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SEA WATER CONVERSION LABORATORY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 3

Covering Period April 9 - August 9, 1968

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

Contract No. 952109
Jet Propulsion Laboratory
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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

"This report contains information prepared by the University of California, Sea Water Conversion Laboratory, Berkeley, under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration.

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ABSTRACT

Construction of a cell suitable for the measurement of different membrane transport properties is reported. In this cell osmosis, electro-osmosis, dialysis, transport number, membrane potential, streaming potential, and conductivity measurements can be performed under uniform hydrodynamical conditions. Various auxiliaries e.g. conductivity cells, conductivity electrodes, and Ag/AgCl electrodes have been made.

The electrical part of a concentration feedback mechanism for the two cell compartments was assembled and tested.

I. INTRODUCTION

This report deals with the construction of the transport cell and of the concentration feedback mechanism. The aim of the project is to construct and test an apparatus in which transport of salt, ions, and water across a membrane can be measured, with differences in chemical potential, electric potential, and pressure as driving forces, and to evaluate the results with a method based on irreversible thermodynamics. The system considered consists of a membrane separating two different solutions of the same electrolyte. When measuring and combining such diverse properties as electric resistance, osmotic and electroosmotic water transport, diffusional and electrical salt transport, pressure-induced salt and water transport, membrane potential and streaming potential, one has to make sure that all these properties are determined with the membrane in very similar states. In other words, membrane-solution interfaces have to be the same in all measurements. Also the concentrations in the two cell compartments should be the same in all measurements in order to obtain a consistent set of coefficients for a given membrane and given solution concentrations. In our first report we have outlined the requirements for such an experimental system. The system which will be used in this project was described and some of the difficulties involved were pointed out. It consists of a two-compartment membrane transport cell (Figure 1) in which all the measurements will be performed. A stirrer is inserted in each cell half and the concentrations in each compartment are kept constant during an experiment by means of a concentration feedback system, containing conductivity cells to sense the concentration changes.

This report describes in detail the transport cell with some auxiliaries and the concentration feedback mechanism, both of which have been constructed in the period covered by this report. The temperature regulation and measuring devices are under construction and testing now and will be described in the next report.

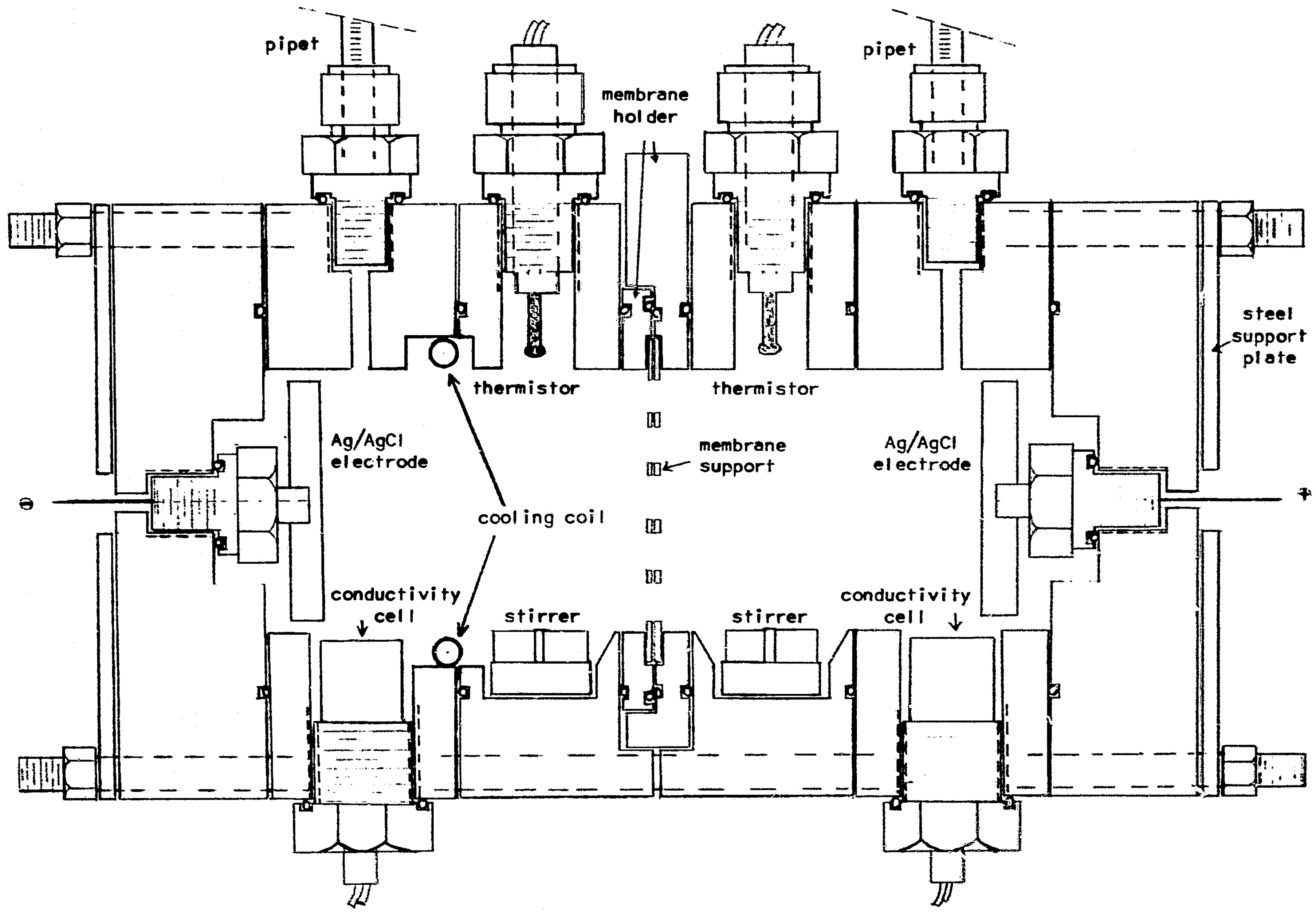

FIGURE 1

MEMBRANE TRANSPORT CELL

II. MEMBRANE TRANSPORT CELL

II-1. Transport Cell

The transport cell, to be used for all measurements, is a cylindrical two compartment cell and consists of interchangeable cylinders and end parts, clamped together by two supporting steel plates and steel rods. Buna N O-rings are used as seals between the various parts. All parts were machined of "Lexan" (General Electric Co. trade name), a transparent polycarbonate plastic (West Lake Plastics, Lenni Mills, Pa.). The cylinders have an outer diameter of 4.5" and an inner diameter of 2". The end parts also have a diameter of 4.5" and are 1-1/8" thick.

The assembly for an electroosmosis experiment is shown in Figure 1. The end part of each compartment contains a mounting hole in which the Ag/AgCl working electrode (described in Section II-3) can be inserted. Two other 1/4" holes are made for connecting the cooling coils (Section II-5) to the outside. The cylinder next to the end part has the connections for the pipet, the inlet and outlet for the concentration feedback system, and the conductivity cell. All holes are 7/16"-20 N.F. (National Fine, i.e. straight thread) for standard "Swagelok" (Crawford Fitting Co., Solon, Ohio) connectors, except the hole for the conductivity cell which is 3/4"-16 N.F. (Section II-4). At the inside of the cylinder 1/2" wide x 5/16" deep grooves are made for the cooling coil. In the next cylinder, provisions are made for accommodating resistance thermometer, a Ag/AgCl measuring electrode (Section II-3) and a magnetic stirrer. The thermistors and the Ag/AgCl electrodes are epoxy-sealed in "Swagelok" connectors ("Zytel"), 3/8" tube o.d. for 9/16"-18 N.F. holes. All "Swagelok" connectors have an O-ring seal. The stirrer is a "Teflon"-enclosed magnet and has the form of a 1/4" high fin on top of a 3/8" high cylinder, 3/4" diameter (Bel Art, Pequannock, N. J.). A cone was made in the bottom of the cell cylinder, leading to a 7/8" wide 1/4" deep cylindrical hole that keeps the stirrer in place.

The membrane holder can be slid out of the cell without disassembling the other parts completely. The membrane is sealed by an O-ring at each side. The two parts of the membrane holder fit together tightly, and a soft rubber gasket is inserted between the left side stirring compartment and the membrane holder. With this design, we expect no evaporation from the membrane edges. Two 1/16" thick membrane supports can be inserted in the membrane holder. They are made of glass-fiber reinforced plastic, each one having 19 holes of 5/16" diameter. This reduces the membrane area from 20.3 cm^2 to 9.40 cm^2. When necessary, different supports can be made and inserted.

For membrane resistance measurements, a different end part than the one shown in Figure 1 is used. This part has a 3/8" hole into which the shaft of the conductivity electrode (Section IV-4) can be fitted. Two O-rings are inserted in the 3/8" hole, spaced at 7/8", to seal the shaft. The distance between the electrodes can be changed and measured by means of an adjusting screw pushing against the electrode shaft.

II-2. Conductivity Cells

The sensors for the concentration feedback systems are the conductivity cells shown in Figure 2. They are made of "Lexan." Platinized platinum electrodes are glued to the sides of the 1/2" long x 3/16" wide x 3/8" deep hole and are connected to a Pt wire leading to the outside via a 1/32" hole.

The threaded electrode holder fits into a 3/4"-16 N.F. threaded hole in the cylinder, O-ring sealed at the outside. Cell constants are between 2 and 10.

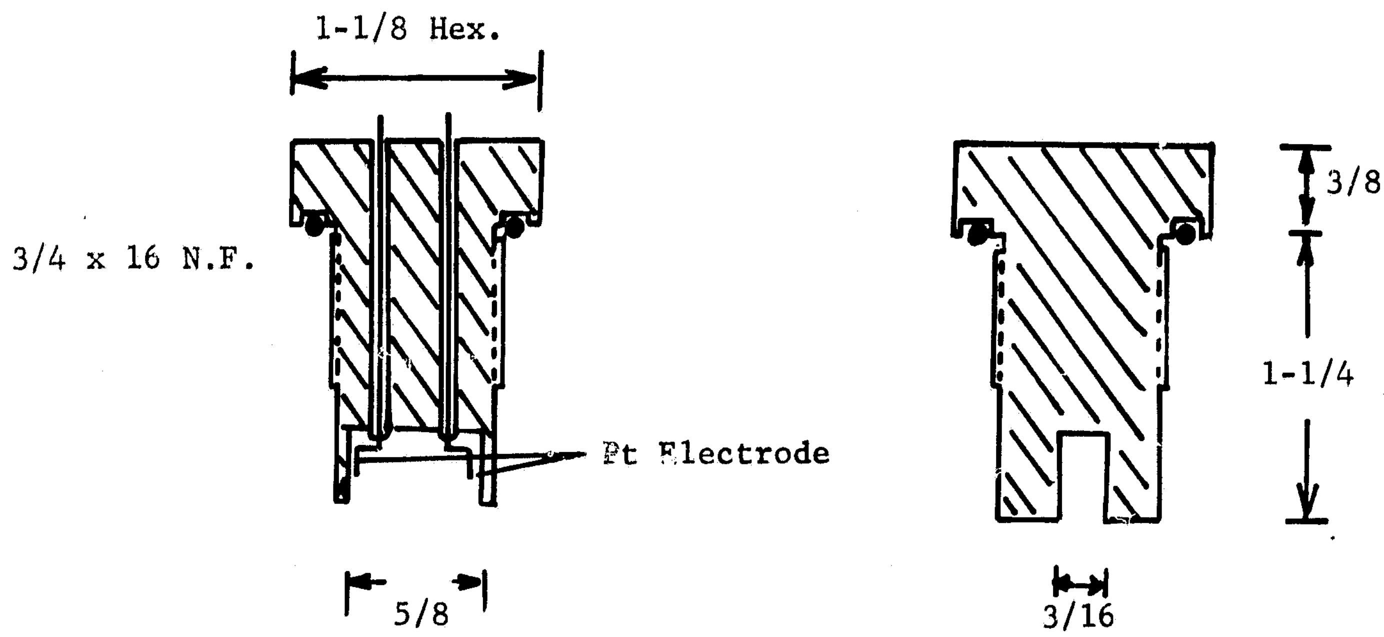

FIGURE 2

CONDUCTIVITY CELL

Material: Lexan

Dimensions are in inches.

II-3. Ag/AgCl Electrodes

Ag/AgCl working electrodes, to be used in the electroosmosis experiments, were constructed. A strip of silver metal, about 25" long, 1/4" wide, and 0.022" thick is wound as a spiral of 1-3/4" diameter (outer circumference). The spiral is mounted on a cylindrical "Lexan" plate, also 1-3/4" diameter and 1/4" thick. This assembly is mounted on a "Swagelok" hose connector, 1/4" hose diameter, 7/16"-20 N.F. thread, which can easily be inserted in the end part of the transport cell (Figure 1). A silver wire is welded to the silver strip and is sealed with epoxy inside the "Swagelok."

Seventy mmoles silver are deposited on the silver spiral out of a $KAg(CN)_2$ solution (10 gram/liter). Then about 35 mmoles are converted to AgCl by electrolysis in a 0.1N HCl solution. By keeping the current density low (<1 ma/cm^2) and stirring well it seems that the whole surface area (approximately 70 cm^2) is covered quite uniformly. During an electroosmosis experiment about 10 mmole of AgCl will be produced or consumed.

The Ag/AgCl potential-measuring electrodes are fitted into a "Swagelok" connector that can be fitted in the section of the transport cell containing the stirrer. Each consists of a silver wire sealed with epoxy into a 3/8" glass tube. The tip of the wire is first plated with silver and then chloridized. Asymmetry potentials of these simple electrodes are smaller than 0.1 mV.

II-4. Conductivity Electrodes

The a.c. resistance of the system solution 1 - membrane - solution 2 will be measured, and by varying the electrode distance, the resistance of the membrane can be determined. The circular electrodes consist of 0.004" platinum foil glued with "Plio-Bond" (Goodyear Tire & Rubber Co., Akron, Ohio) to a "Lexan" plate, 1-7/8" diameter. A platinum wire is welded to the foil and leads to the outside connection through a hollow rod mounted on the disc, perpendicular to its face. This rod is made of "Delrin" (E. I. du Pont de Nemours Co., Wilmington, Del.), a reinforced "Teflon" material, chosen for its strength and low friction. Each of the two assemblies consisting of electrode and rod is introduced into the end part of the cell through a double O-ring seal and can be moved forward and backward by means of an adjusting screw. The distance between the two electrodes is read on a ruler. With the method of variable distance, the resistance of the cell solution can be distinguished from the membrane resistance.

II-5. The Cooling Coils

The heat dissipated inside the cell by the electric current and the stirrer has to be removed to keep the temperature constant at the desired level. The thermal insulation of the liquid by the walls of the cell is very good; therefore we decided to introduce coils cooled by tap water; the flow rate of coolant is regulated by solenoid valves which are actuated by a thermistor sensing system. The coils are made of copper tube, 1/4" o.d. and have a total length inside each half cell of 18 cm. They are introduced through "Swagelok" connectors in the end parts of the cell. A 1/2" wide x 5/16" deep groove at the inside of the cylinder next to the end part leads to a 270° circular groove at the inside of the stirrer compartment. In this way the surface of the coil is exposed directly to the solution without forming an obstacle for the current passing between the working electrodes. The outer surface of the coils is coated with a thin epoxy layer to prevent corrosion and distortion of the electric current lines. It was determined that this coating approximately halves the heat transfer rate. However, a sufficient amount of heat can be taken out of the solution if cooling water of about 20°C is used.

A description of the total cooling system and its performance will be given in the next report.

III THE CONCENTRATION FEEDBACK MECHANISM

III-1. General Description

The concentration feedback mechanism was devised in order to keep the concentration in each of the two cell compartments constant with time. A brief description of the system was given in the first report. The total system diagram is shown in Figure 3. The resistance of the conductivity cell described in Section II-2 is continuously compared to that of a reference cell by an impedance comparator bridge (Section III-2). The output signal of this bridge is amplified and when the difference between standard and unknown exceeds a presettable value a relay is actuated, which at the donating side starts the motor of an automatic buret filled with a concentrated salt solution, while at the receiving side the relay opens a solenoid valve to a mixed-bed demineralizing column. The electronic and electrical part of this system has been constructed and tested and will be described in detail in the following paragraphs.

III-2. Impedance Comparators and Amplifiers

When the temperature of the solutions in the reference cell and the transport cells is kept within very narrow limits, the resistance difference is a measure for the concentration difference between the two solutions. An accurate 1605 AH impedance comparator (General Radio Company, West Concord, Mass.) is used to compare the two resistances. This instrument measures the difference of the total impedance and the phase angle between an unknown and a standard. By using conductivity cells of the same geometry for both unknown and standard, the phase angle difference will be very small and the impedance difference as measured by the comparator is a direct measure for the resistance

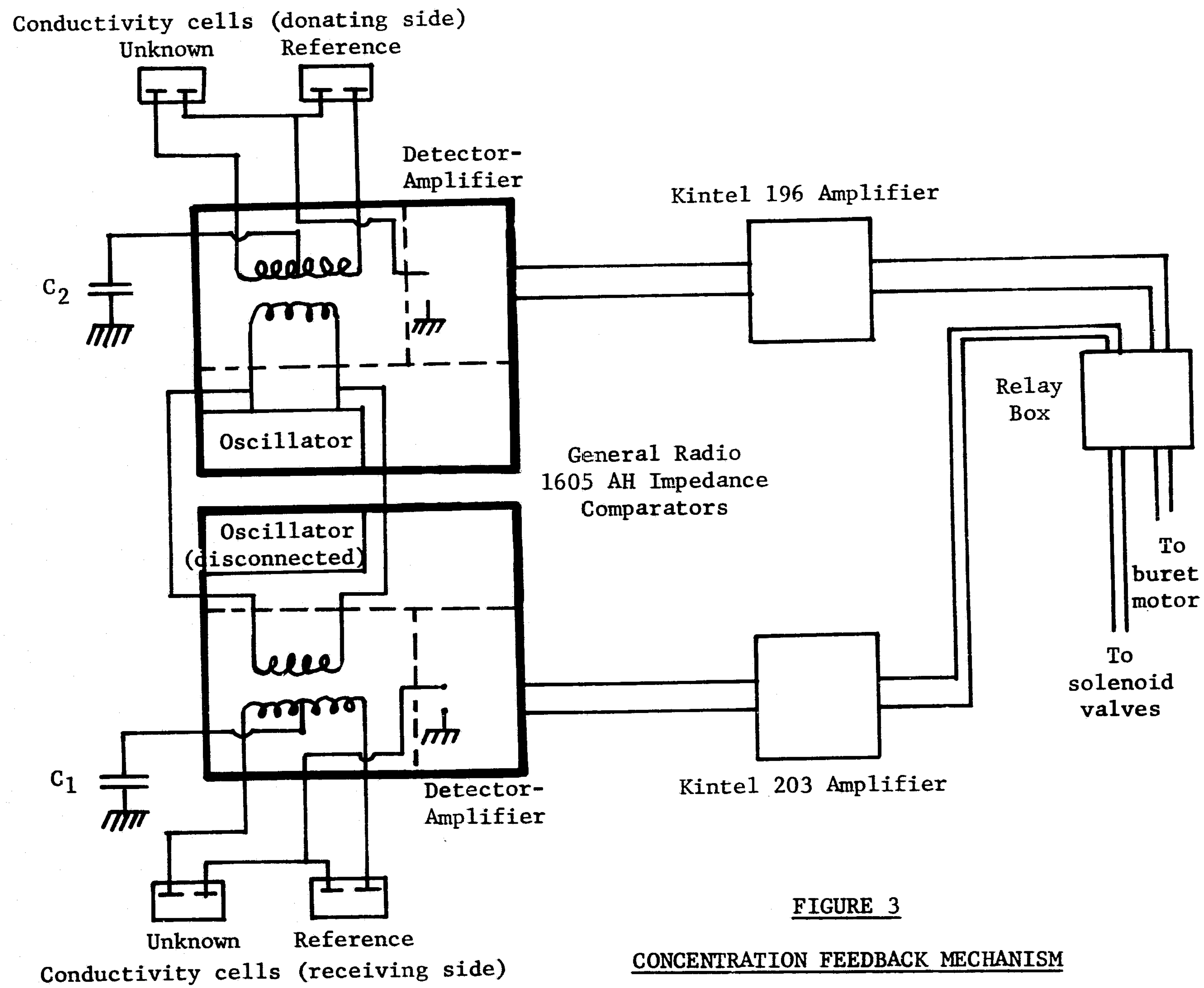

FIGURE 3

CONCENTRATION FEEDBACK MECHANISM

$C_1 = 20\ \mu F$

difference between the two conductivity cells. The General Radio 1605 AH has impedance difference ranges of 0.1, 0.3, and 3% full scale. The read-out accuracy is 3% of full scale. This means that by using the lowest scale, resistance differences as low as 0.005% can be detected and measured, approximately equivalent to 0.005% concentration difference between reference and standard solution. When working on the lowest scale, a variable resistor is used to compensate differences in cell constant between reference and unknown. The limiting factor in the accuracy of the concentration invariance is expected to be the temperature control.

The output of the comparator is ± 60 mV ± full scale; the output resistance is 600 ohm. Since the sensitive relay has a coil resistance of 480 ohm and needs 0.28 ma actuation current, an amplifier has to be used. Because the output of the comparator is at 45 V above ground, the input of the amplifier has to be floating. Amplifiers of very low drift are necessary. At one side we use a Model 196 amplifier, at the other side a Model 203A electrometer-amplifier (Kintel, San Diego, Calif.). With the amplifiers at gain 30, the relays are actuated when the impedance differences are 5% of the full scale deflection. This means for the lowest range a concentration difference of 0.005%; by using different ranges and different gains any impedance difference between 0.003% and 1% can be used as actuation limit.

Special difficulties are caused by the fact that we want to use two comparators for measuring the resistance of two conductivity cells which are electrically connected via the solutions and the membrane. First, the input circuits of the comparators are grounded, which will cause a direct current leak via conductivity cell 1 - ground - conductivity cell 2 when there is a potential difference between the two cell compartments (e.g. in an electroosmosis experiment). To prevent this, the comparator input is connected to ground via large blocking capacitors (C_1, C_2 in Figure 3, 20 mF ± 5%, polystyrene) which will not influence the resistance measurement but effectively block any d.c. leaks. Second, the oscillators of the two comparators generally being out of phase, an alternating loop current would pass through the bridges via the conductivity cells, the membrane cell solutions and the membrane. This was avoided by internally disconnecting the oscillator of one comparator and using the oscillator of the other for driving both.

III-3. Electromechanical Parts

A polarized relay has to be used for actuation by the amplifier output, so that the solenoid valves or buret motor will be switched on only when the concentration exceeds or respectively falls below a presettable region around the reference concentration. A polarized relay (MDP1007, Potter and Brumfield Division, American Machine and Foundry Co., Princeton, Ind.) is used. These d.c. relays have a coil resistance of 480 ohm and need a pull-in current of 0.28 ma. The output power is too small to actuate the valves, pump, and motor directly; therefore, a second relay (KAP11AG, Potter and Brumfield) working on 115 V a.c. is used in series with the first one.

It was found that the sparks between the contact points of the relays at the moment of switching influenced the reading of the comparators, causing an oscillation of the whole system. This was completely suppressed by connecting 0.1 μF capacitors parallel to the output contacts of each relay. The diagram for the constructed relay box, which can handle the two signals, is shown in Figure 4. The solenoid valves used are a 51P19N14-8 two-way valve and a 54C18D3B three-way directional flow valve (Valcon Engineering Corp., Kenilworth, N. J. 07081). Both have "Nylon"

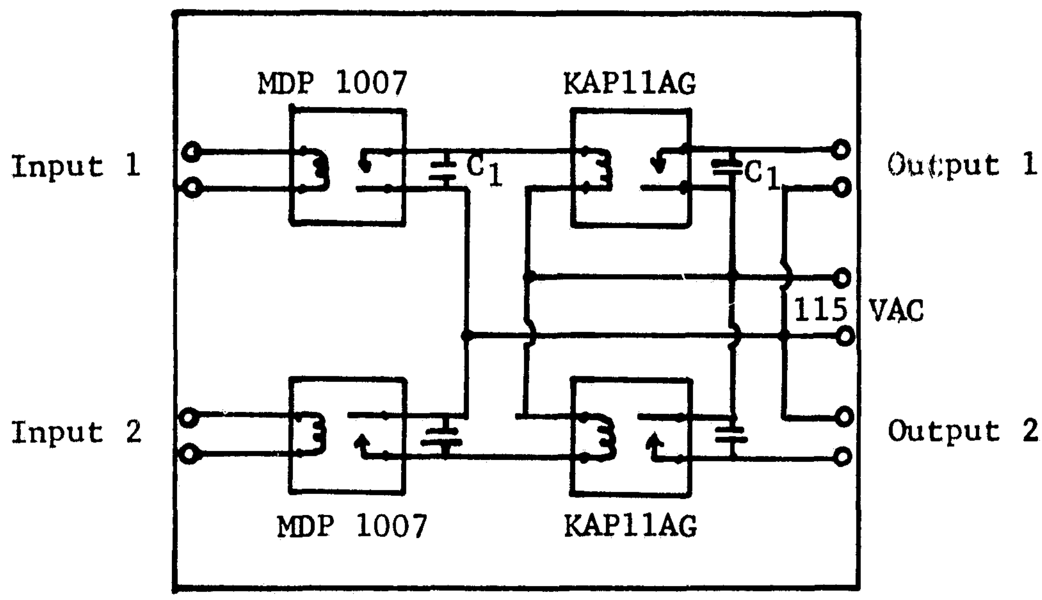

FIGURE 4

RELAY BOX FOR TWO FEEDBACK SYSTEMS

C_1 = 0.1 μF   Relays: Potter and Brumfield bodies and neoprene diaphragms. They can stand line pressures up to 100 psi.

IV. CONCLUSION

The main developments during the period covered by this report were the construction of the membrane transport cell and of the concentration feedback mechanism. The design of the cell makes it suitable for many different experiments. Emphasis has been on constructing a cell in which an accurate and consistent set of experiments can be performed. In particular, the concentration feedback system might prove essential for obtaining accurate and comparable transport parameters. Problems with alternating and direct current leaks via the conductivity cells and the comparators have been solved. The electrical part of the system has been tested with resistors simulating the cell resistances and performed very satisfactorily. Although in principle it should be able to keep the concentrations in the cell compartments constant within 0.01%, other factors, especially the temperature, will probably reduce the constancy to 0.02 - 0.03 percent, which is better than normal chemical analysis.

V. FUTURE WORK

In the coming period the transport cell is to be tested with and without pressure for leaks and pressure expansion. The first transport experiments are planned, to check the performance of the feedback system and to obtain at least approximate values of the various transport parameters. The temperature regulation and measurement system is now under construction and will be described in the next report. The temperature constancy and especially the measuring accuracy are very important for the performance of the feedback mechanism and for the measurement of the volume transported by osmosis or electroosmosis. Equilibrium properties of the membranes to be used will be checked.