

STUDIES ON THE PERMEABILITY OF MEMBRANES.
II. DETERMINATION OF IONIC TRANSFER NUMBERS IN MEMBRANES
FROM CONCENTRATION CHAINS.

By L. MICHAELIS, R. McL. ELLSWORTH, AND A. A. WEECH.

(From the Laboratory of Research Medicine, Medical Clinic, The Johns Hopkins University, Baltimore.)

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1. THEORY.

It has been shown (1) that the P.D. of a concentration chain, e.g. with two KCl solutions in the ratio 10:1, across a membrane of dried collodion, reaches its maximum value better the more dilute the KCl solutions are, and that in higher ranges of concentrations, the effect of the membrane vanishes more and more. So in the latter case the P.D. approaches closely that established without a membrane. This is, in the case of KCl, practically equal to zero.

The interpretation of the effect of the membrane was given as follows: Any potential difference between two aqueous solutions of different electrolytic content, in direct contact with each other, is due to the difference in the mobilities of the different kinds of ions. In the ultracapillary spaces of the membrane, the mobilities of the ions are not only changed with respect to their absolute value, but also to their relative value. In general, the mobility of the anion is considerably more decreased than the cation.

Let us consider a very thin layer of the liquid content within a pore channel confined by two cross-sections through the channel, infinitely close to each other. Let the two sides of the membrane be in contact with two different solutions of the same kind of electrolyte consisting of two univalent ions. A transition zone will be formed across the membrane. Then the P.D. between two infinitely close neighboring cross-sections through this transition zone will be:

$$dE = \frac{RT}{F} \frac{u - v}{u + v} \frac{dc}{c} \quad (1)$$

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where u and v are the mobilities of the cation and anion, respectively, within the concerned cross-section; c is the concentration, or better, the activity of the electrolytes within this infinitely thin layer of the liquid, and dc the change of c from the one cross-section to the neighboring one. In order to find the total P.D. from the one side of the membrane to the other, the above formula must be integrated over all the infinitely small cross-section layers from the one side of the membrane to the other. Let us designate the direction along the axis of the pore channel as the x axis; the integration has to be performed from $x = 0$ to $x = D$, where D is the total thickness of the membrane. Now, from the experiments referred to, we have to infer that u and v within the channel depend considerably on the concentration in a degree much more pronounced than in a free aqueous solution. Usually in an aqueous solution u and v depend only slightly on the concentration. Here, with a certain approximation, we may consider u and v as constant, and the result of the integration becomes:

$$E = \frac{RT}{F} \cdot \frac{u - v}{u + v} \ln \frac{C_2}{C_1} \quad (2)$$

when C_2 and C_1 are the two concentrations of the solution which are in contact with each other and connected by a transition zone. It should be emphasized that this result of the integration does not depend on the manner in which the transition of the one concentration to the other is realized. It does not depend on whether the fall of the concentration is rectilinear or arranged in some other way; whether the transition is realized by a pure diffusion zone or by a zone of mechanical mixtures of the two solutions.

However, within the membrane there is no constancy of u and v over the range of integration, u and v depend strongly on c , and, therefore, also on x . In the integration, the factor containing u and v must not be placed before the integration sign, and the result is:

$$E = \frac{RT}{F} \int_{x=0}^{x=D} \frac{u - v}{u + v} dc \quad (3)$$

If, instead of this accurate formula, we apply formula (2), the letters u and v no longer have the meaning of the mobility of the cation and anion, respectively, but they may be interpreted as some kind of

average mobility,¹ within the range of concentration C_1 and C_2 . Such an average mobility has no simple physical meaning. It need not be the arithmetical mean.

In the ordinary concentration chain without a membrane, we are allowed to calculate the relative value of u and v , or the transfer numbers $t^+ = \frac{u}{u+v}$ and $t^- = \frac{v}{u+v}$ from the measurement of the P.D. availing ourselves of the formula (2) which solved for t^- reads, for a temperature of 20°C.:

$$t^- = 0.5 - \frac{E}{2 \times 58 \times \log^{10} \frac{C_2}{C_1}} \quad (4)$$

where E is the measured P.D. in millivolts.

If we apply this formula to a concentration chain with a membrane, the obtained transfer number of the anion, t^- , is nothing but the calculated average value of t^- , which has not a simple physical meaning. However, when the ratio $C_2:C_1$ is small enough, the variation of t^- for the concentration C_2 and C_1 may be also small, so that with a certain approximation the calculated t^- may be regarded as a useful approximation to both the value of t^- for C_2 and for C_1 . Using this idea, there is obtained a method for calculating, with a certain approximation, the transfer number of the ions of an electrolyte within the pores of the membrane for any concentration of the aqueous solution in contact with the membrane and in equilibrium with the electrolytic content of the membrane pores.

The method consists in the measurement of the P.D. of concentration chains with a membrane, the ratio of concentrations of the two solutions being as small as possible. It is not practical to apply very small ratios, for in this case the measured P.D. becomes very small also and

¹ It should be borne in mind that according to the interpretation given in the previous paper, even the mobility of an ion, especially of an anion, within *one* very thin cross-section layer of a channel, is but an average value, as the anions fixed at the wall and the free anions in the center of the pore have different mobilities. The average value of these mobilities is called here the mobility of that ion within this cross-section. In this present paper the "average" mobility of an ion means the average of the thus defined mobilities, over the range of all of the cross-sections through the channel from its one opening to the other.

the inevitable error of, let us say 0.5 millivolt, which may occur in the measurement of such a chain and which may be due to uncertain and irreproducible liquid junction potentials, has too high an influence on the results. The best ratio of concentrations seemed to be the one of 2:1. The maximum effect, when the mobility of the anion = 0 is in this case 17.6 millivolts for 20°C.²

Several previous authors emphasized the fact that the transfer numbers are altered in membranes. As all of these authors applied methods different from those used in this paper, and as review of these findings is to be made in a subsequent paper, we refrain here from discussing the literature, in order to avoid repetition, especially because the essential point,—the rapid change of the transfer number according to the concentration, has not yet been described so far as we know.

2. *Technique.*

The experiments were carried out with the dried collodion bag membrane, as described in the previous paper. Some series were made with flat membranes which have advantages to a certain extent; particularly in that they maintain their original properties as measured by the *Co P* virtually permanently. Such flat membranes were used by the authors through many successive experiments over months, the *Co P* having remained constant within some tenths of a millivolt. Flat collodion membranes have been used in the past, *e.g.* by Bethe and Toropoff (2), Bigelow and Gemberling (3), Bartell and Carpenter (4), and Hitchcock (5), and they have been used also long ago for ultrafilters by Bechhold, Zsigmondy, and others. But these authors worked with more or less well permeable, not completely dried collodion membranes. It is very easy to obtain this kind of membrane in a flat form, but it requires special technique to make completely dried membranes in a flat form. Recently Collander (6) described the flat form for the dried collodion membrane emphasizing its great stability. The difficulty consists in the fact that the flat membranes, while drying, shrink and shrivel and become inelastic and rigid, so

² The error involved in the fact that a concentration ratio is used instead of one between activities, is so small for a ratio of 1:2 as to be negligible with respect to other errors involved.

that they cannot be fastened without a leak to any opening of a vessel. One has to fix the membrane, in a half dried condition, to the rim of a vessel and then allow it to dry. The authors found the following method best.

A 5 per cent solution of celloidin Schering in 75 per cent ether and 25 per cent alcohol was poured on a mercury surface in a Petri dish, as Bartell suggested, in an amount sufficient to cover easily the whole surface by the spontaneous spreading of the viscous solution. The collodion is allowed to dry to such an extent that the consistency is just suitable for cutting with a knife. At this time, the periphery adjacent to the rim of the Petri dish is cut and the membrane taken out and put over the opening of a bell jar shaped glass, such as is shown in Fig. 1. The diameter is 2 cm. smaller than that of the Petri dish in a cross-section. The rim is



FIG. 1. Glass bell jar used as supporting frame for flat membranes.

represented by an even ring 1 cm. broad with ground surface. The rim is wet with a layer of collodion solution immediately before the half dried membrane is put on. By means of this the membrane is glued on the rim. While the drying process is going on, the main part of the membrane covering the opening of the jar is prevented from shrinking. However, the peripheral portion of the membrane shrinks in such a way that a circular sulcus outside the glass rim is formed, the concavity being directed toward the pointed part of the jar. Now the jar is turned over and collodion solution is poured into this sulcus. This fills in the leaks which may be left between the membrane and the glass rim. Moreover, while drying and shrinking, the peripheral collodion ring shrinks and rolls so that finally a tight band hermetically seals all leaks. The membrane has to stand 3 or 4 more days to complete dryness which can be recognized by electrification after rubbing with hair. The membrane is exposed to an enormous

stress, and too thin a membrane sometimes will crack. Those membranes which have withstood the stress have turned out to be virtually invariable in any respect. The *Co P*, even after months of experiments, remains constant within a fraction of a millivolt. It is true, in consequence of the complete lack of shrinking, the *Co P* does not reach such high values as sometimes is obtained in the shrunk bag membranes. Usually a *Co P* of about 48 millivolts was obtained, whereas the other form sometimes gives 52 to 53 millivolts. In the second place, on account of the thickness, a long time is necessary to reach a stationary condition when measuring the P.D. To measure, for example, the *Co P*, the membrane has to stand at least some hours in contact with the solution, the latter being several

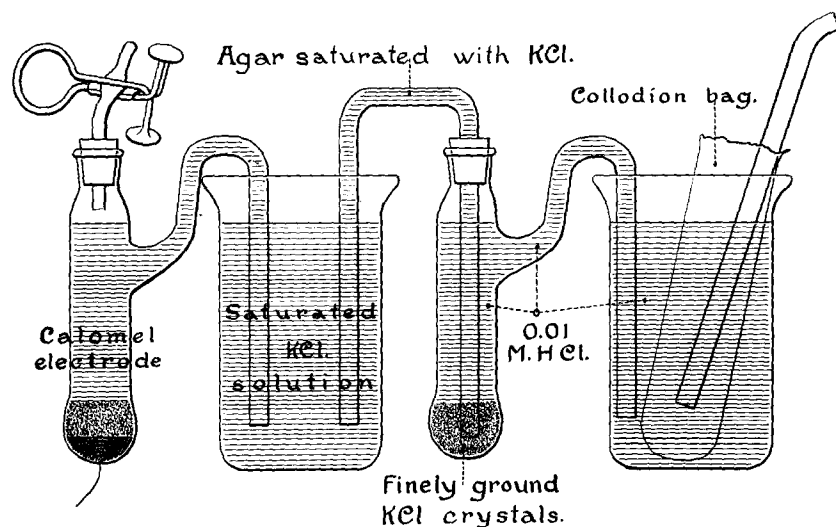


FIG. 2. Method of connecting calomel half-cell with membrane system to avoid diffusion potentials and diffusion.

times renewed. However, after the stationary condition has been established, the P. D. keeps astonishingly constant for any period.

When a membrane used for one experiment is to be used for another with different solutions, the previous solutions must be washed out at least 24 hours; and in certain cases, *e.g.* in the transition of KCl chain to a LiCl, where any trace of the much more movable K will spoil the value of the Li chain, the washing process should be prolonged several days. Inconvenient as that may be, the labor is rewarded by very constant and reproducible results, and on account of its invariability,

such a membrane can be used for comparative successive experiments with different solutions much better than the bag membrane.

As an error of even 1 millivolt has a relatively great influence on the calculation of the transfer numbers, the errors involved in liquid junction potential should be eliminated as far as possible. In chains with KCl there is no trouble in this respect, but for other electrolytes the arrangement shown in Fig. 2 was used. This represents a .01 M HCl solution outside the membrane connected with the leading off calomel half cell. The same arrangement was used to connect the inside solution of the collodion bag with the other electrode. This arrangement is based on the principle of Michaelis and Fujita (7), interposing between the HCl solution and the saturated KCl solution another HCl solution of the same concentration as the first one, but also saturated with KCl. We may be sure that the liquid junction potential is reduced to a fraction of 1 millivolt at least. The two calomel half cells, saturated with KCl, were often checked against each other and when a small P.D. was observed between them, a suitable correction for the P.D. of the chains in the experiments was made.

3. Results and Discussion.

Table I shows the P.D. of a chain with a dried collodion bag membrane between two KCl solutions of the concentration 1:2, in different ranges of concentration. The last column gives the transfer number for Cl evaluated according to formula (4) (Fig. 3, lower curve).

Table II shows a similar experiment with a flat membrane. Here the constancy of all values is best, though long time and repeated change of the solution was necessary to reach these constant potentials. The definite value of this series is most trustworthy of all, and the smoothness of the interpolation curve (Fig. 4) confirms this assumption.

Table III gives a series of experiments with a fairly stable bag membrane and with the chlorides of H, K, Na, and Li. The entire series would have consumed too much time, had it been made with a flat membrane. So the results may not be quite so accurate in an average, though much care was taken to obtain a really stationary condition by extended observation and repeated renewal of the solution before definite readings were made. The results are plotted in Fig. 5.

Although the transfer number of Cl is low in any case, especially in low concentration ranges, still the difference can be plainly seen in the different alkali chlorides. The experiments with HCl were not carried out up to the same concentration as in the other electrolytes on account of doubt as to whether liquid junction potentials might be insufficiently abolished. It should be borne in mind that an error of 1 millivolt, according to the particular circumstances, may have a great influence on the evaluated transfer number. That is also the reason why these figures are not utilized in further computations

TABLE I.
Celloidin Membrane, Bag Form.
Change of the P.D. with the Change of the Concentration Range. The Ratio of Concentration of Each Chain is Always 1:2. All Experiments with the Same Membrane.

KCl solutions	P. D.				f_{Cl}
	1st series of experiments (22°C.)	2nd series (22°C.)	3rd series (20.5-22°C.)	Average	
	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
M/400 : M/200		17.8	17.7	17.7	0
M/200 : M/100	15.3		17.8	16.6	0.040
M/100 : M/50	14.7		16.2	15.5	0.059
M/50 : M/25			15.3	15.3	0.065
M/25 : M/125			12.5	12.5	0.145
M/20 : M/10	13.2	13.0	12.9	13.0	0.130
M/12.5 : M/6.25			9.5	9.5	0.230
M/6.25 : M/3.125			5.5	5.5	0.309
M/2 : M/1	4.8	3.9	3.8-3.1 (Aver. = 3.4)	4.0	0.386

Theoretical maximum value at 22° = 17.6 millivolts.

but only shown in the diagram where the interpolation curves, obtained a little arbitrarily, give an idea about the differences. The order of the transfer number of Cl in the different chlorides is the same as in aqueous solutions; the absolute values, however, strongly diminished in comparison with the latter, and the fact that the transfer number depends largely on the concentration, is obvious for all of these electrolytes, whereas in free aqueous solutions the influence of concentration is known to be small. Further discussion must be delayed.

TABLE II.
Celloidin Membrane, Flat Form.

Concentrations of KCl	Temperature	P. D.	t_{Cl}
		<i>mv.</i>	
N/1 : N/2	18.5°	3.5	.399
N/2 : N/4	18.5°	5.45	.343
N/4 : N/8	19.5°	9.55	.226
N/8 : N/16	19.5°	11.75	.163
N/16 : N/32	19.5°	14.5	.085
N/32 : N/64	20.5°	15.4	.060
N/64 : N/128	20.5°	16.35	.033

TABLE III.
Celloidin Membrane, Bag Form.
Temperature $20^{\circ} \pm 0.5^{\circ}\text{C}$. Theoretical Maximum Value of a Concentration Chain for This Temperature: 17.4 Millivolts.

	Concentration range	P. D.	Transfer Number of Cl
	<i>M</i>	<i>mv.</i>	
LiCl	.01-.02	15.1	.066
	.02-.04	13.4	.115
	.04-.08	11.4	.173
	.08-.16	8.3	.262
	.16-.32	5.2	.351
NaCl	.01-.02	15.5	.055
	.02-.04	14.8	.075
	.04-.08	13.5	.112
	.08-.16	10.5	.198
	.16-.32	6.2	.322
KCl	.01-.02	16.05	.026
	.02-.04	15.4	.058
	.04-.08	13.6	.109
	.08-.16	10.8	.190
	.16-.32	7.3	.290
HCl	.01-.02	17.2	.006
	.02-.04	17.1	.009
	.04-.08	15.65	.050
	.08-.16	15.5	.055

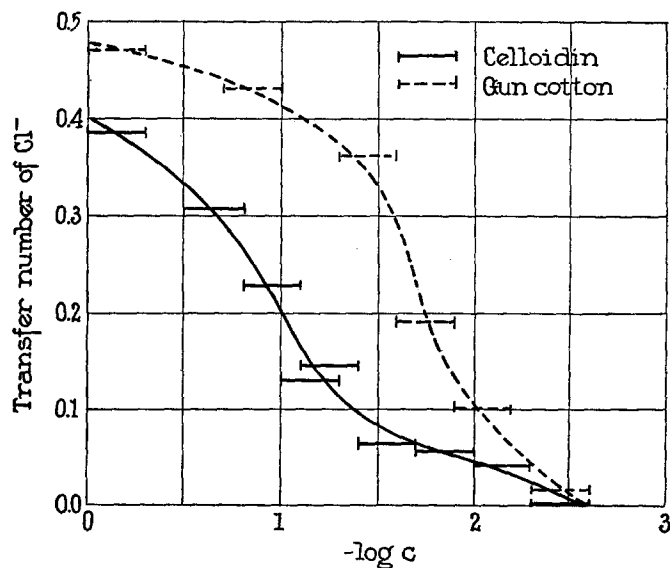


FIG. 3. Magnitude of the transfer number for Cl through the different concentration ranges with two membranes of the bag type.

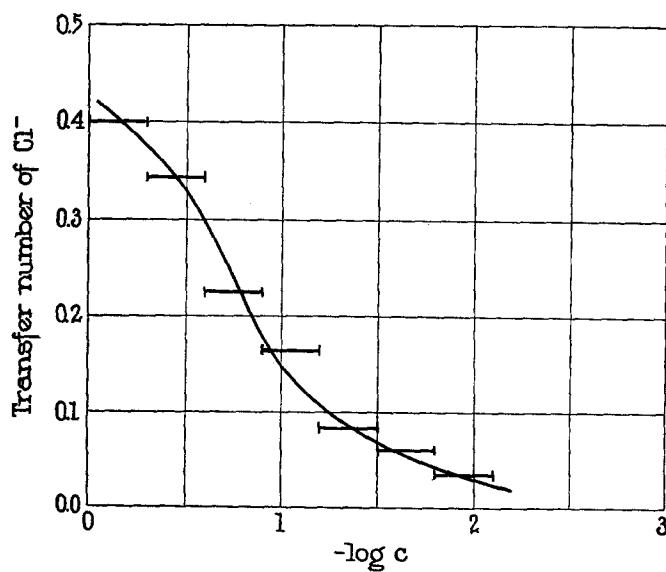


FIG. 4. Magnitude of the transfer number for Cl through the different concentration ranges with a collodion membrane of the flat bell jar type.

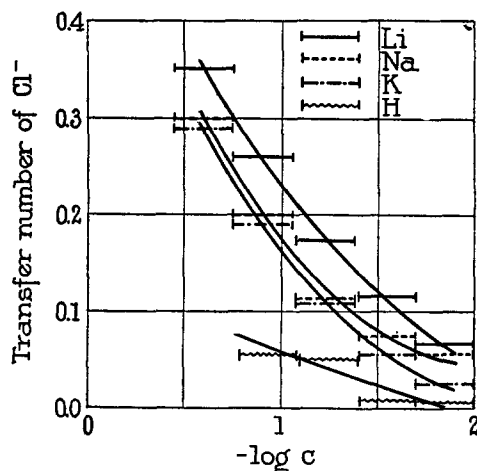


FIG. 5. Concentration chain curves showing the transfer numbers for Cl in the form of chlorides of different cations.

TABLE IV.

Gun Cotton Membrane, Bag Form.

Temperature 26.5°C. Maximum Value Calculated 17.7 Millivolts

KCl solutions	P. D. <i>mv.</i>	t_{Cl}^- calculated
M/1 : M/2	1.10	0.47
M/5 : M/10	2.60	0.43
M/10 : M/20	4.05	0.40
M/20 : M/40	5.55	0.36
M/40 : M/80	10.90	0.19
M/80 : M/160	14.25	0.10
M/160 : M/320	17.1	0.017
M/10 : M/100 (that is : <i>Co P</i>)	21.4*	0.306†

* 2 days ago 23.0.

† Theoretical maximum value for this chain = 55 millivolts. Corresponding to the value of the interpolation curve for a concentration = M/40.

In order to show that this behavior of the membrane is connected with their relatively high CoP , being only a couple of millivolts below the possible maximum value, a gun cotton membrane with a lower CoP (21 to 23 millivolts) was used for a similar series with KCl (Table IV and Fig. 3, upper curve). It can be seen that the transfer number of Cl is always greater than the one with a good celloidin membrane (lower curve, Fig. 3) through the same concentration range. However, in principle, the course of the curve is the same.

It should be borne in mind that the calculation of the transfer numbers in this paper are completely based on the assumption that the P.D. of the concentration chains with the membrane are due to the difference of the mobilities of the cation and the anion. This assumption was till now only an attempt to control the phenomena in membranes by a simple hypothesis, and the present paper shows some consequences of this hypothesis. Subsequent papers will have to deal with the problem of whether this hypothesis is sufficient or requires an addition or correction.

SUMMARY.

The ionic transfer number in an electrolyte solution in the pores of a narrow pored collodion membrane depends much more on the concentration than it does in a free aqueous solution. The potential difference of two solutions of the same electrolyte in different concentration depends largely on the concentration range. The ratio of the concentrations on the two sides was always 1:2 in the experiments; the concentration range was varied. It is shown that the transfer number of Cl, calculated from the P.D. measured, is very small in dilute solution (down to .02 and less in some cases), whereas it approaches the value .5 holding for free aqueous solutions when the concentration range is raised. The differences for the transfer number of Cl, according to the cation (H, K, Na, Li), can be recognized and show the same order as in free aqueous solution. But even in LiCl, where in an ordinary aqueous solution the transfer number of Cl is always $> .5$, this number is very low in the case of the membrane (*e.g.* $< .05$ in .01 M solution).

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