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SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
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"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 10

July 15, 1970

K. S. Spiegler, Principal Investigator
J. C. T. Kwak
D. A. Zelman
J. Leibovitz (part time)

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Contract No. 952109
Jet Propulsion Laboratory
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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

This report describes a complete series of transport measurements achieved by the concentration-clamp technique. The following measurements were performed:

a) Dialysis-osmosis; membrane bounded by 0.5 M and 0.1 M NaCl solutions.
b) Electromigration-electroosmosis with a concentration gradient.
c) Pressure permeation with a concentration gradient.
d) "Combined experiment", in which differences in concentration, pressure and electrical potential were applied simultaneously.

The same specimen of AMF C-103 (American Machine and Foundry Co., Stamford, Connecticut) cation-exchange membrane was used throughout all the experiments. All the phenomenological coefficients can be calculated from these data, except for the membrane conductance.

Additivity of salt and water fluxes was also checked. Further studies under hydrostatic pressure confirmed previous observations of a decrease in hydraulic permeability as a result of the pressure gradient applied across the membrane. This is probably caused by changes in the membrane structure. Although the membrane tested is relatively sturdy, the results clearly indicate that the transport coefficients are functions of the generalized forces themselves. The calculations of the coefficients will be presented in the next report.

Electromigration-electroosmosis experiments under uniform concentration are to be performed in the future. Transport coefficients can be determined without making any assumptions on how to average over the existing concentration gradients; the theoretical evaluation in terms of friction coefficients can thus be made more accurate.

List of Symbols

a_k	Chemical activity of species k, mole cm^{-3}
A	Effective surface area of membrane, cm^2
C_s, c_w	Concentration of salt and water respectively, mole cm^{-3}
δc_s	Change in concentration of salt in a half-cell with time, mole cm^{-3}
ΔE	Total E.M.F. measured between Ag/AgCl reversible electrodes, volt
$\mathcal{F}$	Faraday's constant, $9.6491 \cdot 10^4$ amp sec eq^{-1}
i	Current density, amp cm^{-2}
I	Electric current, amp
J_s, J_w	Flux of salt and water, mole sec^{-1} cm^{-2} (positive from left to right)
J_V	Volume flux, ℓ sec^{-1} cm^{-2}
M_s, M_w	Molecular weight of salt and water respectively, g $mole^{-1}$
n_s, n_w	Moles of salt and water, respectively
P	Hydrostatic pressure, atm
R	Gas constant, 8.314 watt sec deg^{-1} $mole^{-1}$
t	time, sec
T	Temperature, °C
V	Volume, cm^3
$\dot{V}_L$	Rate of solution loss of a half-cell, cm^3 sec^{-1}
Δ	Denotes difference, right minus left
δ	Denotes difference, final state minus initial state
$\tilde{\mu}$	Electrochemical potential, cm^3 atm $mole^{-1}$
μ^c	Chemical potential, cm^3 atm mole
π	Osmotic pressure, atm
ρ	Solution density, g cm^{-3}

ψ	Electric potential, volt

Superscripts

'	Single prime denotes "property of the demineralizing column half-cell"
"	Double prime denotes "property of the auto-buret side"
c	Denotes "measured under a positive concentration difference", $C_s'' > C_s'$
c-P	Denotes "measured under a positive concentration difference and a negative hydrostatic pressure difference"
c-P-i	Denotes "measured under a positive concentration difference, a negative pressure difference and a negative current density"
-i	Denotes "due to negative current density alone"
-P	Denotes "due to negative hydrostatic pressure difference alone", $\Delta P < 0$
-c-i	Denotes "measured under a negative concentration difference and a negative current density"

Subscripts

Bu	Buret
Col	Demineralizing column
L	Leak
s	Salt
w	Water

I. Introduction

This is the tenth quarterly report of a research program designed to (a) construct one apparatus in which transport of salt, ions and water across membranes can be determined with differences in concentration, electric potential and pressure as driving forces, together with the measurement of membrane and streaming potential, and (b) perform a variety of transport measurements in it to determine the range in which linear relationships between fluxes and forces exist. This will permit us to study the performance of separators and membranes from a minimum number of basic characterization measurements. The experimental system has been described in the first annual report (November, 1968). Minor alterations in this system have been reported in the fifth (February, 1969), sixth (May, 1969) and seventh (August, 1969) quarterly reports and the extended eighth quarterly report (January, 1970) which serves as the second annual report. This report describes in detail the measuring systems (voltage, pressure, electric current) which have not been previously discussed. A full description of the various transport measurements is outlined.

II. Experimental

A complete and detailed description of the "concentration-clamp" cell and feedback system has been outlined in the previous quarterly reports (November, 1968; August, 1969) and especially in the eighth quarterly report (January, 1970), together with the experimental procedure for the determination of the salt and water flows. For the sake of completeness, we report here the description of the constant-current and constant-pressure apparatus, together with the voltage-measuring system.

II.1. Constant-Current System

The following scheme was used to provide a predetermined constant d.c. electric current which was then passed through the membrane in electromigration experiments. See Figure 1 for a diagram of the system.

The power supply (Model KG 25-0.2, Kepco, Inc., Flushing, New York) for the constant d. c. current could supply a maximum of 25 volts and 200 ma. It had a continuously adjustable, 10-turn voltage control; the resolution was 0.05% of maximum output. For isolation, the resistance between output and ground was 10 kilomegohm; this large resistance was necessary to prevent significant current loops between the comparators and the power supply via ground and the cell solution.

The value of the current was accurately determined by measuring the voltage drop across a ten ohm resistor which had a 20 ppm(°C)$^{-1}$ temperature coefficient. The potentiometer (Section II-2) measured the voltage drop to better than 0.01%. The accuracy of the current measurement was therefore determined by the accuracy of the value of the fixed resistance. The resistance was determined to ±0.04% by comparison with a 10 ohm calibration resistance (type 1433, decade resistor, General Radio Co., Concord, Mass.), using an accurate 1605AH impedance comparator (General Radio Co., West Concord, Mass.). A milliammeter (Simpson Electric Co., Chicago, Ill.) and a silver coulometer were connected in series with the working electrodes. In the experiments described in Section III, there was agreement of 0.1% or better for the value of the electric current as calculated from the coulometer and from the voltage across the 10 ohm resistor.

II.2. Voltage Measurement System

The streaming potential, the membrane potential and the voltage across the ten ohm resistor (Section II.1) were measured in the following manner (the schematic diagram is shown in Figure 2).

A storage battery was used as the power supply for a potentiometer

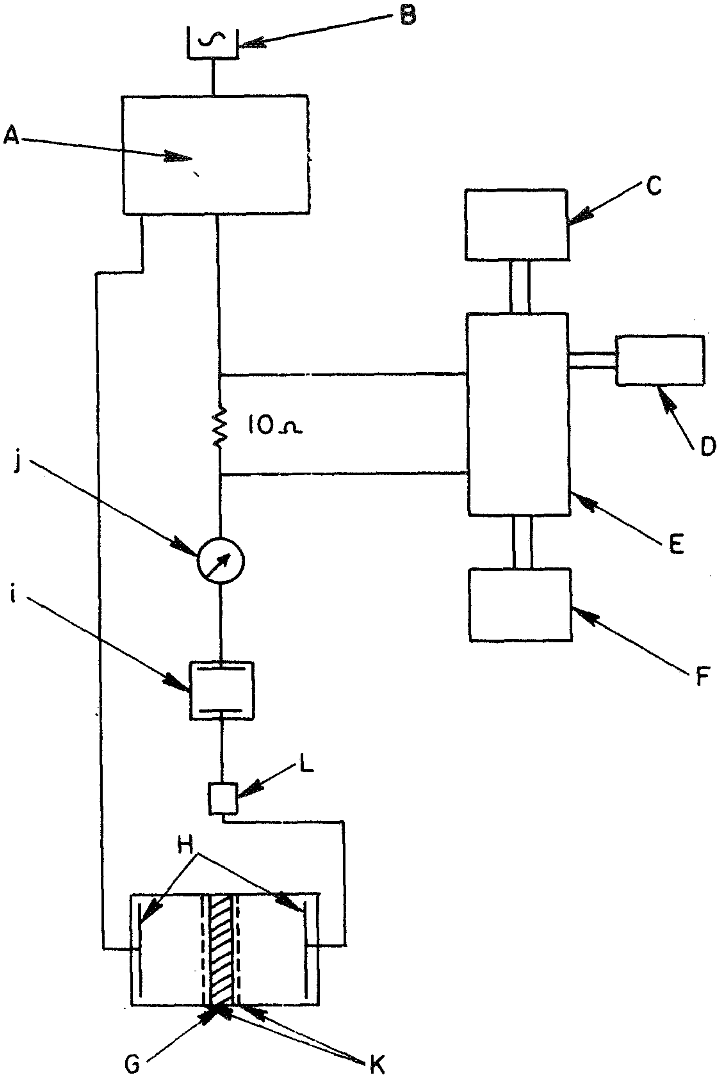

Figure 1: Constant-Current System. A, constant-current power supply; B, linepower; C, storage battery; D, standard cell; E, potentiometer; F, null detector; G, membrane; H, Ag/AgCl working electrodes; i, coulometer; j, milliammeter; K, membrane support; L, toggle switch.

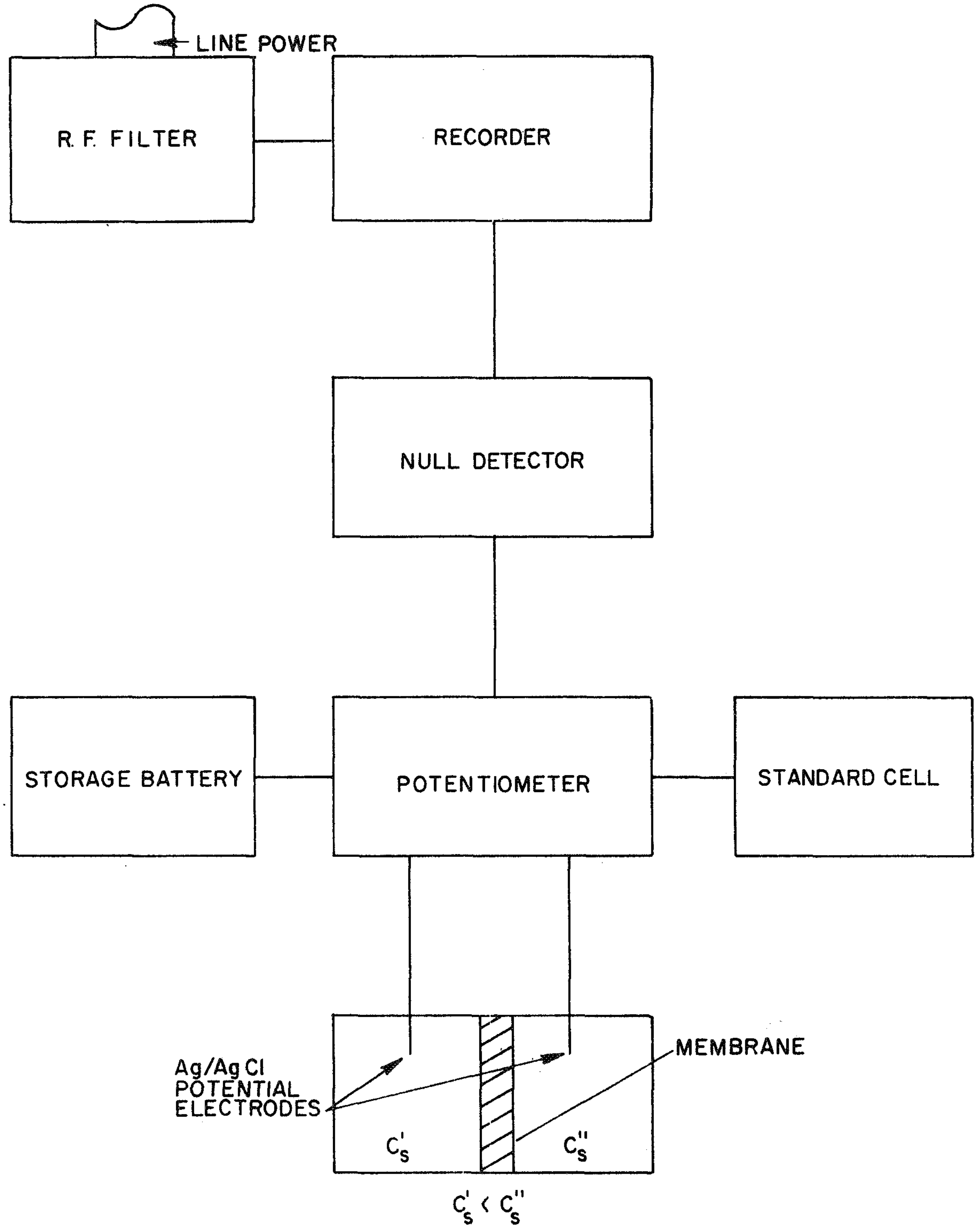

Figure 2: Voltage-Measuring System.

(Type K-5, Leeds and Northrup, Philadelphia, Pa.). The null detector for the potentiometer was a microvoltmeter (Model 150B, Keithley Instruments, Inc., Cleveland, Ohio 44139) which had a circuit ground-to-chassis resistance of 10^9 ohms. On battery operation it was completely isolated from line power and ground. The accuracy of the meter was ±3% of full scale on all ranges; of course the sensitivity of the instrument is much greater when it is used as a null detector than when it is normally operated. The 100 mv recorder output of the microvolt meter was connected to a chart recorder (Cat. 93506, Beckman Instruments, Inc., Fullerton, Ca.). Due to the current loop between the recorder and the comparators through ground, the feedback system could not operate when the recorder was connected to the null detector output. As a consequence, the periods of potential recording were kept to less than the time interval necessary to cause 0.5% change in concentration (3 hours) on the low-concentration side.

II.3. Pressure System

The pressurizing system was designed to maintain constant pressures up to 5 atmospheres for several days. This was accomplished in the following manner (Figure 3).

A five-liter tank was connected to a brass bellows valve (H-series, B-4H, Nupro Co., Cleveland, Ohio) which served as the inlet to the pressure system. The tank was connected to the cell via a brass 1/4" tube (silver-soldered to a hole drilled in the tank), and a short piece of hard plastic tubing connected to the brass tubing by a "Swagelok" union. The hard plastic tubing was connected to a 5 ml pipet which was connected to the cell by a "Swagelok" O-ring connector. Also connected to the tank was a Bourdon tube pressure gauge (Model "CMM", Heise Bourdon Tube Co., Newtown, Conn.) which had an automatic thermal compensator, slotted link (for sudden release protection), full scale deflection of 5 atm and divisions of

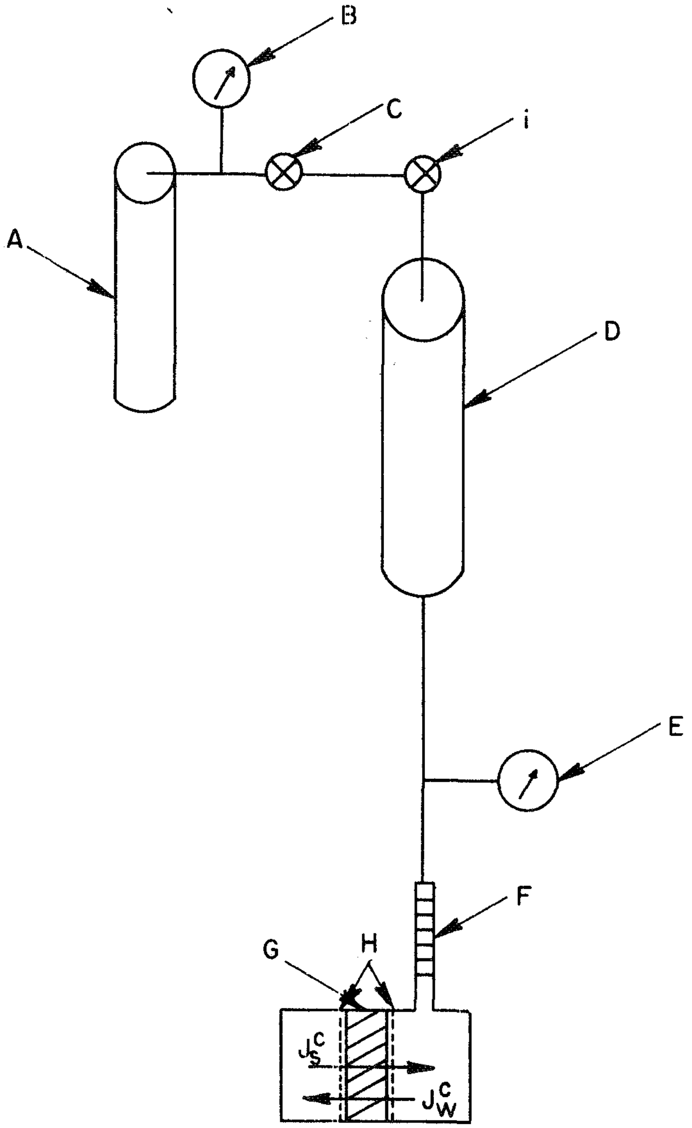

Figure 3: Pressurizing System. A, high pressure nitrogen tank; B, pressure gauge; C, shut-off valve; D, five liter tank; E, Heise pressure gauge; F, five ml. pipet; G, membrane; H, membrane support; i, reducing valve.

0.005 atm. Hydrostatic pressure was only applied to the demineralizing side of the cell because the auto-buret could not withstand pressure. An accurate measurement of volume and salt concentration transport was only possible on the low-pressure side (auto-buret side). The demineralizing side expanded with pressure; however the ion exchange column did serve as an order-of-magnitude-check on the salt transport.

The system was pressurized with industrial grade nitrogen. Fluctuations in pressure due to temperature variations in the temperature of the N_2 (±0.05°C) were about 0.002 atm which was less than the smallest increment of pressure that could be read on the Heise pressure gauge.

III. Results and Discussion

We have performed four types of experiments, the results of which are discussed here. Each experiment has been designed to study one or a combination of the driving forces, i.e. concentration gradient, electrical potential gradient, or pressure gradient. In our eighth quarterly report (January, 1970), we described the transport measurement results in terms of salt and volume fluxes. Because the partial molar volumes of salt and water depend upon salt concentration, volume is not a strictly conserved quantity. Therefore, when discussing transport measurements we shall describe them here and in the future, in terms of water flux, J_w, rather than volume flux, J_V. The derived equations will be outlined in the next report.

III.1. Dialysis - Osmosis Experiment

The dialytic and osmotic fluxes which result from a concentration difference of 0.5 - 0.1 M NaCl ($\Delta\pi$ = 18.17 atm) were measured in this experiment. The large concentration difference was chosen because the AMF C-103 cation-exchange membrane (American Machine and Foundry Co., Stamford, Conn.) has a low permeability to salt. Even when using a membrane of surface area 7.88 cm^2, three days were required to transport approximate 3 mmoles of salt, this amount being the minimum consistent with accurate analytical determination. The results of a typical experiment are shown in Figure 4. This figure demonstrates the high degree of linearity of the dialytic and osmotic fluxes with time. Using the least-square method, we obtained the following flux values:

$$J_w^c = (+\ 130 \pm 1) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$

$$J_s^c = (-\ 1.21 \pm 0.01) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$

As can be clearly seen in Figure 4, the standard deviation of the data points was quite small. Several experiments using identical conditions were performed consecutively over a period of six days and gave roughly identical results.

In the first two dialysis experiments, the salt flux as calculated from the demineralizing-column data was 10% lower than that calculated using buret data. It was discovered that during the elution of the demineralizing column, small air bubbles formed which interfered with the elution process. These were eliminated by eluting with $NaNo_3$ solution, which had been deaerated. Thereafter, agreement between salt fluxes was within 1%.

III.2. Electromigration - Electroosmosis Experiments

This series of experiments was performed using two driving forces, concentration difference and electrical potential gradients, (see Figures 5 and 6). Furthermore in successive experiments, the concentration gradient was both in the direction of positive electric current and opposite to it. A current density of 2 ma cm^{-2} was chosen because this value gave an electroosmotic water flux at least twice that of the osmotic water flux;

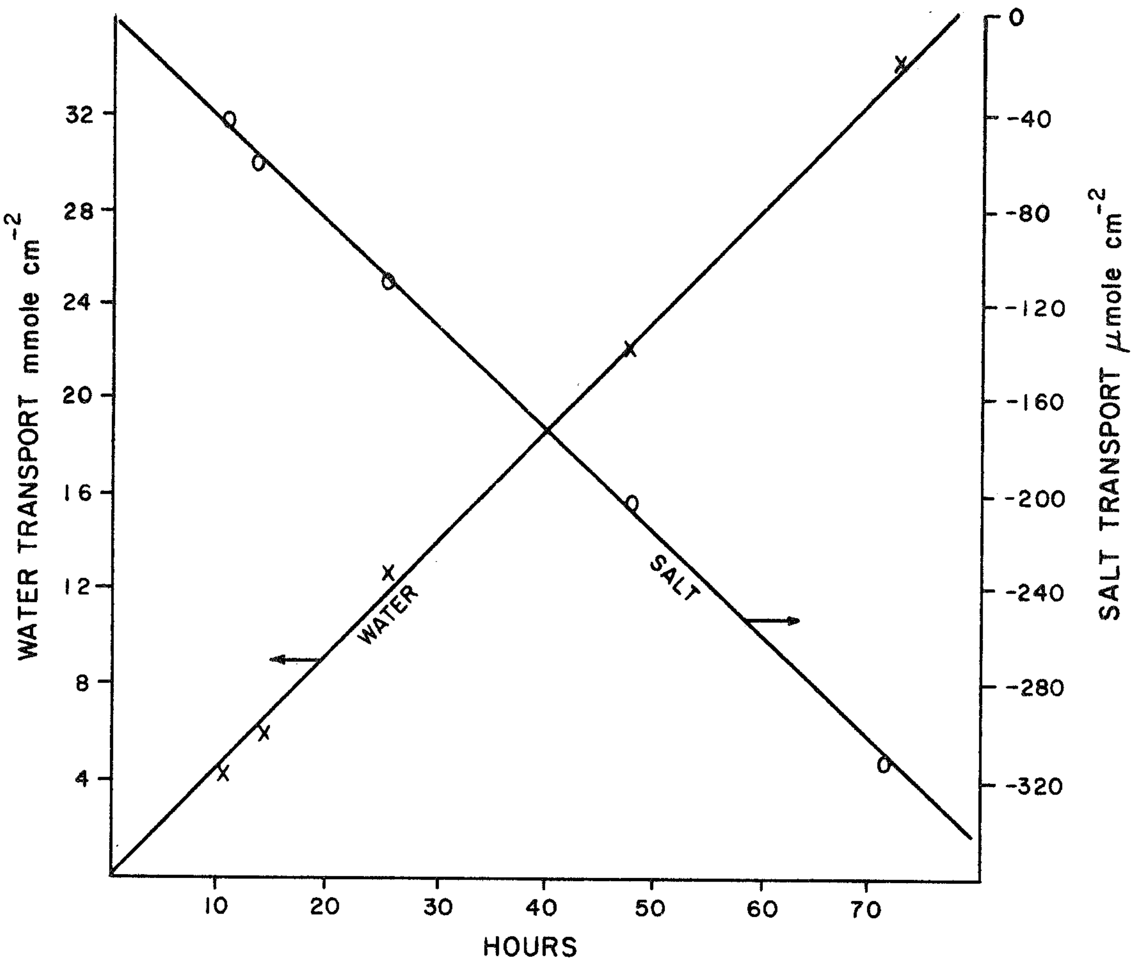

Figure 4: Dialysis→Osmosis Experiment.

Concentrations: $C_s' = 0.1$ M NaCl; $C_s'' = 0.5$ M NaCl,

Membrane: AMF C-103; T = 25.00 ± 0.01°C

From Figure:

Salt flux: $J_s = -4.36 \pm 0.04$ µmole cm^{-2} hr^{-1},

Water flux: $J_w = + 467 \pm 4$ µmole cm^{-2} hr^{-1}.

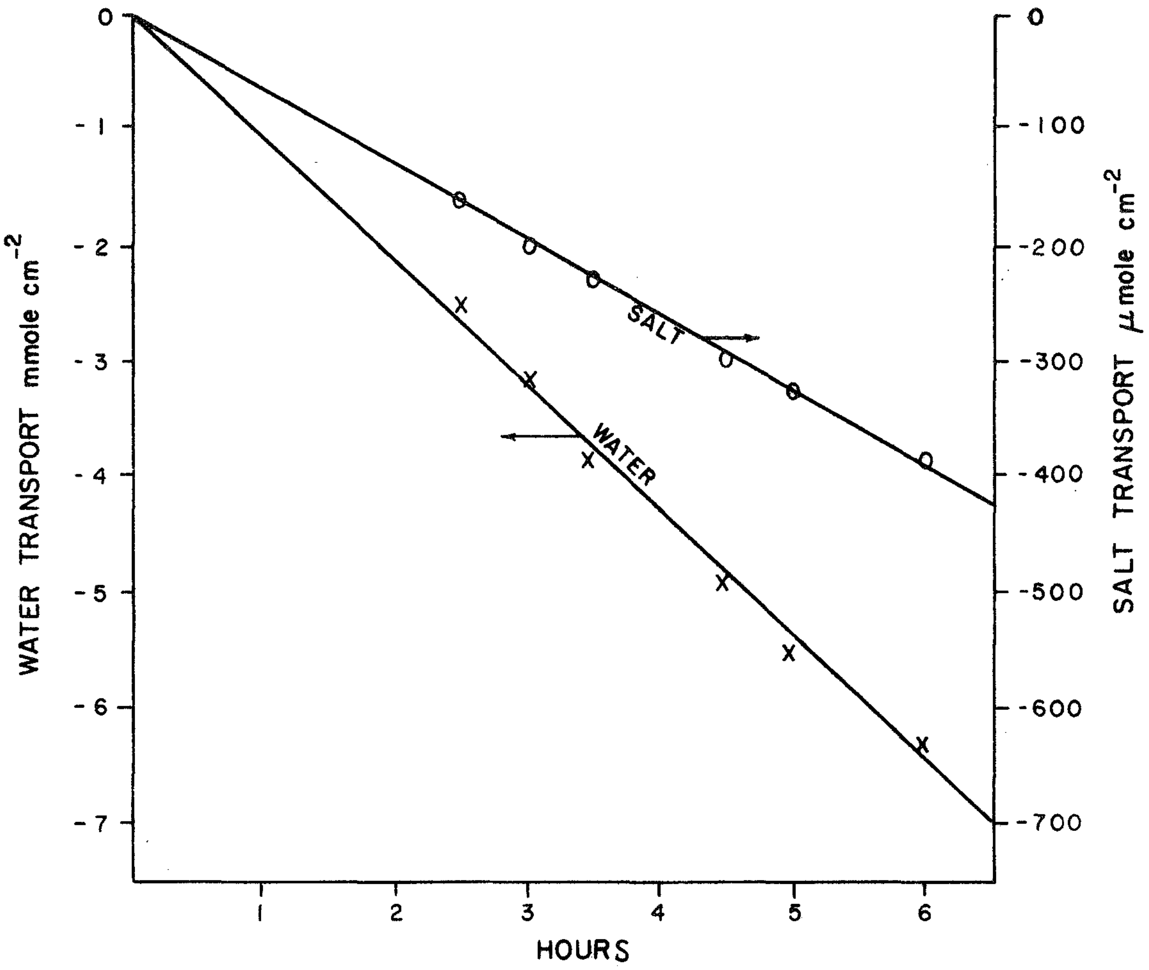

Figure 5: Electromigration - Electroosmosis Experiment I.

Concentrations: $C_s' = 0.5$ M NaCl; $C_s'' = 0.1$ M NaCl; i = - 2 ma cm^2;

AMF C-103 membrane; T = 25.00 ± 0.01°C

From figure:

Salt flux: $J_s = -66.2 \pm 0.5$ μmole cm^{-2} hr^{-1}
Water flux: $J_w = -1118 \pm 6$ μmole cm^{-2} hr^{-1}

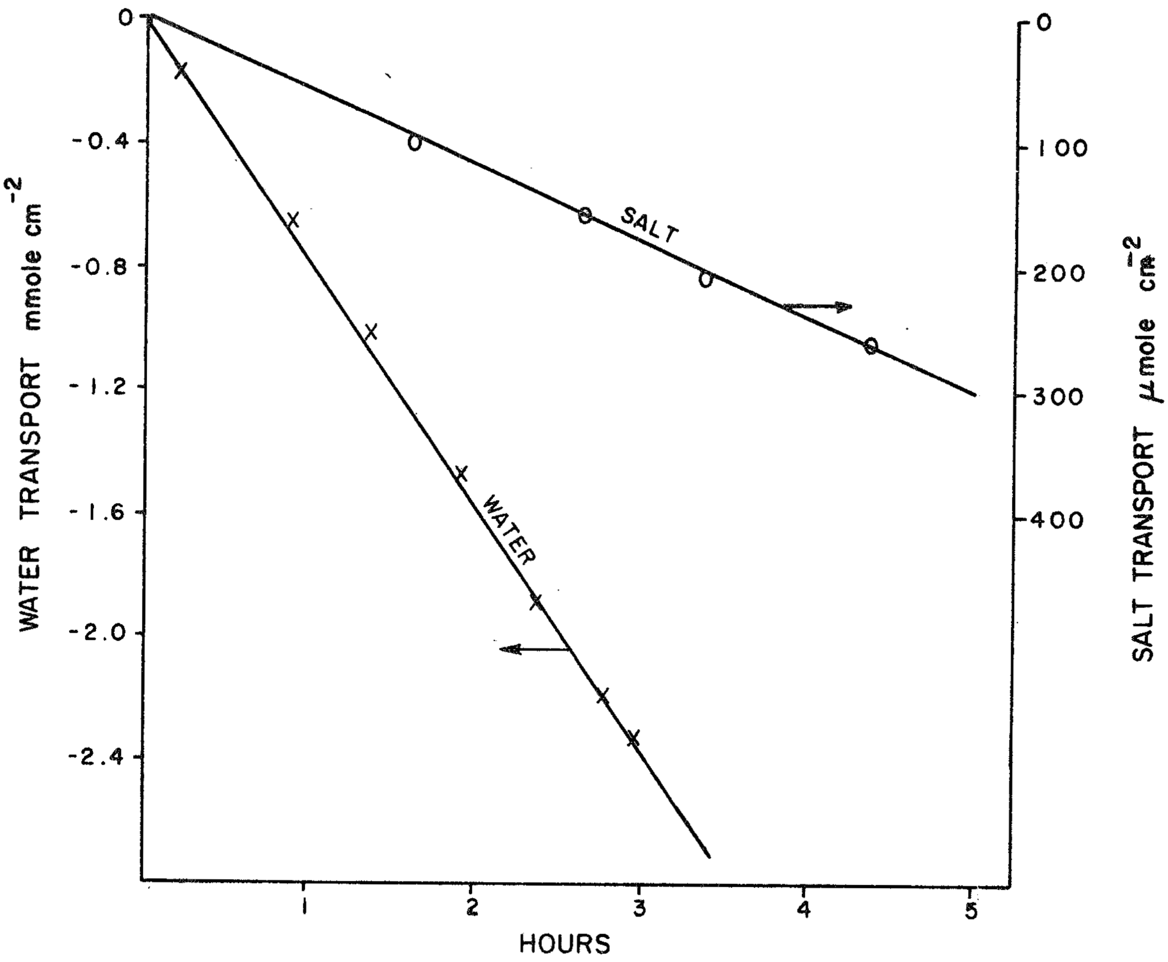

Figure 6: Electromigration - Electroosmosis Experiment II.

Concentrations: $C_s' = 0.1$ M NaCl; $C_s'' = 0.5$ M NaCl; $i = -2$ ma cm^{-2};

AMF C-103 membrane; T = 25°C ± 0.01°C

From figure:

Salt flux: $J_s = -75.3 \pm 1.2$ μmole cm^{-2} hr^{-1}

Water flux: $J_w = -528 \pm 2$ μmole cm^{-2} hr^{-1}

the concentration difference across the membrane for all electromigration experiments was 0.5 - 0.1 M NaCl. Since the column half-cell always removes salt, and the buret side adds salt, and since electromigration is the dominant factor in salt transport, the current must always be made to flow from the buret to the column side. Hence when the osmotic and electric forces are to be in the same direction, the buret side must be more concentrated; if the forces are opposed, the column side is the more concentrated. In the latter case, this requirment introduces a problem: in the period preceding the passage of the current, the feedback system cannot maintain the steady state because dialysis is proceeding in the direction opposite to that which can be corrected by the feedback mechanism. Therefore, the initial concentrations were established and maintained manually by injecting deaerated water and concentrated salt solutions into the half-cells until the electric current was turned on. After this time, the feedback system started to maintain steady-state conditions.

For positive current (left to right), the following flux values were calculated:

Experiment I $\qquad \underleftarrow{i = -2}\ \text{ma/cm}^2$

$$\text{Cathode}/C_s' = 0.5\ \text{M NaCl} \ // \ C_s'' = 0.1\ \text{M NaCl} \ /\ \text{Anode}$$

$$J_w^{-c-i} = (-311 \pm 2) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$$

$$J_s^{-c-i} = (-18.4 \pm 0.1) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$$

Experiment II $\qquad \underleftarrow{i = -2}\ \text{ma/cm}^2$

$$\text{Cathode}/C_s'' = 0.1\ \text{M NaCl} \ // \ C_s'' = 0.5\ \text{M NaCl} \ /\ \text{Anode}$$

$$J_w^{c-i} = (-147 \pm 0.6) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$$

$$J_s^{c-i} = (-20.9 \pm 0.3) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$$

III.3. Pressure Permeation Experiments

The results of the experiments, in which concentration and pressure difference were applied simultaneously, were used to calculate the salt and water fluxes (J_s, and J_w respectively). The streaming potentials were measured simultaneously. Using the experimental conditions: $C_s'' = 0.5 - 0.1$ M NaCl and $P'' - P' = -1.5$ atm, we found that the water flux reached steady state within a few minutes while the salt flux required about two days. Figure 7 demonstrates the linearity of the salt and water transport with time during a pressure experiment which includes concentration control. Calculated values of the fluxes are the following:

$$J_s^{c-p} = (-0.442 \pm 0.008) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$
$$J_w^{c-p} = (+ 101 \pm 0.6) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$

Comparing these values to those obtained in the absence of the pressure gradient (Section III.1) we see that both the salt and the water flux decreased (in absolute value) with application of pressure. The decrease of the salt flux is not surprising, because the pressure opposes the dialysis flow. The hydraulic and osmotic driving forces for the water flux are in the same direction, however, and one should therefore expect higher water flux under pressure than in the absence of pressure. It is possible that this result is due to membrane compaction, but further experiments have to be done to confirm this working hypothesis. It is seen that by application of pressure the water flux decreased from the dialysis value (Section III.1) of 130 to 101 x 10^{-9} mole sec^{-1} cm^{-2}.

Measurement of the streaming potential was accomplished using Ag/AgCl electrodes. The concentration difference was: $C_s'' - C_s' = 0.5 - 0.1$ M NaCl. Streaming potential was taken as the voltage difference across the membrane under a pressure difference minus that measured without a pressure difference. The pressure difference was increased in steps of 0.1 atm ranging from 0.0 atm. to -1.5 atm. Figure 8 shows that the streaming

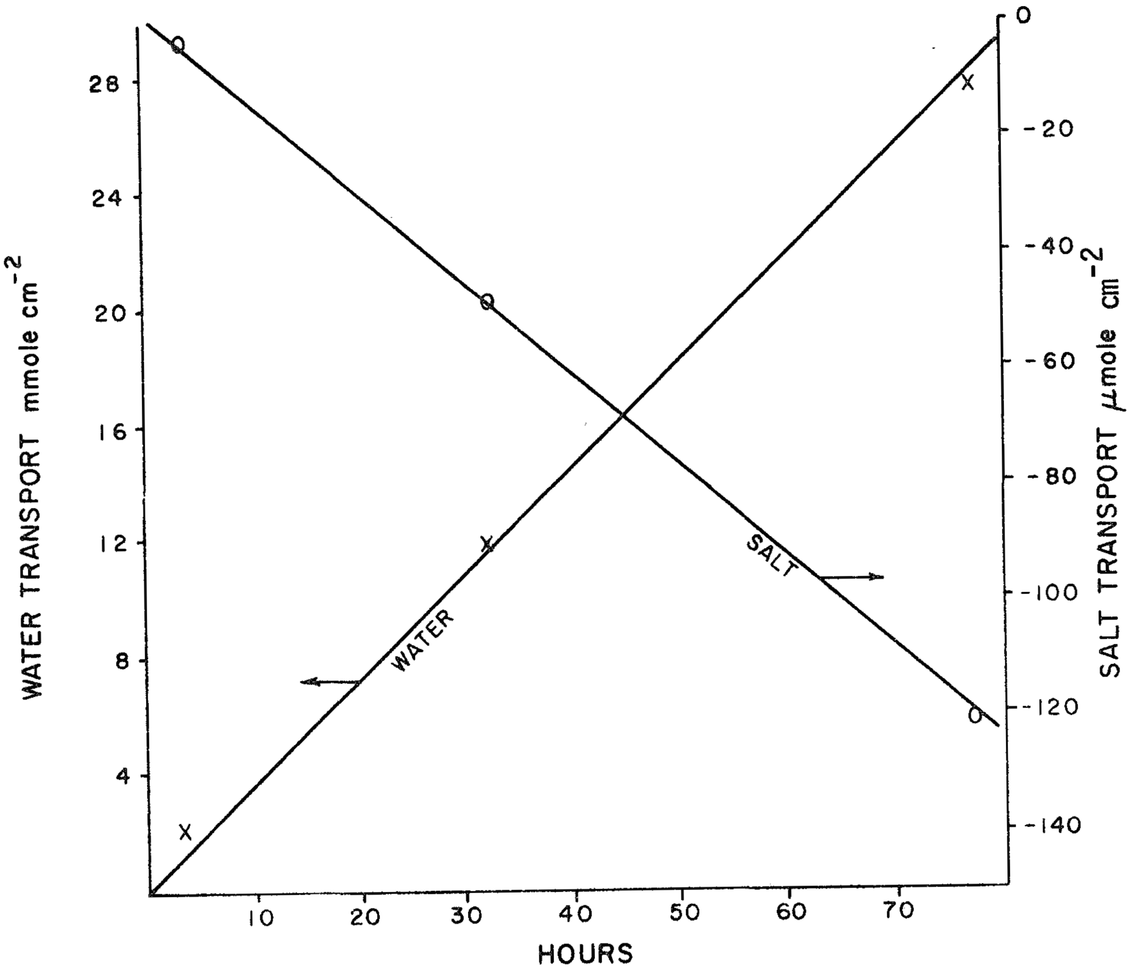

Figure 7: Dialysis + Osmosis with Pressure Gradient.

Concentrations: $C_s' = 0.1$ M NaCl; $C_s'' = 0.5$ M NaCl,

$P'' - P' = 1.5$ atm; $T = 25.00 \pm 0.01$°C; AMF C-103 membrane

From figure:

Salt flux: $J_s = -\ 1.59 \pm 0.03$ µmole cm^{-2} hr^{-1}

Water flux: $J_w = +\ 362 \pm 2$ µmole cm^{-2} hr^{-1}

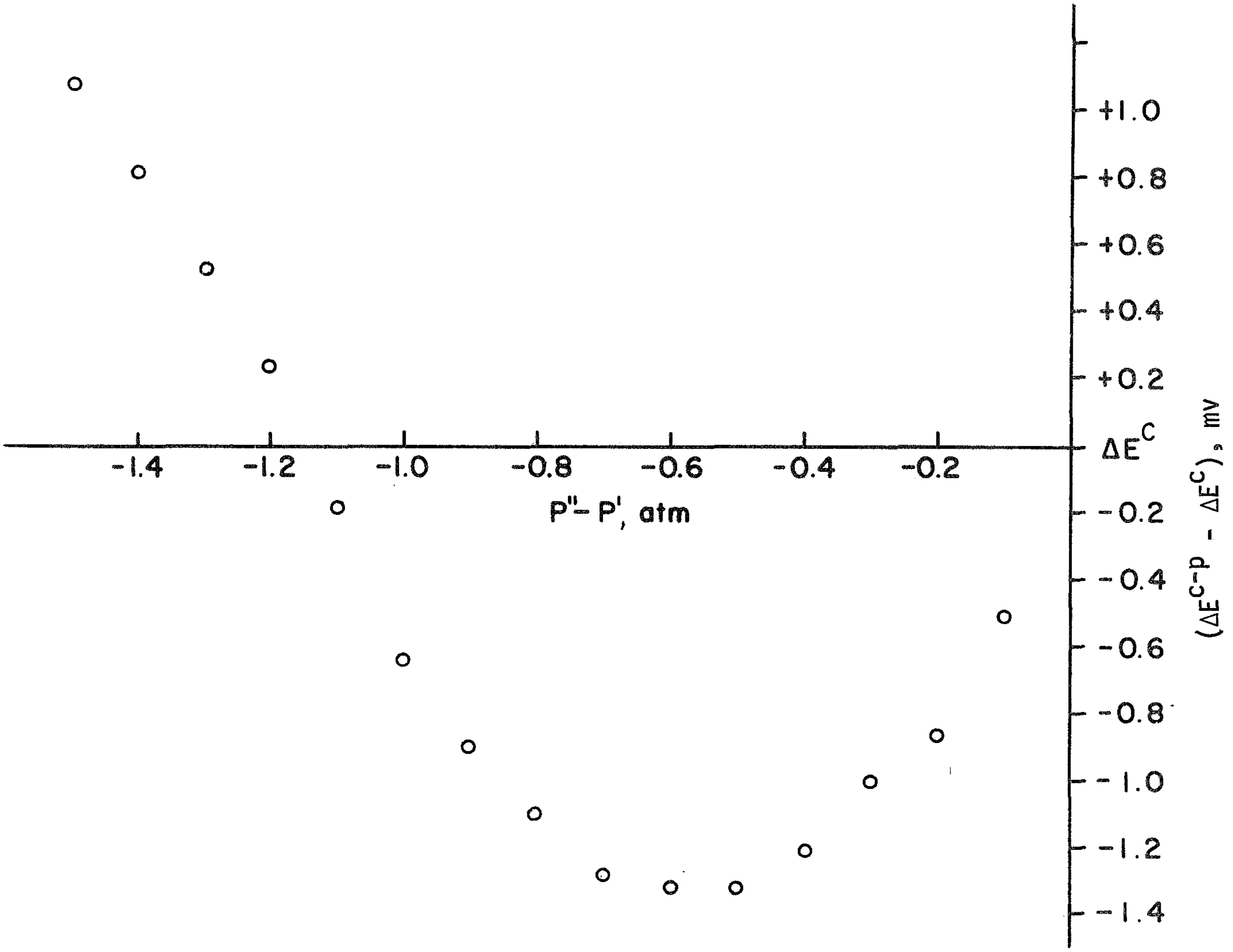

Figure 8: Streaming Potential with a Concentration Gradient.

Concentrations: $C_s' = 0.1$ M NaCl; $C_s'' = 0.5$ M NaCl,

AMF C-103 membrane; T = 25.00 ± 0.01°C

Voltage without pressure difference: $\Delta E^C = -65.4 \pm 0.1$ mv potential increased to a maximum value of 1.3 mv when $\Delta P = -0.5$ atm, and than decreased fairly linearly with a slope of -2.2 mv atm^{-1}.

The voltages measured by this incremental pressure sequence were quite reproducible; however, when all pressure difference was removed the voltage due to concentration difference alone, ΔE^c, reached its original value only within ± 150 μv. These data indicate the existence of a non-linearity and of a hysteresis effect which requires further study.

In order to create conditions of $\Delta P \simeq \Delta\pi$, one can either impose pressure differences approximating the osmotic pressure difference due to the commonly used concentration difference (18.17 atm in the case of $\Delta C = 0.5 - 0.1$ M NaCl) or one can adjust the concentration difference so that the osmotic pressure approximates a predetermined pressure difference. The former is by far the preferred experimental technique; however, in this case the mechanical properties of the membrane support prohibit application of pressure differences greater than 1.5 atm. Thus, we have adopted the latter procedure for the last group of volume transfer measurements. These were performed with the concentration difference of: $C_s'' - C_s' = 0.08 - 0.1$ M NaCl ($\Delta\pi = -0.8922$ atm). These experiments were only of a few hours duration, and the feedback system was not used because the concentration changes were very small.

The following results were obtained:

$$J_v^c = (-1.48 \pm 0.03) \times 10^{-10} \ \ell \ \mathrm{sec}^{-1} \ \mathrm{cm}^{-2}; \ P'' - P' = 0.000 \ \mathrm{atm}$$

$$J_v^{c-p} = (+1.41 \pm 0.03) \times 10^{-10} \ \ell \ \mathrm{sec}^{-1} \ \mathrm{cm}^{-2}; \ P'' - P' = -0.985 \ \mathrm{atm}$$

$$J_v^{c-p} = (+2.80 \pm 0.06) \times 10^{-10} \ \ell \ \mathrm{sec}^{-1} \ \mathrm{cm}^{-2}; \ P'' - P' = -1.490 \ \mathrm{atm}$$

When plotting these volume fluxes against pressure, one finds an almost linear relationship.

In experiments employing pressure gradients, neither salt nor water flux can be calculated using data recorded on the pressurized demineralizing half-cell since the "Lexan" and the polyethylene tubing housing of this system expand with pressure in an irreproducible, non-linear way. While it is impossible to measure volume changes in the demineralizing half-cell, it is still possible to calculate the salt flux using auto-buret data, and to check their accuracy using the elution data of the demineralizing column.

III.4. "Combined" Experiment

In this experiment the imposed forces were differences of concentration, pressure and electric current, applied simultaneously. The conditions were $C_s'' - C_s' = 0.5 - 0.1$ M NaCl, $P'' - P' = 1.5$ atm and an electric current density of $- 2$ ma cm^{-2} passed, such that the anode occurred on the high concentration (auto-buret) side of the membrane.

The following flux values were calculated from the results:

$$J_s^{c-i-p} = (- 20.5 \pm 0.2) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$

$$J_w^{c-i-p} = (- 98.1 \pm 0.9) \times 10^{-9} \text{ mole sec}^{-1} \text{ cm}^{-2}$$

These results together with the former ones will serve to calculate the required conductance coefficients, the salt and water permeabilities, and the various transport numbers determined in our system.