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ELECTROMOTIVE FORCE OF TRANSFER SYSTEMS CONTAINING MEMBRANES*

Leslie F. Nims and Jean Kuo

**Biology Department, Brookhaven National Laboratory,
Upton, Long Island, New York**

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**Send proofs to: Leslie F. Nims
Biology Department
Brookhaven National Laboratory
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ABSTRACT

LESLIE F. NIMS AND JEAN KUO. Electromotive force of transfer systems containing membranes. Am. J. Physiol.

If a chemocouple is defined as an isothermal closed circuit, composed of two or more homogeneous ionic aqueous phases separated by two or more barriers of different sets of ionic transport numbers, we find that a spontaneous electric current flows in the closed circuit. The euf of the simplest chemocouple, containing two aqueous sodium chloride solutions is

$$\mathfrak{F} E_s = (t_{Na^+}^1 - t_{Na^+}^2) \Delta \mu_{ClNa}$$

in which $\mathfrak{F}$ is the Faraday constant, $t_{Na^+}^1$ and $t_{Na^+}^2$ are the transport numbers of the sodium ions in the two membranes, and $\Delta \mu_{ClNa}$ is the chemical potential difference of the ion pair between the two phases. The spontaneous electric current in the chemocouple is due to the circulation of anions and cations around the closed circuit in opposite directions. The energy required to sustain this flow of electric current is derived from some fraction of the free energy of dilution of one phase with the other.

The following report is concerned with a few experiments designed to test the validity of some of the conclusions reached by a general analysis of those systems in which chemical energy can be converted to electric energy (1). In particular, evidence is presented for the appearance of a spontaneous electric current in an isothermal closed circuit, composed of two membranes, which have different sets of ionic transport numbers, interposed between two phases of different ionic compositions.

EXPERIMENTAL DETAILS

The apparatus constructed for a study of ion distribution patterns in the idealized physiological transfer unit, phase α , membrane, phase β , (2) was used in the majority of the present experiments. Electrodes reversible to the chloride ion, formed by the thermal decomposition of a silver oxide paste held in the coils of a platinum spiral, and electrolytically plated with a coherent deposit of silver chloride, Type 2 as described by Harned (3), were inserted in the two homogeneous phases of the distribution apparatus. The electromotive force that appeared between the copper terminals of the chemical source of electric energy so constructed was measured potentiometrically. In studies on closed circuit systems, called for convenience chemocouples, two Ag-AgCl electrodes, which had an asymmetry potential of less than 0.1 mv, before and after an experiment, were placed at selected positions in the external homogeneous phase of the chemocouples (See Fig. 4).

Two sets of experiments were done in the distribution apparatus. In the first set, the emf and the compositions of the phases were determined at arbitrarily selected values of the flow rates of water through the membrane. The membrane was a millipore filter, grade PH, previously described (2), or a cellophane dialyzing membrane, grade 600. A solution 0.5 molar in either NaCl or KCl was placed in the large compartment and varied but more dilute solutions of the same salt were placed in the small compartment of the apparatus. An arbitrary flow of water through the membrane in the direction from the dilute to the concentrated salt solution was established. The stirrers were placed in operation, and after at least thirty minutes to allow the electrodes to come to equilibrium and the phases to become homogeneous, the emf at 30°C. was determined. The positive electrode was always the chloride

electrode in the more dilute solution. As soon as possible thereafter, samples were taken from the two phases in order to determine the concentration differences that corresponded to a given emf reading. Great care had to be taken in collecting the samples, particularly when the millipore filter was used and appreciable pressure differences existed across the membrane, in order to obtain representative samples.

The concentrations of sodium chloride or potassium chloride were determined in the more concentrated solutions, both by evaporation to dryness and by flame spectrophotometry of diluted aliquots. The concentration of the more dilute solutions was determined by flame spectrophotometry alone. From a knowledge of the compositions of the phases, and the activity coefficient data listed by Harned and Owen (4), it was possible to calculate the chemical potential difference of an ion pair between the two phases for each value of the recorded emf. The results obtained are illustrated by Fig. 1, in which the observed emf readings are plotted as a function of the chemical potential difference of an ion pair.

In the second set of experiments, done with the millipore filter alone, the composition of the two phases was initially identical. The flow rates of water through the cellophane membrane at the pressure gradients feasible with the apparatus were so small that they could not be measured with any degree of precision. A selected flow rate of water through the filter was established and was kept constant thereafter. The emf in the system was determined from time to time. Fig. 2 contains the observed results in which the flow rate of water was 0.66 cc per minute, and the system contained KCl solutions. The emf at 30°C. is plotted as a function of the time. Note that as the system approaches a stationary state, the emf approaches a constant

magnitude. From the results of several such experiments, the stationary state emf of the system, designed as E[∞] can be obtained as a function of the flow rate of water through the membrane. Such results so obtained are plotted in Fig. 3.

In the third set of experiments, a chemocouple was constructed with the dimensions given in Fig. 4. At the start of an experiment the internal phase was a concentrated solution, near saturation, of a particular salt; the external phase was a dilute solution of the same salt. A matched pair of Ag-AgCl electrodes was placed in the external phase. Rapid stirring at a rate as constant as possible insured the homogeneity of the two phases. The internal phase had a volume of 55 cc, and the external phase had a volume of 1500 cc. After an interval of an hour or so, to ensure equilibration of the electrodes with the external phase and the stabilization of the diffusion processes at the two membranes, the electrodes were connected to a potentiometer or to a sensitive galvanometer. These experiments were done at room temperature, $25^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$

The electrochemical field in the external solution was then explored. The current paths and orthogonal electrochemical potential surfaces were found to be complex geometrically. The emf appearing at the copper terminals of the electrodes depended upon the position of the electrodes with respect to each other and with respect to the two membranes. The electrode nearest the cellophane filter was always positive and the emf's obtainable ranged from fractions of a millivolt up to one millivolt or so.

In Fig. 5 are plotted the galvanometer deflections as a function of time, obtained in a typical experiment in which NaCl solutions of different concentrations made up the external and internal phases. The galvanometer had

a sensitivity of 0.0012 microamps per division, a resistance of 688 ohms, and a period of 3.7 sec. This experiment was done with the electrodes in a fixed geometrical position, and with the stirring rate held as constant as possible. Note that the current through the galvanometer declined with time, and approached zero asymptotically as the diffusion process at the two membranes brought about the equalization of the concentration of the salt throughout the system.

DISCUSSION

If two identical electrodes, reversible to the chloride ion, are placed in the two phases of the idealized physiological transfer unit, phase α , membrane, phase β , and if the phases α and β contain solutions of NaCl at different concentrations, the emf of the system

Cu, Pt, Ag-AgCl, NaCl sol. 1, membrane, NaCl sol. 2, Ag-AgCl', Pt', Cu' so formed should be given by the expression

$$3E_{Cu} = t_{Na^+} \Delta \mu_{ClNa} \quad (1)$$

in which t_{Na^+} is the transport number of the sodium ion in the membrane, 3 is the Faraday constant, and $\Delta \mu_{ClNa}$ is the chemical potential difference of the ion pair, chloride and sodium, between the two phases. As the results depicted in Fig. 1 indicate, the emf of the system is almost linearly proportional to $\Delta \mu_{ij}$. This means that t_{Na^+} is practically constant over the range of concentrations present in the membrane in these experiments. Furthermore, it was found that the emf was independent of the flow rates of water and salt through the membrane, that is, the "purely chemical" processes (5) accomplishing transfer.

The slopes of the solid lines in Fig. 1 are equal to the transport numbers of the sodium or potassium ion through the membranes concerned, since

only one salt at a time is present in the system. Table 1 lists the values of the transport numbers of sodium and potassium ions in the two membranes studied, and for comparative purposes, values for water are listed at infinite dilution and a concentration of 0.2 mol. The differences in the transport numbers of the anions in the millipore filter and in water probably result from some density of fixed positive charge which the millipore filter acquires in contact with the salt solutions used. A small degree of fixed charge density alone would not be expected to modify markedly the ratio of the ionic transport numbers. The differences in ratio of the transport numbers in the cellophane membrane from those in water indicate specific interactions of sodium and potassium ions with cellophane.

To further demonstrate that the emf of the system is independent of the actual flows occurring across the membrane in the non-stationary state, experiments of the type illustrated in Fig. 2 were done. From these, it is readily seen that the emf is a function of the period of time a constant flow of water is maintained, and becomes constant only after an infinite time, that is, when the stationary state is reached. If we compare systems in which different stationary states are produced by different rates of flow of water, we see, as Fig. 3 demonstrates, that the emf of the system can then be said to be a function of the flow rate of water.

The demonstration of electric current flow in the chemocouple depends upon the fact that an emf appears between two identical electrodes placed in an ionic homogeneous phase when, and only when, an electric current is circulating through the homogeneous phase. The observed emf's were sufficient to drive a small electric current through a galvanometer connected to the electrode terminals. Theoretically, the E_s of the chemocouple could be

obtained from the measured E and I by the equation

$$E_{Cl^-} = IR_{ei}'' = E_s - IR_{ai}'' \quad (2)$$

If the electric resistances between the equielectrochemical potential surfaces were known. However, due to the geometrical configuration of the present apparatus, the two electric resistances would be exceedingly difficult to calculate or to measure. If the circuit is opened through either phase, and the reversible chloride electrodes are inserted in the terminal phases, the system will have a E_{Cl^-} which is given by

$$3E_{Cl^-} = (t_{Na^+}^I - t_{Na^+}^A) \Delta \mu_{ClNa} \quad (3)$$

The direct measurement of E_{Cl^-} is difficult experimentally, for the spontaneous diffusion processes at the two membranes would make it burdensome to keep phase 1 and 1' identical for any length of time, unless the volumes of all phases were inordinately large, or unless further flow systems were added to the apparatus to keep the compositions of the phases constant in time.

A much simpler procedure is to open the circuit and split the chemocouple into the two idealized physiological transfer units. The two E_{Cl^-} 's for each membrane system can then be determined as was done in the experiments illustrated in Fig. 1. The algebraic sum of these emf's would be the E_{Cl^-} of the system,

Ag-AgCl, sol.1, mem.1, sol.2, mem.2, sol.1', Ag-AgCl'

which is equal to the E_s of the system,

solution 1, membrane 1, solution 2, membrane 2, solution 1'

or the emf in the chemocouple. Thus the dotted line in Fig. 1 represents the E_s of a chemocouple constructed from NaCl solutions, a cellophane^{membrane} and a millipore filter, for various values of the ion pair differences in chemical potential.

The chemocouple, even in its simplest form is more complicated theoretically than the thermocouple. In the thermocouple there are only three flows to consider, the flows of heat at different rates through the two limbs of the thermocouple from the hot to the cold junction, and the flow of electrons around the closed circuit. In the chemocouple, there are six flows to be considered, the countercurrent flows of water and salt at different rates through the two membranes, and the countercurrent flows of the positive and the negative ions around the closed circuit. Opening the circuit in a chemocouple does not abolish the countercurrent flows of water and salt. The free energy dissipation accompanying these flows in an open circuit is equal to the free energy of dilution of the phases with each other. In a closed circuit, some fraction of the free energy of dilution can be recovered and made to do external electric work. The magnitude of this fraction depends upon the geometry of the circuit, the various specific resistances in the circuit, and the sites at which electrodes are inserted in the circuit.

The chemocouple is an excellent model by which to represent the behavior of physiological sources of electric energy. For example, when the axon of a nerve is cut, a chemocouple is produced. The two phases of different ionic compositions are the axioplasm and the exterior phase; the two barriers with different sets of transport numbers are the axon membrane and the liquid junction formed between the axioplasm and exterior phase of the cut end. A living cell already contains two phases, the interior phase and the exterior phase. The membrane may be isotropic around a living cell, in which case there would be no spontaneous electric current produced by the cell in question. If now some portion of the limiting membrane of the cell is altered by any means, ^{to produce} a second barrier with changed transport numbers, a

spontaneous electric current will appear. In fact, the conducted neuronal impulse can be considered as ^{the activity of} a moving chemocouple. Here again we have two phases, the axioplasm and the external phase, and a non-isotropic membrane with a graded set of ionic transport numbers from the excited region to the unexcited region.

CONCLUSIONS

A spontaneous electric current circulates in a chemocouple. In order to have a spontaneous electric current in a chemical system, composed solely of aqueous phases and membranes, the only requirements are that at least two aqueous phases of different ionic compositions be separated by two membranes with different sets of ionic transport numbers and the phases and membranes be arranged to form a closed circuit. Whereas such a two by two system is a chemical source of electric energy, the system contains no electrodes and does not depend upon electrode reactions to furnish the energy for the production of a spontaneous electric current. The source of electric energy is some fraction of the free energy of dilution of one phase with another, and the electric current is the circulation of anions and cations in opposite directions around the closed circuit.

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FOOTNOTE

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Table 1. The transport numbers of sodium and potassium ions in a millipore filter of grade "PH" and a cellophane membrane as determined from emf measurements at 30° C. Listed for comparison are the transport numbers of the anions in aqueous solutions of NaCl and KCl at 0 and 0.2 m concentration at 25° C. (4, p. 699).

	Water 0 m.	Millipore filter	Cellophane membrane	Water 0.2 m.
t_{K^+}	0.491	0.446	0.499	0.489
t_{Na^+}	0.396	0.362	0.418	0.382
t_{K^+}/t_{Na^+}	1.24	1.23	1.19	1.26

Fig. 1. The emf that appears between reversible Ag-AgCl electrodes when they are inserted into the homogeneous aqueous phases of the idealized physiological transfer unit, phase α , membrane, phase β , plotted as a function of the chemical potential difference in the ion pair between the two phases. Note that the emf depends upon which salt and which membrane is present in the transfer unit. The dotted line in this figure represents the difference in emf of two transfer units containing NaCl solutions but having different membranes, and is the E_s of the system.

NaCl sol. 1, membrane 1, NaCl sol. 2, membrane 2, NaCl sol. 1'

in which E_s is given by

$$3E_s = (t_{j+}^1 - t_{j+}^2) \Delta\mu_{ij}$$

Fig. 2. The emf in the system

Ag-AgCl, NaCl sol. 1, millipore filter, NaCl sol. 2, Ag-AgCl' plotted as a function of time when the flow rate of water is maintained constant. Solution 1 and solution 2 had the same compositions at zero time. Note that the emf asymptotically approaches a constant value, E^∞ , as the time increases and the system approaches a stationary state.

Fig. 3. The magnitude of the emf, E_{Cl}^{∞} , of the system Ag-AgCl, salt sol. 1, millipore filter, salt sol. 2, Ag-AgCl' when the system is in a stationary state produced by a constant flow of water through the millipore filter. The emf_A is plotted against the flow rate of water. Note that the emf in the stationary state is a function of the flow rate of water, and depends upon which salt is present in the system.

Fig. 4. A diagram drawn to scale of the chemocouple studied in these experiments. The container was a two liter beaker which held 1200 cc of a dilute salt solution. The internal phase was a nearly saturated solution of the same salt of a volume of 55 cc. The two membranes employed were the millipore filter and the cellophane membrane. The reversible Ag-AgCl electrodes were placed at arbitrary distances apart in the homogeneous external phase, and the electrode nearest the cellophane filter was always positive to the second electrode.

Fig. 5. The electric current obtained when a sensitive galvanometer was connected to the terminals of two reversible chloride electrodes inserted in the external phase of a chemocouple composed of sodium chloride solutions of different concentrations, and two barriers, a millipore filter and a cellophane membrane. The electric current in terms of galvanometer deflections is plotted as a function of the time. Note that the electric current declined as the spontaneous diffusion processes at the two membranes brought about an equalization of the concentrations of salt in the internal and external phases.

END