sources of error were found during the first experiments:

1. The solutions in both cell-halves were circulated with the aid of air-lifts. However, these promoted evaporation, upsetting the results. Therefore they were removed.

2. Before the experiment the apparatus must be perfectly dry. With drying however, some water is withdrawn also from the membrane, so that too small a quantity of water is estimated. This difficulty was solved by rinsing the apparatus previously with alcohol, after which humid aid was blown through.

The number of gram equivalents, present at the end of the experiment was calculated with the aid of the transport numbers in

the membrane and the reaction at both AgCl electrodes. The transport measurements should be perfectly reproducible (deviations not greater than 1‰). This was not the case in our experiments. Probably the AgCl electrodes are not completely reversible. Our results for a number of transport number measurements in a Dowex 50-polyethylene membrane are given in table 7. The total current amounted to 25 mA, the duration of the experiment was 45 minutes. For a ideally selective membrane one should find for the quantity of electrolyte transported $\dfrac{45 \times 60 \times 25}{96480}$ mg eq. = 0.700 mg eq.

Table 7
Reproducibility of transport measurements through a
Dowex 50-polyethylene membrane.

number of experiment	cathode cell	anode cell
1	+ 0.73 mgeq.	- 0.71 mgeq.
2	+ 0.67	- 0.68
3	+ 0.70	- 0.72
4	+ 0.68	- 0.68
5	+ 0.72	- 0.72
6	+ 0.68	- 0.70
averaged	+ 0.70	- 0.70

On the average we find 0.70 mgeq. but the accuracy does not exceed 4%. Therefore this method was not practicable. For this reason we changed over to the capillary method. To that end the cells were provided with two horizontally placed capillaries. 10 mm displacement of the meniscus corresponded to 0.004 ml transport of water. The apparatus was placed in a thermostat filled with transformer oil. The temperature of the bath was 25°C. The whole was placed in a conditioned room with a temperature of 20°C.

At first we obtained very irregular values. It appeared that reproducible results could be obtained only if the capillaries were thoroughly cleaned. It proved to be desirable to replace the capillaries occasionally. Moreover, the method of supporting the membrane exerts some influence. A support with openings of 5 mm diameter gave low values of the water transport. Supporting with a coarse glass filter caused polarization of the membrane. Satisfactory results were obtained using a support having holes with a diameter of 3 mm. Thickness: 1 mm. Total active membrane area = 2.62 cm^2.

The displacement of the meniscus was plotted against time. An example of these plots is given in fig. 25. At the beginning we observed an increasing velocity of the meniscus. After some time a constant value was reached. This phenomenon is due to changes

in shape of the membrane. At the end, when the current flow is stopped, the displacement continues for some time as a result of the membrane restoring its initial shape. Corrections were made for the changes in volume of the electrodes and for changes in volume due to alterations in NaCl concentration. Calculating the first correction we used the following values:

spec. weight of AgCl = 5.56
spec. weight of Ag   = 10.5
Per Faraday ΔV of the electrode reaction AgCl $\longrightarrow$ Ag equals

$$- \frac{143.5}{5.56} + \frac{107.9}{10.5} = - 15.5 \text{ ml } H_2O.$$

This corresponds to -0.86 gmol H_2O/F. For the calculation of the apparent molal volume of the various salts we used the formula:

$\Phi_v = \Phi_v^\circ + s_v \sqrt{c}$ ml, where

Φ_v = apparent molal volume

c = number of moles per 1000 ml of solution

Φ_v° and s_v are constants.

Values for Φ_v° and s_v are borrowed from table (8-5-1) of "The Physical Chemistry of Electrolytic Solutions" by Harned and Owen (1950).

For NaCl Φ_v° = 16.40; s_v = 2.153

For KCl Φ_v° = 26.52; s_v = 2.327

For HCl Φ_v° = 18.20; s_v = 0.85

In 0.1 N salt solutions we get for:

NaCl Φ_v = 17.1 ml $\sim$ 0.95 mole H_2O.

KCl Φ_v = 27.3 ml $\sim$ 1.5 mole H_2O.

HCl Φ_v = 18.5 ml $\sim$ 1.0 mole H_2O.

For 0.1 N NaCl the total correction amounts to
+ 0.86 - 0.95 = - 0.1 mole H_2O.
For 0.1 N KCl: + 0.86 - 1.5 = - 0.6 mole H_2O.
For 0.1 N HCl: + 0.86 - 1.0 = - 0.1 mole H_2O.

For 0.1 N AgNO₃ the correction is $- \dfrac{107.9}{10.5 \times 18}$ mole = - 0.6 mole H_2O.

Previously the membranes were shaken for some hours in the 0.1 N salt solution concerned. The total current was 12 mA. Every 15 minutes the position of both menisci was read. The measurements lasted for some hours. For each membrane 3 to 5 experiments were carried out. The standard deviation was calculated. The results of the measurements are given in table 8.

Table 8
Water transport through cation selective membranes

membrane	salt solution	water transport number	standard deviation
Dowex 50	0.1 N NaCl	9.3	± 0.2
Stamex K	0.1 N NaCl	7.5	± 0.3
IRC 50	0.1 N NaCl	12.9	± 1.2
A 71	0.1 N NaCl	16.9	± 1.2
A 58	0.1 N NaCl	10.5	± 1.3
Dowex 50	0.1 N KCl	6.3	± 0.6
Stamex K	0.1 N KCl	3.9	± 0.1
IRC 50	0.1 N KCl	7.1	± 0.2
A 71	0.1 N KCl	7.8	± 0.7
A 58	0.1 N KCl	7.0	± 0.3
Dowex 50	0.1 N HCl	1.4	± 0.1
Stamex K	0.1 N HCl	1.7	± 0.3
IRC 50	0.1 N HCl	2.7	± 0.2
A 71	0.1 N HCl	2.2	± 0.1
A 58	0.1 N HCl	1.8	± 0.1
Dowex 50	0.1 N AgNO$_3$	3.3	± 0.3
Stamex K	0.1 N AgNO$_3$	3.1	± 0.3
IRC 50	0.1 N AgNO$_3$	7.2	± 0.3
A 71	0.1 N AgNO$_3$	5.2	± 0.1
A 58	0.1 N AgNO$_3$	5.2	± 0.2

5. Measurements of the selectivity constant $K_2^{\frac{1}{2}}$

It is assumed that if a cation exchange membrane is placed in a solution with different cations, a Donnan equilibrium is established for which is valid, in the case of univalent cations:

$$\frac{a_2'}{a_1'} = \frac{a_2}{a_1} = \frac{\gamma_2 \, c_2}{\gamma_1 \, c_1} = K_2^{\frac{1}{2}} \frac{c_2}{c_1}$$

a_1' and a_2' are the activities of the ions 1 respectively 2 in the solution, a_1 and a_2 are the corresponding values in the membrane. The measurements were carried out as follows: about 1 gram of the membrane in a suitable salt form was brought to equilibrium with a solution, containing a mixture of the cations 1 and 2. After that the number of both cations in the membrane was determined. The total concentration of both cations always amounted to 0.1 N. For each combination of cations 1 and 2 three series of measurements were carried out with a concentration ratio of 9/1, 1, and 1/9. Most measurements were carried out in triplicate. To check the experiments the H$^+$ exchange capacity of the sample

was also estimated. For this purpose the membrane was shaken for 21 hours in 100 ml of 1 N sulphuric acid. The solution was replaced after 3 and 18 hours. It was then shaken 3 x one hour in 100 ml 0.1 N sulphuric acid and squeezed lightly twice between filter-paper. After that the membrane is shaken with 0.1 N sodiumhydroxide for about 10 hours. The excess of sodiumhydroxide is titrated back with 0.1 N sulphuric acid on methyl red.

a) Ag^+ - H^+ series.

Initially the experiments were carried out as follows: ± 1 g of the membrane was transferred into the H^+-form by shaking with 100 ml 0.1 N nitric acid for 24 hours. After that the acid was removed by shaking with distilled water. Then the membrane was shaken in 100 ml of the salt mixture for 24 hours. The solution was replaced regularly. Then it was squeezed twice between filter-paper and shaken with 100 ml 1 N KNO_3 for one hour. This was repeated twice with fresh KNO_3 solution. The three portions were collected and the silver content was determined according to Volhard. The acid was titrated with 0.1 N NaOH. In this manner the equilibrium concentrations in the Dowex 50, the Stamex K and A 58 membrane were determined for $C_{Ag^+}/C_{H^+} = 1$.

In all other instances the membrane first was converted into the sodium form by shaking with 100 ml 1 N NaOH for 21 hours. After three and eighteen hours the NaOH solution was replaced. Then the membrane was shaken in distilled water until free of alkaline. After that it was shaken in the salt mixture for 21 hours. After 3 and 18 hours the solution was renewed. Then it was squeezed twice between filter-paper. The Ag^+ and a part of the H^+ ions on the membrane were removed by shaking three times in 100 ml 1 N $Ca(NO_3)_2$. The rest of the H^+ ions were estimated by shaking the membrane in an excess of 0.1 N NaOH solution and back titrated. Ag^+ and H^+ were determined as stated above. All experiments with silver salt solutions were carried out in blackpainted flasks to prevent reduction of the silver ions by light. The results of the experiments are given in table 9.

b) Na^+ - Ag^+ series.

α. Dowex 50, Stamex K and IRC 50 membrane. The Dowex 50 and Stamex K membrane were first converted into the H^+ - form, the IRC 50 membrane into the Na^+ - form. After that they were shaken for 21 hours with 100 ml of the solution of silvernitrate and sodiumnitrate. The solution was replaced several times. Then the membrane was squeezed twice between filter-paper and shaken in 100 ml 1 N HNO_3 for 21 hours. The solution was renewed three times. The solutions were collected and neutralized with a 25% NH_4OH solution. Ag^+ was determined according to Volhard. Na^+ was estimated flamephotometrically. The NH_4^+ - ion did not disturb the determinations.

β. The A 58 and A 71 membrane were first brought in the NH_4^+ - form by treating with 1 N NH_4OH solution. Then they were shaken for 21 hours in 100 ml of the salt mixture. After that the Ag^+ and Na^+ - ions were removed by shaking in 3 x 100 ml 1 N HNO_3. The solutions were collected, neutralized with a 25% NH_4OH solution,

and made up to 1000 ml. In 500 ml Ag^+ was estimated. The other half was used to determine Na^+ flamephotometrically. In the latter instance it proved to be useful to first remove the Ag^+-ions. To that end a little ammoniumchloride was added and the colloidal precipitate was removed by absorbing it on cuttings of filter-paper. The results are given in table 10.

c) Na^+ - H^+ series.

The membranes were first converted to the NH_4^+-form. They were shaken for 21 hours in 100 ml of a solution containing NaCl and HCl in a fixed ratio. After 3 and 18 hours the solution was renewed. After that the membrane was squeezed as before and shaken in an excess of 0.1 N KOH for 21 hours. The excess of alkali was back titrated with 0.1 N H_2SO_4. Then the membrane was shaken three times in 100 ml of 1 N HNO_3 for 21 hours. The solutions were collected and the liquid being left after the titration, was added. Then the solution was neutralized with 25% NH_4OH. In this solution Na^+ was estimated flamephotometrically. The results are given in table 11.

d) Na^+ - K^+ series.

At first all membranes were converted to the NH_4^+ - form. Then each membrane was shaken for 21 hours in 100 ml of a salt solution, containing NaCl and KCl in a fixed ratio. The solution was renewed after 3 and 18 hours. The membrane was squeezed as before and shaken in 100 ml of a 1 N HNO_3 solution for 21 hours. This was repeated three times. The solutions were collected and neutralized with 25% NH_4OH. Na^+ and K^+ were determined flame photometrically. The results are given in table 12.

The capacity of the membrane sample was also measured in all cases to check the experiments. It is necessary that the sum of the cations measured is equal to the exchange capacity of the sample for H^+ ions. In general the agreement was satisfactory. Only in the instance of the A 58 membrane was the sum of both cations in most series much higher than the exchange capacity. We found that the capacity for Ag^+ - ions of an A 58 sample was 0.28, whereas the capacity for H^+ - ions was merely 0.12. The cause of this phenomenon was not further investigated.

Selectivity constants $K_2^1 = \gamma_2/\gamma_1$.

Table 9

$\gamma_{H^+}/\gamma_{Ag^+}$

Membrane	Dowex 50	Stamex K	A 58	A 71	IRC 50
Concentration ratio C'_{Ag^+}/C'_{H^+}					
9/1	3.1	0.31	0.31	0.07	0.13
1/1	7.5	4.2	1.6	0.43	0.0075
1/9	4.7	3.6	0.40	0.18	0

Table 10

$$\gamma_{Ag^+} / \gamma_{Na^+}$$

Membrane	Dowex 50	Stamex K	A 58	A 71	IRC 50
Concentra-tion ratio C'_{Na^+}/C'_{Ag^+}					
9/1	0.26	0.18	0.61	0.17	0.034
1/1	0.28	0.22	0.66	0.31	0.018
1/9	0.22	0.30	4.76	1.2	0.032

Table 11

$$\gamma_{H^+} / \gamma_{Na^+}$$

Membrane	Dowex 50	Stamex K	A 58	A 71	IRC 50
Concentra-tion ratio C'_{Na^+}/C'_{H^+}					
9/1	1.1	0.20	0.37	0.054	0.03
1/1	1.5	1.3	1.2	0.19	0.003
1/9	1.4	1.2	1.6	0.44	0.02

Table 12

$$\gamma_{K^+} / \gamma_{Na^+}$$

Membrane	Dowex 50	Stamex K	A 58	A 71	IRC 50
Concentra-tion ratio C'_{Na^+}/C'_{K^+}					
9/1	0.57	0.42	0.64	0.78	1.12
1/1	0.65	0.55	0.89	0.82	1.25
1/9	0.70	0.70	0.74	0.74	1.36

Remark. The standard deviation in the estimation of the selectivityconstants amounts for Dowex 50 and Stamex K 1 to 5%; for A 58 and A 71 5 to 20%; for IRC 50 1 to 5%, with the exception of $C'_{Ag^+}/C'_{H^+} = 1/1$; $C'_{Na^+}/C'_{Ag^+} = 1/1$ resp. 1/9; and $C'_{Na^+}/C'_{H} = 1/1$ resp. 1/9 where it amounts to 20 to 40%.

6. Measurements of the conductivity

The membrane was clamped in between two half-cells in which the relevant salt solutions were circulated with the aid of air-lifts, operated with nitrogen. The active membrane-area amounted to 0.28 cm^2. A part of each circulation circuit was surrounded by a mantle. This mantle formed part of a circuit in which a thermostat was taken up to a temperature of 25°C ± 0.01°. The whole apparatus was placed in a conditioned room with a temperature of 20°C ± 1°. The cell was provided with two circular platinized platinum electrodes. The cell-resistance was measured with an accurate Wheatstone bridge with amplifier and indicator tube. The membrane resistance was estimated as the difference of the cell resistance with membrane and without membrane. Three samples were measured of each membrane. The membrane first was converted into the relevant salt form and then brought to equilibrium with the corresponding 0.1 N salt solution by shaking for 21 hours. Measurements were carried out in respectively 0.1 N NaCl, 0.1 N KCl, 0.1 N HNO$_3$ and 0.1 N AgNO$_3$. To prevent hydrolysis of the weak acid membranes, the pH of the solutions was brought up to 8. Each membrane sample was converted successively into the different salt forms. To eliminate errors, caused by irregularities of the membranes, the same area of each membrane sample was measured on each occasion. The resistance of the cell with membrane was measured every five minutes over a period of half an hour. After that the resistance of the cell without membrane, but with the circulating solutions was measured.

In table 13 the ratio of the mobilities of the ions in the membrane is given, using the formula $u_1/u_2 = R_2/R_1$, in which R_1 and R_2 are the resistances of the membrane when fully in the 1 respectively 2-form.

Table 13

u_1/u_2

Membrane	Dowex 50	Stamex K	A 58	A 71	IRC 50	Ratio of limiting equivalent conductivity
Mobility ratio						
u_{Ag^+}/u_{H^+}	0.14	0.07	0.26	0.24	0.39	0.18
u_{Na^+}/u_{Ag^+}	1.14	1.84	0.76	0.94	5.33	0.81
u_{Na^+}/u_{H^+}	0.16	0.13	0.20	0.23	2.06	0.14
u_{Na^+}/u_{K^+}	0.72	0.49	0.76	0.70	0.46	0.68

Remark. The standard deviation in the estimation of the mobility ratios amounts to 1 to 10%.

IV. DISCUSSION

Plotting the B. I. P.'s against the logarithm of the varying activity in general results in a straight line with a slope, corresponding with a change of 58 mV in B. I. P. for each tenfold change in activity (see fig. 2 to 11). However, for the cellophane membranes in some instances the slopes of the straight lines were too small.

From the tables 3 to 6 can be read that there is agreement within the experimental error between the "transport ratios" derived from B. I. P. measurements and from transport measurements in about one half of the cases investigated. In the remaining part there is no agreement. As there was a possibility that water transport through the membrane caused the discrepancies, water transport numbers were measured for all the membranes (see table 8). The influence of water transport on the B. I. P. can be calculated approximately, according to

$$E' = \frac{RT}{F} . \bar{t}_W \ln \frac{a_W^\omega}{a_W^\alpha} \qquad (4-1)$$

$\bar{t}_W$ = mean value of the water transport number in the membrane equilibrated with a solution of the ions 1 and 2 respectively.

a_W^α = activity of the water in solution 1.

a_W^ω = activity of the water in solution 2.

The values for the water activities were calculated with the help of the numerical tables of J. Kielland (1939) for the osmotic coefficients starting from the definition of the molal osmotic coefficient

$$\ln a_W = - \frac{\nu \, m \, W_W}{1000} \Phi \qquad (4-2)$$

Φ = molal osmotic coefficient.
W_W = molecular weight of water.
m = molality of the solution.
ν = number of moles of ions formed from 1 mole of electrolyte.

On closer view it proved that the correction for water transport on the B. I. P. was very small, as the activity coefficients of

water in dilute salt solutions are only slightly below one. We shall now give the calculation for the most unfavourable case, namely an A 71 membrane, separating a 0.1 N NaCl and a 0.01 N KCl solution.

The activity coefficient for water in 0.1 N NaCl is 0.99664; in 0.01 N KCl: 0.99966. For the water transport number of an A 71 membrane, placed in 0.1 N NaCl we found 16.9; in 0.1 N KCl 7.8; $\bar{t}_w$ = 12.4. Thus

E' = 58.16 x 12.4 x 0.4343 (- 0.00336 + 0.00034) mV = - 0.94 mV.

The maximum deviation caused by water transport is consequently about 1 mV. So water transport cannot be the cause of the discrepancies.

It is possible that the differences are due to the term

$$\frac{\Sigma_i^+ \, m_i \, u_i \, d \ln u_i / \gamma_i}{\Sigma_j^+ \, m_i \, u_i}.$$

Scatchard himself states that this term may be very small, without giving further arguments. As has been said in the theoretical part, experimental estimation of this term is exceedingly cumbersome, as transference numbers, mobilities and activity coefficients have to be determined across the whole membrane. Although serviceable data in the literature are very scarce, we shall try to make a rough estimate of the magnitude of this correction term. Instead of

$$\frac{\Sigma_i^+ \, m_i \, u_i \, d \ln u_i / \gamma_i}{\Sigma_i^+ \, m_i \, u_i}$$

we may write: $\Sigma_i^+ \, t_i \, d \ln u_i / \gamma_i$, as $m_x u_x$ is almost zero.

As for u_i, only a few data have been published. B. A. Soldano and G. E. Boyd (1953) determined self-diffusion coefficients for different cations in various sulphonated polystyrene exchangers. In the instance of a nominal 8.6% DVB (divinylbenzene) exchanger they found for the pure Na^+ salt a self-diffusion coefficient of $9.44 \times 10^{-7} cm^2/sec.$ for the Na^+ ions. At an exchanger composition of 31% Na^+ and 69% H^+ this figure was $9.36 \times 10^{-7} cm^2/sec.$ At a composition of 7% Na^+ and 93% H^+ it was $8.82 \times 10^{-7} cm^2/sec.$ The change in u_{Na^+} is in this instance only 7%. Moreover the greater change occurs at lower Na^+ content where t_{Na^+} is small. In this instance

$$\int_\alpha^\omega t_{Na^+} \, d \ln u_{Na^+}$$

is very small. However, it is possible that in other cases the change of the mobility in the membrane is higher. To evaluate

$$\int_\alpha^\omega t_i \, d \ln \gamma_i$$

we applied Harned's rule (1950) to the resin phase following Glueckauf (1952) and Soldano, Larson and Meyers (1955).
This means that this phase is considered as a concentrated solution of salts. We get:

$$\log \gamma_1 = \log \gamma_1^\circ - \alpha_{12} \, m_2$$

$$\log \gamma_2 = \log \gamma_2^\circ - \alpha_{21} \, m_1 \tag{4-3}$$

γ_1 and γ_2 are the activity coefficients of the ions 1 and 2. γ_1° and γ_2° are the corresponding values for the pure resin salt of 1 and 2. α_{12} and α_{21} are constants depending only on m, the total molality of the solution which is constant throughout the membrane. Applying this, we arrive at

$$d \log \gamma_1 = -\alpha_{12} \, d \, m_2 = +\alpha_{12} \, d \, m_1$$

$$m_1 + m_2 = m$$

$$d \log \gamma_2 = -\alpha_{21} \, d \, m_1 = +\alpha_{21} \, d \, m_2$$

Thus

$$\int_\alpha^\omega \alpha_{12} t_1 \, d \, m_1 = \int_\alpha^\omega \alpha_{12} \frac{u_1 \, m_1}{u_1 \, m_1 + u_2 \, m_2} \, d \, m_1$$

$$= \alpha_{12} \left(\frac{m}{1 - u_2/u_1} - \frac{m}{u_1/u_2 - 2 + u_2/u_1} \ln u_1/u_2 \right) \tag{4-4}$$

We suppose u_1/u_2 to be constant.

$$\int_\alpha^\omega \alpha_{21} t_2 \, d \, m_2 = \int_\alpha^\omega \alpha_{21} \frac{u_2 \, m_2}{u_1 \, m_1 + u_2 \, m_2} \, d \, m_2$$

$$= \alpha_{21} \left(\frac{m}{u_1/u_2 - 1} - \frac{m}{u_1/u_2 - 2 + u_2/u_1} \ln u_1/u_2 \right) \tag{4-5}$$

For a sulphonated polystyrene exchanger Soldano et al (1955) estimated α_{12} and α_{21} for different combinations of the ions 1 and 2 with the aid of a "tracer selectivity" technique. Some of their data are compiled in table 14.

Table 14

Interaction coefficients for a sulphonated polystyrene exchanger

2/1	α_{12}	α_{21}
Ag/Na	0.0066	0.07
Ag/H	0.045	0.013
Na/H	-	-0.059
K/Na	0.02	-

To estimate the order of magnitude of the correction term, we calculated this for the systems Ag/H and Ag/Na. For the Dowex 50 membrane we found u_{Ag^+}/u_{H^+} = 0.14. Thus u_2/u_1 = 0.14; α_{12} = 0.045; α_{21} = 0.013. Substituting these values we get:

$$\int_\alpha^\omega \alpha_{12}\, t_1\, d\, m_1 + \int_\alpha^\omega \alpha_{21}\, t_2\, d\, m_2 =$$

(0.045 x 0.76 - 0.013 x 0.24) m = 0.031 m.

For our Dowex 50 membrane the capacity amounted to 2.0 mgeq/g dry. The water content was 37% of dry weight. This corresponds with m = 5.4 molal. Thus the correction term amounts to 58 x 0.031 x 5.4 mV = 9.7 mV.

For the Ag/Na system u_{Ag^+}/u_{Na^+} = 1/1.14 = 0.88; u_2/u_1 = 0.88; α_{12} = 0.0066; α_{21} = 0.07.

$$\int_\alpha^\omega \alpha_{21}\, t_1\, d\, m_1 + \int_\alpha^\omega \alpha_{21}\, t_2\, d\, m_2 =$$

(0.0066 x 1.5 + 0.07 x 0.5) m = 0.045 m

The correction term amounts to: 58 x 0.045 x 5.4 mV = 14.1 mV.

In both cases the term has a rather high value and cannot be neglected. However, it is possible that the influence of the change of the activity coefficient in some instances is partially compensated by the change of the mobility. As will be shown below, a decrease in activity coefficient (i.e. an increase in affinity) is often attended by a decrease in mobility. Assuming for the moment a value for the correction term of 14.1 mV in the case of $Na^+/Dowex\ 50/Ag^+$ we find that the value $u_{Na^+}\gamma_{Ag^+}/u_{Ag^+}\gamma_{Na^+}$ obtained from the plot has to be multiplied by 1.75 (as 0.045 x 5.4 = log 1.75) to get the actual "transport ratio". For the system $H^+/Dowex\ 50/Ag^+$ the value $u_{Ag^+}\gamma_{H^+}/u_{H^+}\gamma_{Ag^+}$ obtained from the plot has to be devided by 1.45 if we assume a value of 9.7 mV for the correction term. It is evident that this correction term requires much more investigation.

Another possible cause of the discrepancies, viz. film diffusion, was suggested by Helfferich (1956) at the Nottingham symposium. In deriving the B.I.P. formula it is supposed that the layers near the membrane have the same composition as the respective bulk

solutions. During the experiment, however, exchange occurs between the "critical ions" of the two solutions. In general the layers near the membrane will have a composition different from that of the bulk solution. Helfferich distinguishes two extreme cases: ideal membrane control and ideal film control. In the first case the diffusion potential in the films vanishes and a real B.I.P. is measured. In the second case the membrane potential vanishes and the measured potential is equal to a diffusion potential in which the mobility of the common anion is zero. The effect of film forming can be suppressed by violently stirring the solutions and by using not too low concentrations.

Considering our data it is striking that in the deviating cases the "transport ratios" from B.I.P. measurements are in between the "transport ratios" from transport number measurements and the ratios of limiting equivalent conductivities. Therefore it seemed worth-while to investigate the effect of film diffusion.

As the cellophane type membranes have a great permeability, it could be expected that this type above all should show the effect. So some measurements were repeated, comparing the B.I.P.'s at a flow rate of 2 l/h with those of 30 l/h (see fig. 13 to 18). In the case of $AgNO_3$ - $NaNO_3$ the values for A 71 and A 58 were about 1 to 3 mV higher at the 30 l/h flow rate (fig. 13 and 14). The slopes of the curves remained unchanged. In the case of KCl - NaCl the influence of the flow rate was small for the A 58 and A 71 membrane (fig. 17 and 18). In the case of HCl - NaCl for the A 58 membrane the influence of increasing flow rate was high. The straight line for a_{NaCl} = 0.009, however, showed at higher flow rate a greater deviation from the theoretical slope (fig. 16). The Dowex 50 membrane showed for the HCl/M/NaCl system hardly any difference in B.I.P.'s for the two flow rates.

The "transport ratios" from B.I.P. measurements at 2 l/h and 30 l/h are given in table 15.

Table 15

$$\frac{u_1 \; \gamma_2}{u_2 \; \gamma_1}$$

solu 1/M/solu 2	Flow rate 2 l/h	Flow rate 30 l/h
$NaNO_3$/A71/$AgNO_3$	0.69 ± 0.02	0.60 ± 0.04
$NaNO_3$/A58/$AgNO_3$	0.80 ± 0.02	0.72 ± 0.03
NaCl/Dowex 50/HCl	0.21 ± 0.01	0.21 ± 0.00
NaCl/A58/HCl	0.09 ± 0.01	0.06 ± 0.02
NaCl/A58/KCl	0.64 ± 0.08	0.61 ± 0.09
NaCl/A71/KCl	0.62 ± 0.07	0.67 ± 0.09

In general the "transport ratios" show a tendency to move in the direction of higher selectivity of the membrane as the flow rate increases. However, the increase in flow rate probably is

not sufficient to eliminate film diffusion completely. Helfferich (1956) states that stirring by usual methods only reduces the films to a thickness of about 10^{-3} cm. A reduction to below 10^{-4} cm is difficult to achieve. Helfferich himself could reduce the thickness of the film to 5.10^{-5} cm by using a glass turbine giving a flow rate of about 90 cm/sec. along the membrane.

Gregor and Wetstone (1956) used a flat paddle stirring at high speed, and achieved a flow rate of about 400 cm/sec. They assume a film-thickness of 1μ. However, it was found that even this very high flow rate in some cases did not produce maximum potentials. Dray and Sollner (1955), measuring B.I.P.'s and starting from equal concentrations of the "critical" ions on either side of the membrane, observed a lowering of the B.I.P. values below a few hundredth normal. They attributed this effect to film diffusion and remarked that the diffusion layers continue to exist, even with very violent stirring. It is therefore likely that the chosen constant concentration of 0.01 N was too low, but a higher concentration would be imcompatible with the requirement of perfect selectivity, on account of the poor selectivity of the cellophane membranes at higher salt concentrations.

As the Dowex 50, Stamex K and IRC 50 membranes permit a higher constant concentration, for the first two of these membranes some B.I.P. measurements were carried out at a constant concentration of 0.1 N (see fig. 20, 21 and 23). For the system NaCl/Dowex 50/HCl $u_{Na^+} \gamma_{H^+}/u_{H^+}$. γ_{Na^+} was 0.31 ± 0.04. This value agrees within experimental error with the value obtained from transport measurements: 0.36 ± 0.04.

For the system $NaNO_3$/Dowex 50/$AgNO_3$, two series of B.I.P. measurements were carried out at constant concentrations of 0.1 N and 0.05 N. At 0.1 N we found $u_{Na^+}\gamma_{Ag^+}/u_{Ag^+}\gamma_{Na^+} = 0.45 \pm 0.02$ at a flow rate of 30 l/h and 0.45 ± 0.04 at a flow rate of 2 l/h. These values are lower than the "transport ratio" 0.62 ± 0.02 obtained from transport number measurements. Accounting for the first correction term gives as a rough approximation for the real "transport ratio" $0.45 \times 1.75 = 0.79$. At a constant concentration of 0.05 N, the corresponding values were 0.47 ± 0.01 at 30 l/h and 0.53 ± 0.01 at 2 l/h.

For the system $NaNO_3$/Stamex K/$AgNO_3$ we found at a constant concentration of 0.1 N $u_{Na^+}\gamma_{Ag^+}/u_{Ag^+}\gamma_{Na^+} = 0.25 \pm 0.03$ at 30 l/h and 0.27 ± 0.03 at 2 l/h; at a constant concentration of 0.05 N the corresponding values were 0.28 ± 0.04 at 30 l/h and 0.35 ± 0.03 at 2 l/h. These values are lower than the "transport ratios" from transport number measurements, being 0.40 ± 0.01. Accounting for the first correction term gives as a rough approximation for the real "transport ratio" $0.25 \times 1.75 = 0.44$. Though it is premature to draw a definite conclusion we may say that in both instances the correction points into the right direction and even leads to remarkably good agreement in the second example.

In principle it might be possible that surface layers have in-

fluenced the transport number measurements as well. If a membrane is placed in a solution containing two "critical" ions, and if this membrane shows an increased transport for one of these ions, there is a possibility that the surface layer on the side of the membrane from which the ions are withdrawn, changes its composition in such a way as to contain relatively less of the ion preferred. This would result in a decrease of the transport of the preferred ion. This phenomenon will occur especially at low concentrations of the solution, at high current density and in unstirred solutions.

Gregor and Wetstone (1956) reported transport ratio measurements for potassium and calcium ions at a total concentration of 0.02 N at current densities varying from 0.1 mA/cm^2 to 10 mA/cm^2. At the highest current density the membranes were virtually non-specific, whereas at low current densities the transport number of calcium was about 3-4 times that of potassium.

In our experiments we used a relatively low current density (0.5 mA/cm^2). The total concentration was rather high (0.1 N) and the flow rate amounted to 2 l/h. It is to be expected that under these circumstances film diffusion plays only a minor part. Nevertheless, we have repeated some transport measurements, varying the current density from 0.125 mA/cm^2 to 0.5 mA/cm^2.

In the case of a Dowex 50 membrane placed in a solution containing NaNO$_3$ and AgNO$_3$ in an equal concentration and at a total concentration of 0.1 N we found for the transference number of Ag$^+$ at a current density of 0.5 mA/cm^2 0.60 ± 0.00; at 0.25 mA/cm^2 0.62 ± 0.02; at 0.125 mA/cm^2 0.60 ± 0.04. So our transport measurements have not been upset by surface-layers. Resuming we may draw the following conclusions:

1. In about half of the instances there is agreement within experimental error between the ratios of the transference numbers obtained by direct measurement and those derived from B.I.P. measurements, but considerable discrepancies as well do occur.
2. It is likely that the term correcting for changes in mobility and activity coefficient may reach rather high values. Further investigation is required.
3. Diffusion layers may upset severely the B.I.P. measurements. From the literature it is known that even with violent stirring these layers cannot always be removed.
4. In general it is not permitted to derive ratios of transference numbers from B.I.P.'s without checking the results. It is to be expected that even in the case of ions for which the membrane has a specific selectivity erroneous results will be obtained.

As a third possibility to check the B.I.P. values in the theoretical part we suggested comparing the "transport ratios" $u_1\gamma_2/u_2\gamma_1$ from B.I.P. measurements with the product u_1/u_2 and

γ_2/γ_1, u_1/u_2 being obtained from conductivity measurements and γ_2/γ_1 from selectivity measurements.

The u_1/u_2 values are given in table 13; the selectivity constants $K_2^1 = \gamma_2/\gamma_1$ in table 9 to 12.

In the theoretical part we remarked that this procedure is only permitted if u_1, u_2, γ_1 and γ_2 are constant across the whole membrane. Thus γ_2/γ_1 also should be constant across the membrane. This is not the case, as γ_2/γ_1 can be shown from table 9 to 12 generally to vary strongly with the ratio of the concentrations of the ions 1 and 2 in th solution.

u_1 and u_2 were estimated from conductivity measurements, the membrane being in equilibrium with a 0.1 N solution of the respective salt. However, it is known from the literature that u_1/u_2 too depends on the ratio of the concentrations of the two ions in the membrane. Spiegler and Coryell (1952) found that when the ratio of the mobilities in an ion exchange resin in the 1^+ respectively 2^+ form is higher than unity, the ratio of these mobilities in the resin containing a mixture of the two ions, will decrease.

Thus the theoretical conditions are not satisfied. Wyllie and Kanaan (1954), contrary to our procedure, calculated ratios of mobilities from B.I.P. measurements and selectivity constants. They rather arbitrarily used selectivity constants at equal concentrations of the "critical" ions in the solution.

In the tables 16 - 19 we give the values of $u_1\gamma_2/u_2\gamma_1$, also taking K_2^1 at equal concentrations. For comparison the $u_1\gamma_2/u_2\gamma_1$ values from B.I.P. measurements at a constant concentration of 0.01 N and at a flow rate of 2 l/h are given as well.

Comparison of "transport ratios" obtained from
conductivity- and selectivity measurements with
those obtained from B.I.P.'s

Table 16

Membrane	u_{Ag^+}/u_{H^+} x $\gamma_{H^+}/\gamma_{Ag^+}$		$\dfrac{u_{Ag^+}\gamma_{H^+}}{u_{H^+}\gamma_{Ag^+}}$ from B.I.P.'s
Dowex 50	0.14 x 7.5	= 1.05	0.45
Stamex K	0.07 x 4.2	= 0.29	0.47
A 58	0.26 x 1.6	= 0.42	0.24
A 71	0.24 x 0.43	= 0.10	0.22
IRC 50	0.39 x 0.0075	= 0.004	0.19

Table 17

Membrane	u_{Na^+}/u_{Ag^+} x $\gamma_{Ag^+}/\gamma_{Na^+}$	$\dfrac{u_{Na^+}\gamma_{Ag^+}}{u_{Ag^+}\gamma_{Na^+}}$ from B.I.P.'s
Dowex 50	1.14 x 0.28 = 0.32	0.76
Stamex K	1.84 x 0.22 = 0.40	0.55
A 58	0.76 x 0.66 = 0.50	0.80
A 71	0.94 x 0.31 = 0.29	0.69
IRC 50	5.33 x 0.018 = 0.10	0.52

Table 18

Membrane	u_{Na^+}/u_{H^+} x $\gamma_{H^+}/\gamma_{Na^+}$	$\dfrac{u_{Na^+}\gamma_{H^+}}{u_{H^+}\gamma_{Na^+}}$ from B.I.P.'s
Dowex 50	0.16 x 1.5 = 0.24	0.19
Stamex K	0.13 x 1.3 = 0.17	0.21
A 58	0.20 x 1.2 = 0.24	0.12
A 71	0.23 x 0.19 = 0.04	0.14
IRC 50	2.06 x 0.003 = 0.006	0.10

Table 19

Membrane	u_{Na^+}/u_{K^+} x $\gamma_{K^+}/\gamma_{Na^+}$	$\dfrac{u_{Na^+}\gamma_{K^+}}{u_{K^+}\gamma_{Na^+}}$ from B.I.P.'s
Dowex 50	0.72 x 0.65 = 0.47	0.64
Stamex K	0.49 x 0.55 = 0.27	0.65
A 58	0.76 x 0.89 = 0.68	0.65
A 71	0.70 x 0.82 = 0.57	0.61
IRC 50	0.57 x 1.25 = 0.57	0.48

In most cases the differences between the two values are of the same order of magnitude as those reported by Wyllie and Kanaan. These differences are too great to allow quantitative conclusions. Better agreement may be expected if the ratio u_1/u_2 is determined in the membrane in equilibrium with a solution containing a mixture of the two ions, in composition identical with the one for which K_2^1 is estimated. The values of u_1 and u_2 can be determined by means of radio-active tracers of the ions 1 and 2 respectively.

From the available figures we are nevertheless able to draw the following qualitative conclusions:

1. Generally the preference for an ion increases as its concentration ratio decreases.

2. If an ion is preferred by a membrane, its mobility decreases. However, the first effect prevails, so that the relative transport number of the ion increases. This is clearly shown e.g. in the

case of the Dowex 50 and Stamex K membranes in $NaNO_3$ - $AgNO_3$ solutions.

3. It is striking that, although the affinity of the IRC 50 membrane for silver ions and hydrogen ions is very high, their part in the transport is not increased exceptionally. Apparently the nature of the binding is of great influence too. An increased transport number can be expected only if notwithstanding the great affinity the ionic character of the binding is maintained.

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SUMMARY

The potential which occurs if an ion exchange membrane sepa-
rates two salt solutions with different "critical" ions is called bi-
ionic potential (B. I. P.). These potentials have received consid-
erable interest for the study of specific selective properties of
membranes, caused by an increased affinity for an ion or a group
of ions. In many instances this phenomenon is accompanied by an
increased transference number for the ion concerned. The ratio
of the transference numbers of the competing ions is often derived
from B. I. P.'s. There is, however, hardly any instance in the
literature of experimental checks on the correctness of the B. I. P.
formula.

In the theoretical part of this thesis an attempt is made to give
a critical survey of the existing formulae for the B. I. P. and to
find a connection between the B. I. P.'s and the ratio of the trans-
ference numbers which is theoretically justified.

A literature survey on ion exchange membranes is given, par-
ticularly specifically selective membranes, the measurements of
B. I. P.'s and the water transport through membranes were re-
viewed.

A great number of experiments with different cation selective
membranes and different combinations of univalent "critical" ions
were performed to check Scatchard's B. I. P. formula. For that
purpose the "transport ratios" derived from B. I. P. measure-
ments were compared with those obtained from transference
number measurements.

Measurements on water transport have been made to study its
influence on the B. I. P. It appeared that for the membranes in-
vestigated this effect can be neglected.

A rough estimate was made of the correction term accounting
for changes in the mobilities and in the activity coefficients of the
ions in the membrane. It was found that this term may reach
rather high values. Further investigation on the subject is re-
quired.

It proved that diffusion layers near the membrane surfaces
have a disturbing effect on the B. I. P. These layers occur espe-
cially in unstirred solutions and with low salt concentrations. In
our first series of measurements a constant concentration of
0.01 N of the relevant salt was maintained on one side of the
membrane. This low value was used because the cellophane-type
membrane shows a rather poor selectivity in more concentrated
solutions. For the other types of membranes some measurements
were repeated with a higher constant concentration. The influence
of the diffusion layers on the transference number measurements

may result in a decreased transport of the preferred ion. A very low current density is required to eliminate this difficulty. As for the diffusion layers disturbing the B.I.P. measurements it is stated in the literature that they can never be fully removed. Nevertheless, we found agreement within experimental error between the ratios of the transference numbers obtained by direct measurements and those derived from B.I.P.'s in about one half of the cases investigated, although among the other cases considerable discrepancies did occur.

In general it is not permitted to derive ratios of transference numbers from B.I.P.'s without a check on the results by a direct determining. It can be expected that even in the case of ions for which the membrane has a specific selectivity erroneous results will be obtained.

Finally the "transport ratio" was compared with the product of conductivity ratio and selectivity constant. Although general agreement is lacking, some qualitative conclusions concerning the specific behaviour of the membrane could be drawn.

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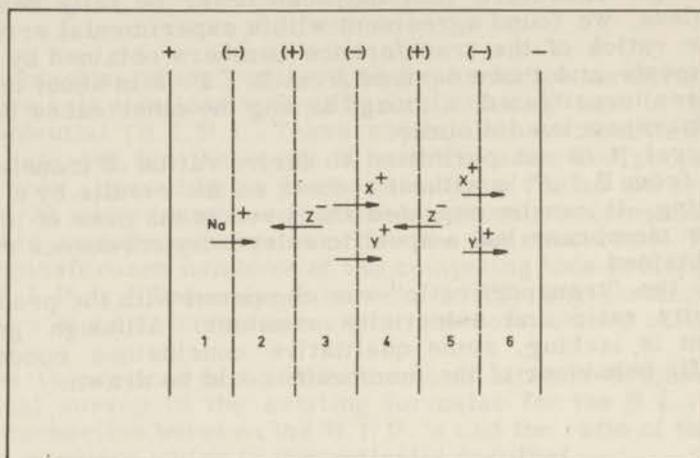
Figure 1
Multicell apparatus used for measurements of
transference numbers (schematically).
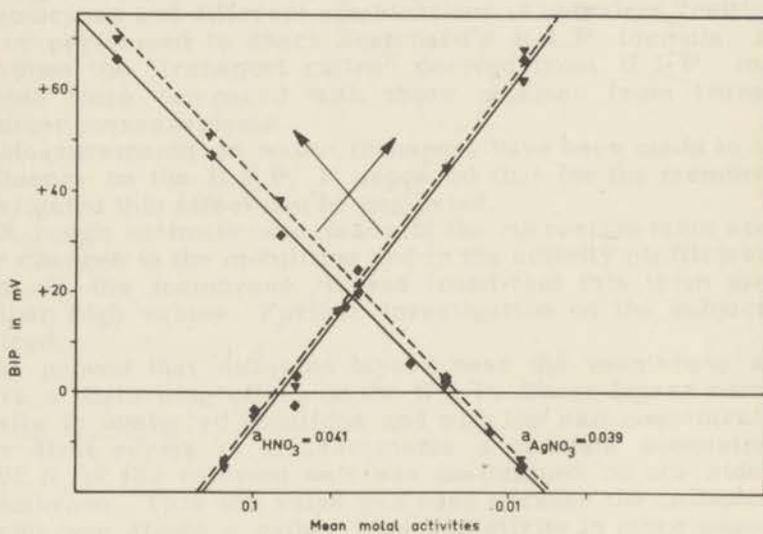
Figure 2
Bi-ionic potentials for HNO₃-AgNO₃ solutions.
▼ -------- Dowex 50 membrane.
◆ ———— Stamex K.
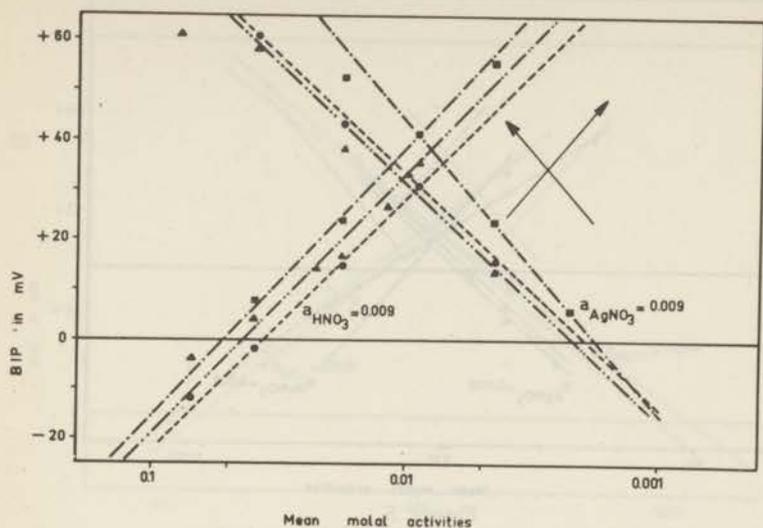
Figure 3
Bi-ionic potentials for HNO₃-AgNO₃ solutions.
- ● --------- A 58.
- ▲ —··—··— A 71.
- ■ —·—·—·— Amberlite IRC 50 membrane.
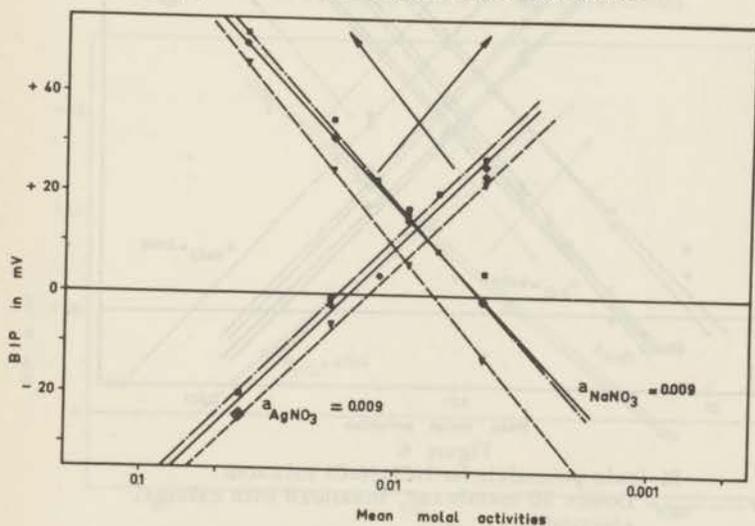
Figure 4
Bi-ionic potentials for AgNO₃-NaNO₃ solutions.
- ▼ — — — — Dowex 50 membrane.
- ◆ ————— Stamex K.
- ■ —·—·—·— Amberlite IRC 50 membrane.
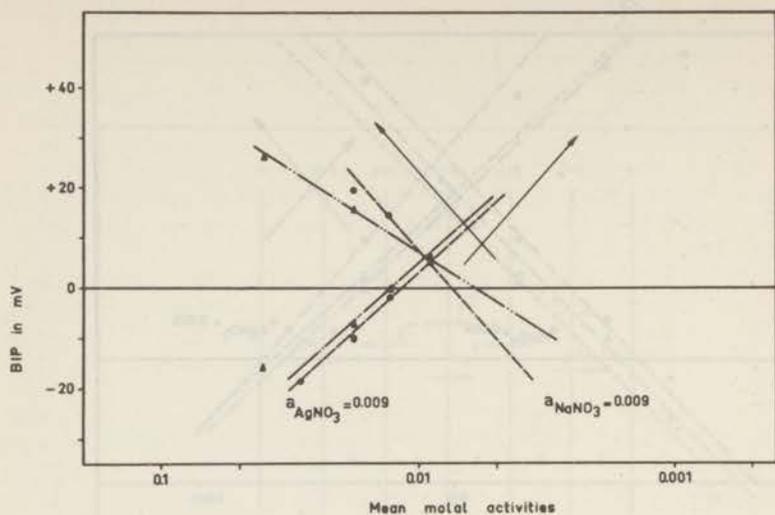
Figure 5
Bi-ionic potentials for AgNO3-NaNO3 solutions.
● ------- A 58.
▲ --·--·-- A 71.
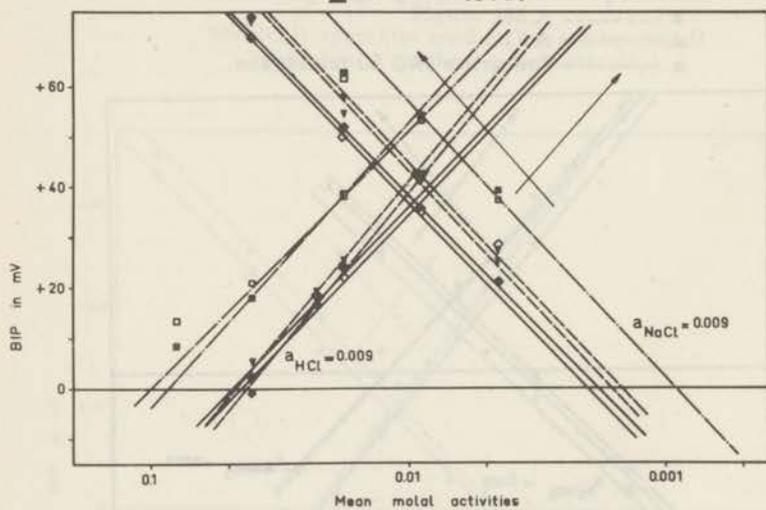
Figure 6
Bi-ionic potentials for HCl-NaCl solutions.
▼ ----- Dowex 50 membrane, measured with calomel
electrodes.
▽ ----- Dowex 50 membrane, measured with AgCl
electrodes.
◆ ——— Stamex K, measured with calomel electrodes.
◇ ——— Stamex K, measured with AgCl electrodes.
■ —·—·- Amberlite IRC 50 membrane, measured with
calomel electrodes.
□ —·—·- Amberlite IRC 50 membrane, measured with
AgCl electrodes.
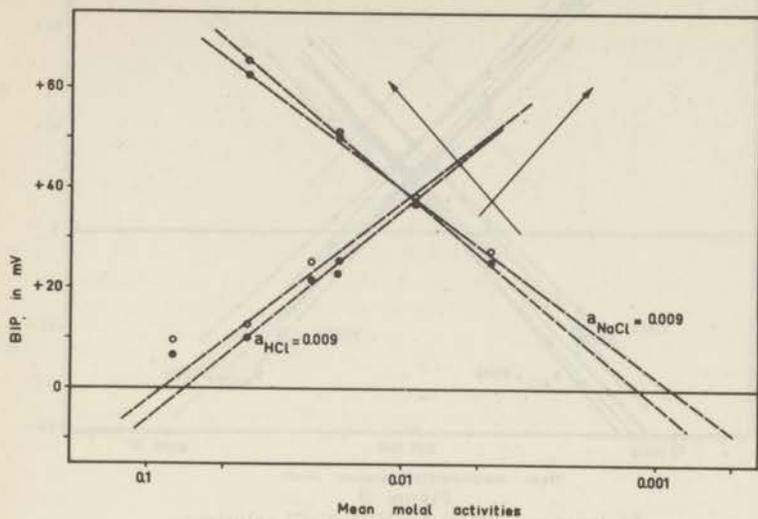
Figure 7
Bi-ionic potentials for HCl-NaCl solutions.
●—————— A 58, measured with calomel electrodes.
o—————— A 58, measured with AgCl electrodes.

Figure 8
Bi-ionic potentials for KCl-NaCl solutions.
▲—·——·— A 71, measured with calomel electrodes.
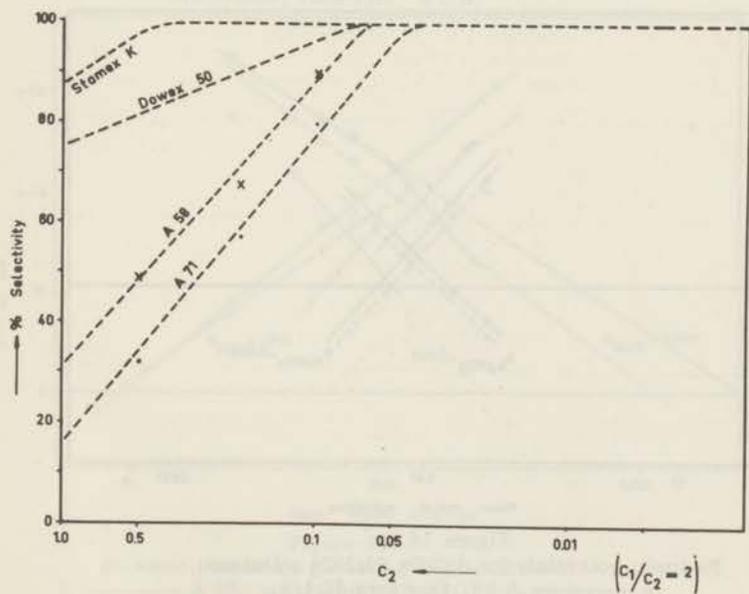△—·——·— A 71, measured with AgCl electrodes.
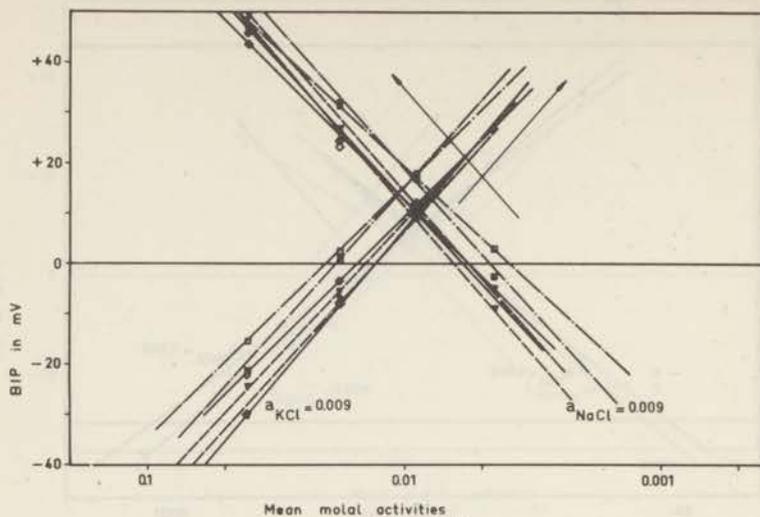
Figure 9
Bi-ionic potentials for KCl_NaCl solutions.

▼ ————— Dowex 50 membrane, measured with calomel
electrodes.
▽ ————— Dowex 50 membrane, measured with AgCl
electrodes.
◆ ————— Stamex K, measured with calomel electrodes.
◇ ————— Stamex K, measured with AgCl electrodes.
■ —·—·— Amberlite IRC 50 membrane, measured with
calomel electrodes.
□ —·—·— Amberlite IRC 50 membrane, measured with
AgCl electrodes.
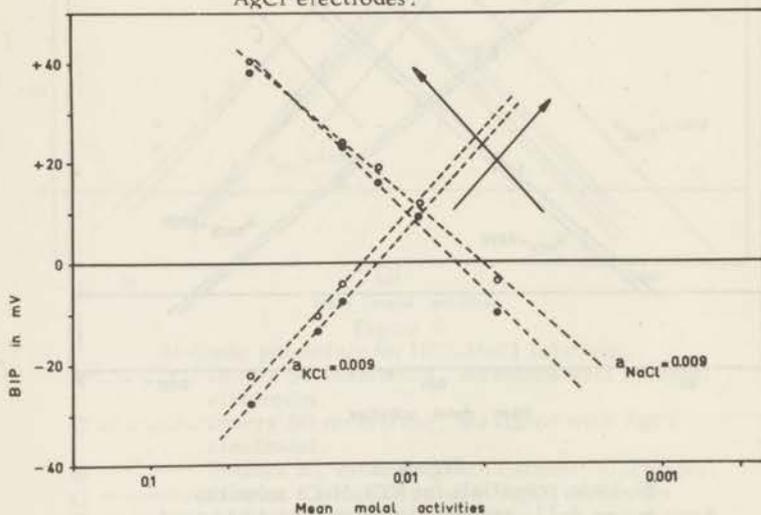
Figure 10
Bi-ionic potentials for KCl_NaCl solutions.
● ———————— A 58, measured with calomel electrodes.
○ ———————— A 58, measured with AgCl electrodes.
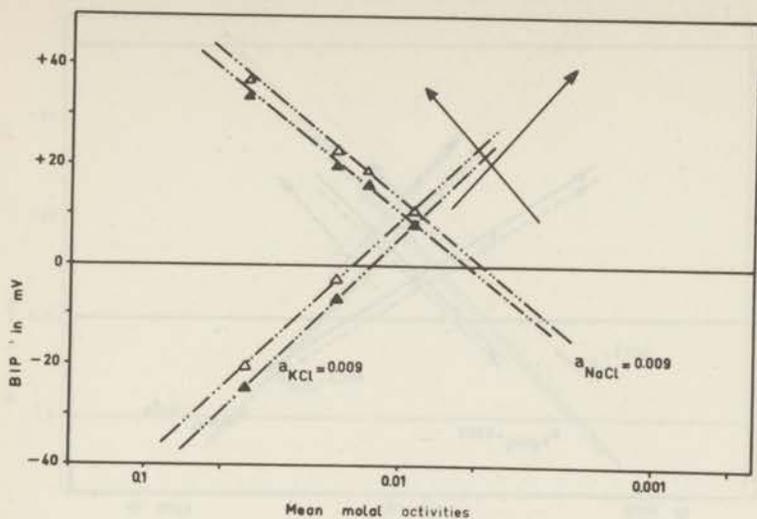
Figure 11
Bi-ionic potentials for KCl-NaCl solutions.
▲ ——·——· A 71, measured with calomel electrodes.
△ ——·——· A 71, measured with AgCl electrodes.

Figure 12
Dependence of the selectivity from solution concentration.
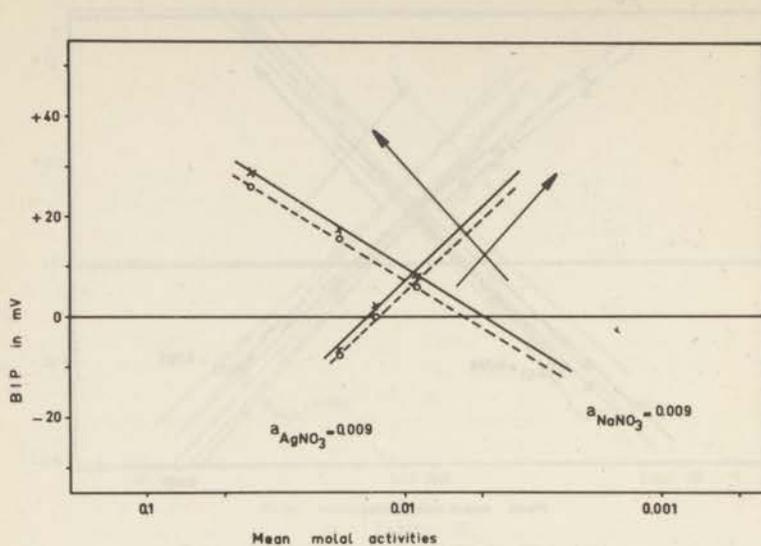
Figure 13
Bi-ionic potentials for $AgNO_3$-$NaNO_3$ solutions.
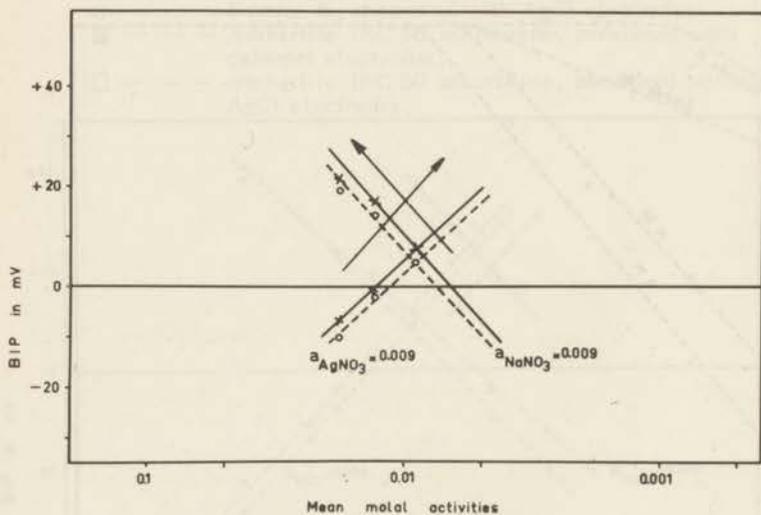x ———— A 71, flow rate 30 l/h.
o -------- A 71, flow rate 2 l/h.

Figure 14
Bi-ionic potentials for $AgNO_3$-$NaNO_3$ solutions.
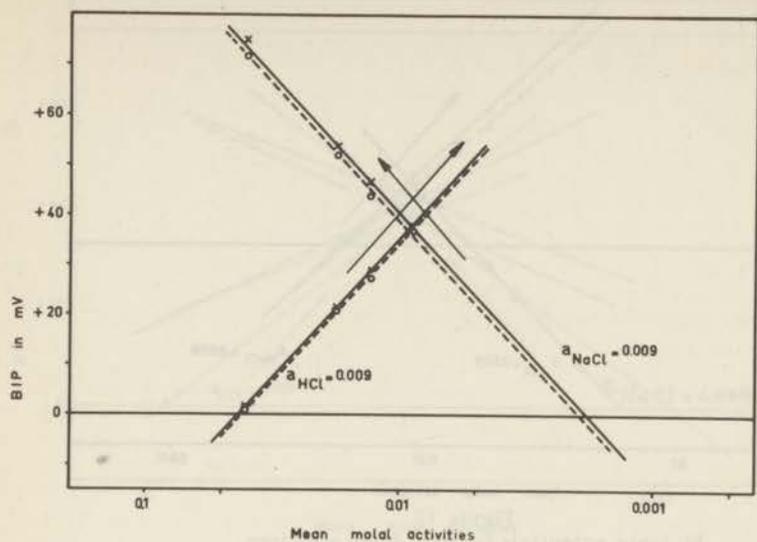x ———— A 58, flow rate 30 l/h.
o -------- A 58, flow rate 2 l/h.

Figure 15
Bi-ionic potentials for HCl-NaCl solutions.
x ———— Dowex 50 membrane, measured with AgCl
electrodes, flow rate 30 l/h.
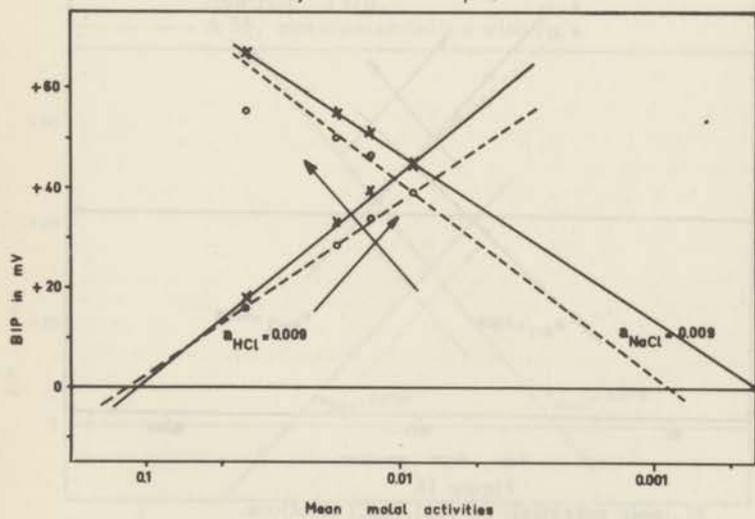o -------- Dowex 50 membrane, measured with AgCl
electrodes, flow rate 2 l/h.

Figure 16
Bi-ionic potentials for HCl-NaCl solutions.
x ———— A 58, measured with AgCl electrodes,
flow rate 30 l/h.
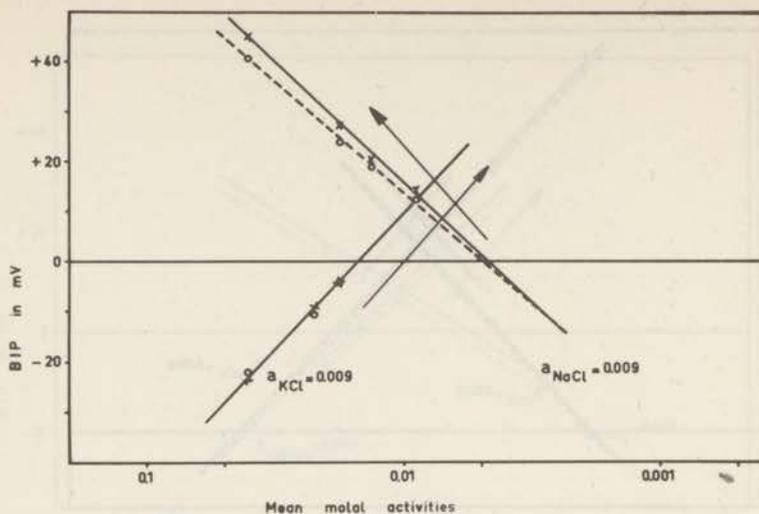o -------- A 58, measured with AgCl electrodes,
flow rate 2 l/h.

Figure 17
Bi-ionic potentials for KCl-NaCl solutions.
x ———— A 58, measured with AgCl electrodes,
flow rate 30 l/h.
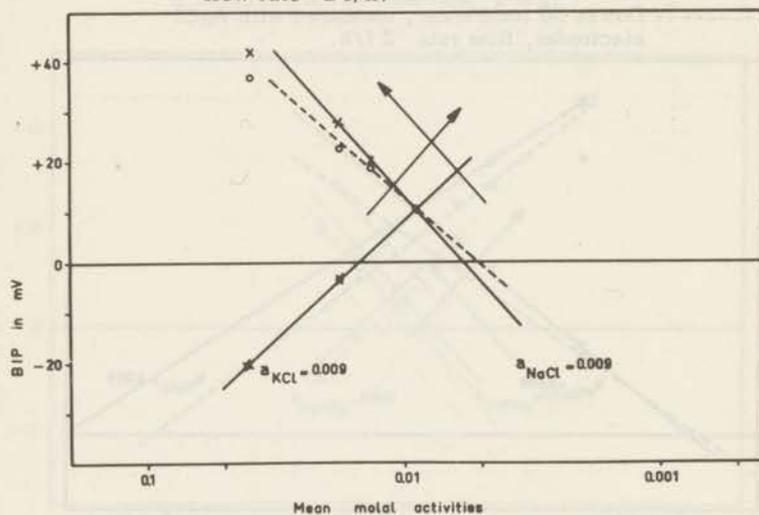o -------- A 58, measured with AgCl electrodes,
flow rate 2 l/h.

Figure 18
Bi-ionic potentials for KCl-NaCl solutions.
x ———— A 71, measured with AgCl electrodes,
flow rate 30 l/h.
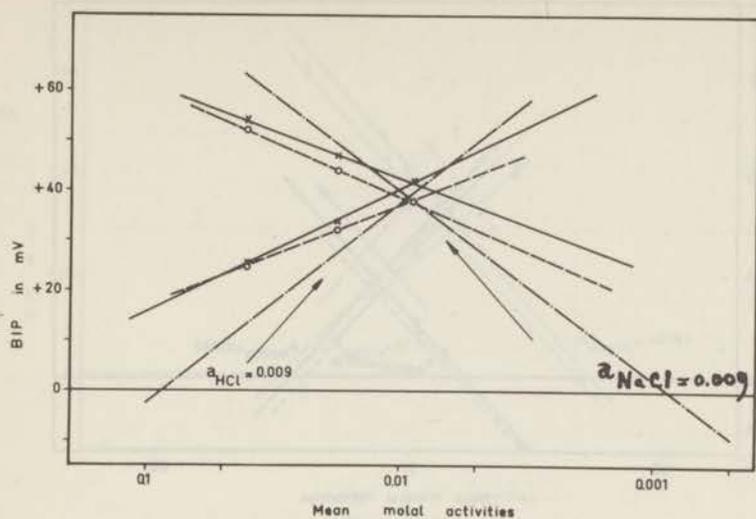o -------- A 58, measured with AgCl electrodes,
flow rate 2 l/h.

Figure 19
Bi-ionic potentials for HCl-NaCl solutions
in the presence of traces of Ag⁺ in the membrane.
x ————— A 58, measured with AgCl electrodes,
          flow rate 30 l/h.
o -------- A 58, measured with AgCl electrodes,
          flow rate 2 l/h.
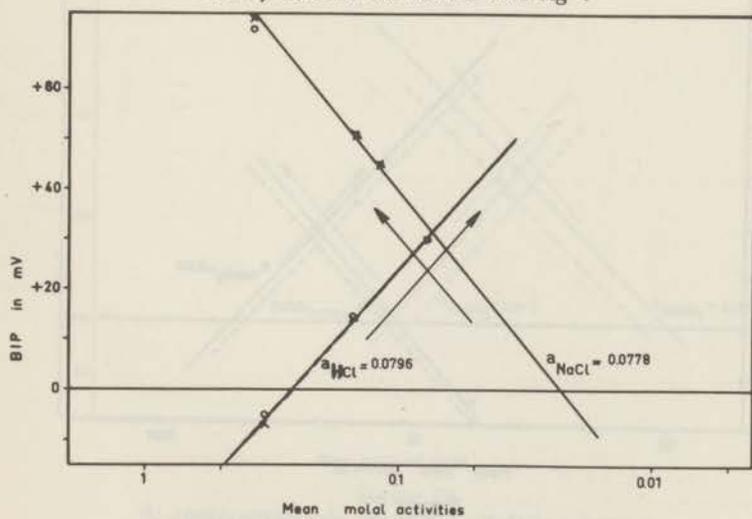—·—·—·— A 58, non-contaminated with Ag⁺.

Figure 20
Bi-ionic potentials for HCl-NaCl solutions
at a constant concentration of 0.1 N.
x ————— Dowex 50 membrane, measured with AgCl
          electrodes, flow rate 30 l/h.
o -------- Dowex 50 membrane, measured with AgCl
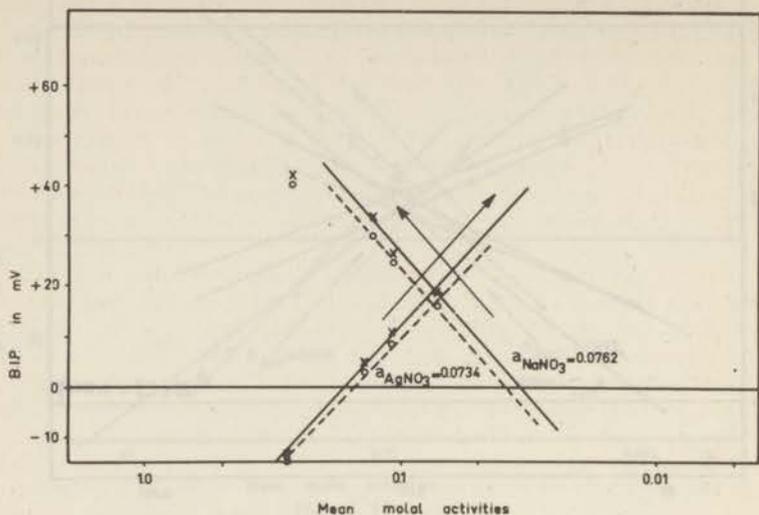   electrodes, flow rate 2 l/h.

Figure 21
Bi-ionic potentials for AgNO3-NaNO3 solutions
at a constant concentration of 0.1 N.
x ————— Dowex 50 membrane, flow rate 30 l/h.
o --------- Dowex 50 membrane, flow rate 2 l/h.

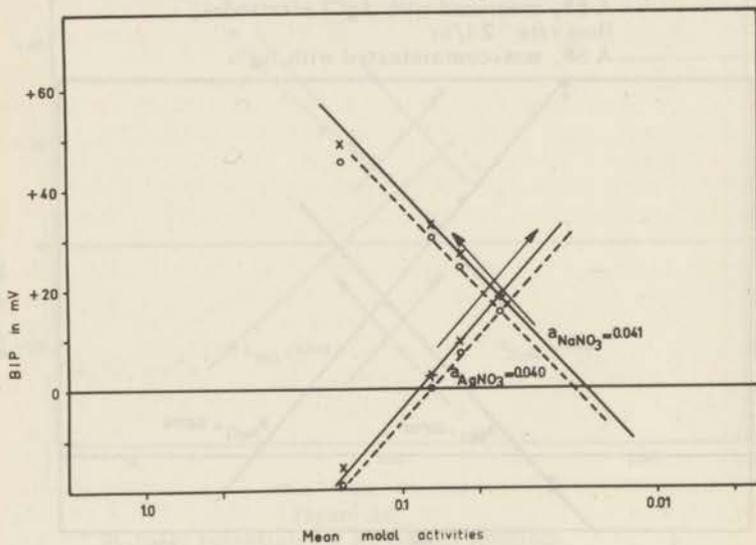Figure 22
Bi-ionic potentials for AgNO3-NaNO3 solutions
at a constant concentration of 0.05 N.
x ————— Dowex 50 membrane, flow rate 30 l/h.
o --------- Dowex 50 membrane, flow rate 2 l/h.

Figure 23
Bi-ionic potentials for AgNO₃-NaNO₃ solutions
at a constant concentration of 0.1 N.
x ————— Stamex K, flow rate 30 l/h.
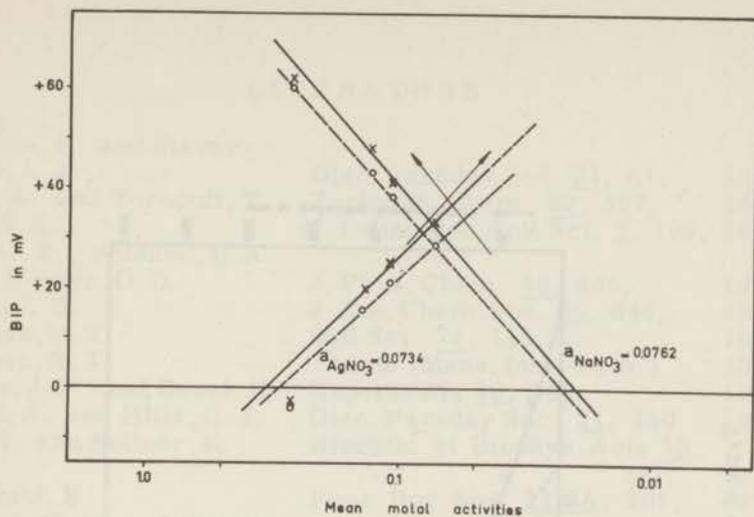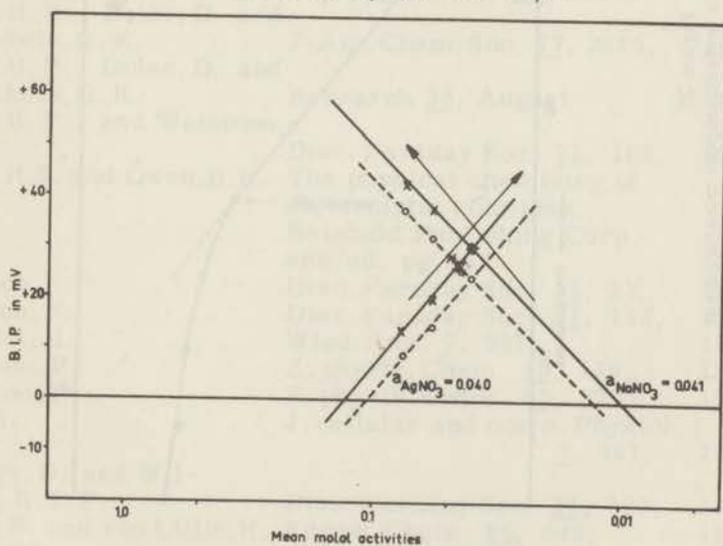o --------- Stamex K, flow rate 2 l/h.

Figure 24
Bi-ionic potentials for AgNO₃-NaNO₃ solutions
at a constant concentration of 0.05 N.
x ————— Stamex K, flow rate 30 l/h.
o --------- Stamex K, flow rate 2 l/h.
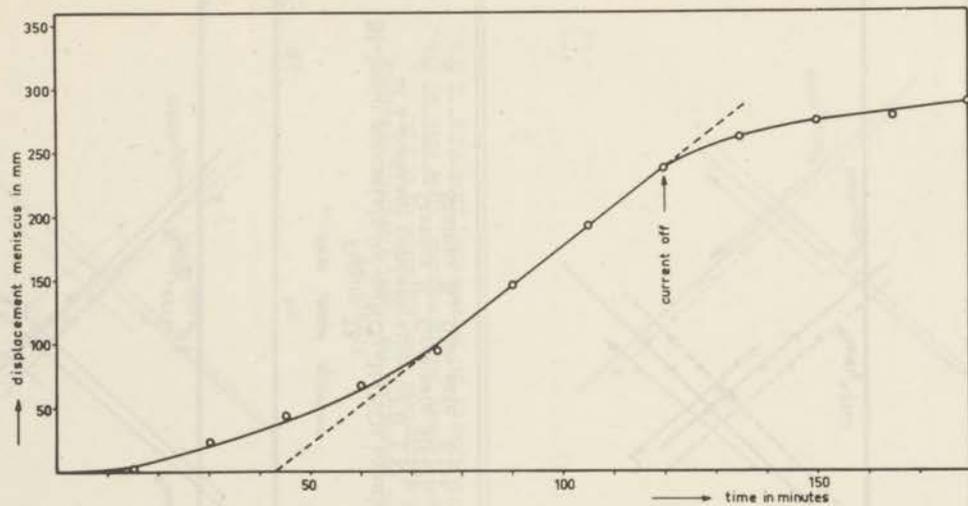
Figure 25
Typical example of a watertransport measurement
with the capillary method.

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    naan, S. L.   J. Phys. Chem. <u>58</u>, 73,   1954 b

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Juda, W. and McRae, W. A.   Ion exchange material and
                            method of making and using
                            the same.
                            U.S. 2,636,851 /July 9,   1949
Rohm and Haas   Improvements in or relating
                            to permselective films of
                            cation-exchange resins
                            Brit. 719,315 /December 17,   1951
Skogseid, A.   Cation-exchange substances
                            U.S. 2,592,350 /April 8,   1952
Staatsmijnen   Cation-selective membrane,
                            obtained by sulphonating a
                            polyethylene film with the aid
                            of chlorsulphonic acid. Dutch
                            Appl. 180,986 /November 15,   1954
T.N.O   Permselective membranes,
                            process for the manufacture
                            of said membranes, and pro-
                            cess for electrodialyzing.
                            Brit. 733,100 /October 26,   1955

Feike Bergsma, geboren 1920 te Oldenzaal, bezocht een jaar de U.L.O. van de Nutsschool aldaar, vervolgens het Carmellyceum, eveneens in Oldenzaal waar hij in 1939 het einddiploma H.B.S. afd. B behaalde. Vervolgens bezocht hij de Hogere Textielschool te Enschede waar hij in 1941 het einddiploma afd. verven verkreeg.

Door een studiebeurs van het Dr. Rudolf Lehmannfonds was hij in de gelegenheid zich in 1941 in te schrijven aan de Universiteit van Amsterdam in de faculteit der wis- en natuurkunde. Van februari 1943 tot de Bevrijding werd de studie onderbroken door een onderduiktijd. In 1946 werd het candidaats-examen, letter e afgelegd. In februari 1950 volgde het doctoraal examen scheikunde cum laude.

Reeds in 1949 trad hij in dienst bij T.N.O., aanvankelijk bij de toenmalige Algemeen Technische Afdeling (ATA), waar hij werkte aan de electrodialytische ontzouting van wei. In 1951 volgde mede op zijn verzoek overplaatsing naar het Kunststoffen-Instituut T.N.O. te Delft in verband met de ontwikkeling van selectieve membranen voor water ontzouting. Later ging hij over naar het Centraal Laboratorium T.N.O., waar ook het in dit proefschrift beschreven onderzoek werd verricht.

STELLINGEN

1. De argumenten die Adison en Lewis aanvoeren om .e weerleggen dat het bestaan van verbindingen als $NOBr_3$ steun geeft aan de aanname van een positief geladen nitrosylgroep, zoals geponeerd door Moeller, zijn weinig steekhoudend.

   C.C.Adison en J.Lewis, Quaterly Revs. 9, 115, 1955.
   Th.Moeller, J.Chem.Education, 23, 441, 1946.
   J.A.A.Ketelaar, Rec.trav.chim. 62, 289, 1943.

2. De verklaring van Chapiro et al. voor het na-polymerisatie effect dat kan optreden bij door straling geïnitieerde polymerisaties is niet volledig.

   A.Chapiro, M.Magat, A.Prévot-Bernas en J.Sebban, J. Chim.Phys. 52, 689, 1955.
   M.Fox en P.Alexander, J.Chim.Phys. 52, 710, 1955.

3. De door Wyllie en Kanaan opgegeven membraan selectiviteiten zijn te laag doordat film-diffusie bij de bi-ionische potentiaal metingen zijn rol gespeeld moet hebben.

   M.R.J.Wyllie en S.L.Kanaan, J.Phys.Chem. 58, 73, 1954.
   Deze dissertatie, Hfdst. IV.

4. De mening van Winger, Ferguson en Kunin dat het netto watertransport door een membraan in zeer geconcentreerde loog oplossingen nul is, is onjuist. De transport getallen voor het kation in 6 N LiOH, NaOH en KOH die zij afleiden uit watertransport metingen zijn meer dan een factor 2 te groot.

   A.G.Winger, R.Ferguson en R.Kunin, J.Phys.Chem. 60, 556, 1956.

5. De door Day en Oestreich berekende verbrandingswarmte voor dimethylfulveen en diphenylfulveen zijn onjuist. Gebruikmaking van de correct berekende verbrandingswarmte voor diphenylfulveen levert een resonantie energie op voor de fulveen kern die minder dan de helft is van de door de auteurs opgegeven waarde.

   J.H.Day en Ch.Oestreich, J.Org.Chem. 22, 214, 1957.

6. De grote vermindering in de treksterkte van water beneden 8°C die Briggs gevonden meent te hebben is niet reëel. De suggestie van Berry en Hough ter verklaring van de schijnbare anomalie verdient nader onderzoek.

   L.J.Briggs, J.Appl.Phys. 21, 721, 1950.
   V.J.Berry en E.W.Hough, J.Appl.Phys. 23, 931, 1952.

7. Ten onrechte menen Koschel en Schlögl dat het elastisch-plastisch gedrag van het door hen onderzochte kation-selective membraan de door hen voorgestelde structuur van dit membraan aannemelijk maakt.

    D. Koschel en R. Schlögl, Z. physik. Chem. N. F. <u>11</u>, 137, 1957.

8. Het structuurbewijs dat Scholtissek geeft voor het door hem verkregen product bij inleiden van phosgeen in pyridine is niet overtuigend.

    C. Scholtissek, Chem. Ber. <u>89</u>, 2562, 1956.

9. Hoewel het, een weinig zwavelzuur bevattende Weston-element van het verzadigde type theoretisch niet geheel voldoet aan de eisen aan een normaal element te stellen, leert een nadere berekening dat het verloop van de E. M. K. door zelf-ontlading geringer zal zijn dan het overeenkomstige verloop voor het „neutrale" element van het onverzadigde type.

    G. W. Vinal, Primary Batteries.
    J. Wiley & Sons Inc. New York, sec. pr. July, 1951.

10. De verklaring die Müller, Fries en Metzger geven voor de vergrote opbrengst van cyclohexanon-oxim door toevoeging van droog zoutzuur gas bij de inwerking van chloor en stik-stof-monoxyde op cyclohexaan onder invloed van ultraviolet licht, is onjuist.

    E. Müller, D. Fries en H. Metzger, Chem. Ber. <u>90</u>, 1188, 1957.

11. Het is waarschijnlijk dat phase-scheiding van de twee componenten van de eluent een rol heeft gespeeld bij de chromato-grafie van steroïden uitgevoerd door Martin.

    R. P. Martin, Biochim. et Biophys. Acta <u>25</u>, 408, 1957.