Physics of Electrical Effects and Energy Conversion on Membranes

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The living cell's electric potential and the electromotive force of a galvanic cell are described here using a nonvolume work thermodynamics and are shown to develop and operate on the same principle, which is that in both external forces perform work at the expense of the system's free energy. The role of the membrane as external-force transmitter could be allowed for only after the momentum conservation principle had been incorporated into the thermostatic description of membrane equilibria and transport. For that it was necessary to introduce an additional term to a species' chemical potential that accounts for its potential interaction with the membrane. Then membrane equilibria, in particular the Nernst equilibrium potential, the Donnan potential, and osmotic pressure, could be properly described. The electric equivalent circuit method supplemented with an electric energy diagram is applied for describing steady-state transport across ion-selective membranes. Then it becomes evident that the system's free energy can be spent on moving across one type of ion when there is free passage for another type of ion. This is due to electric coupling between ionic fluxes accomplished via the resting membrane potential, which is thus to be viewed as an electromotive force, rather than just the electric potential difference.

I. Introduction

The internal energy of a thermodynamic system can change as a result of heat exchanged between the system and its environment and work done by or on the system. Since thermodynamics developed from studies on the heat engine, the system considered was, as a rule, a gas in a cylinder closed by a piston that could move, allowing energy to be exchanged as volume work, whose differential expresses as $p\mathrm{d}V$. If no external forces are present, such work is the only one that a homogeneous system can do, and obviously, it is a far cry from what is happening in nature. Work and energy conversion that occur around us and within us have nothing to do with volume changes, save for the ubiquitous heat engine. In living organisms, the chemical, electrical, and osmotic work is performed. A thermodynamic system can do such types of work at the expense of its free energy only when external forces are present. Such forces are transmitted to the system via the biological membrane, which is a ubiquitous contrivance that surrounds all living cells and cell organelles and has the form of a lipid bilayer with embedded integral and peripheral protein molecules.

It has long been recognized that life processes much depend on the fact that the cell membrane is a highly selective barrier between the cell and its environment. That function is possible due to ion- and nonelectrolyte-specific channels, proteinaceous pores, and carriers present within the membrane. They are there not only to allow passive diffusion of solutes and water but also mainly to enable the cell to accumulate and extrude metabolites. That active role of the cell membrane involves work performed by a thermodynamic system and is the subject of the present report. So the membrane as a force transmitter and energy converter comes to the fore here.

In the first section the simplest possible version of nonvolume work thermodynamics is presented. The simplicity comes from the assumption that only the diffusive type of mass transport is possible within membrane channels of a few nanometers in diameter and that it is an equilibrium thermodynamics of virtual displacement. By combining the Gibbs−Duhem equation with the mechanical equilibrium condition, we get an equation that requires an augmented chemical potential of all the solution components to have the same value throughout the system, i.e., $\nabla\mu_i(x) = 0$, no matter whether a component is membrane permeant or not. This requirement is consistent with a constant Gibbs free energy density throughout the system.

The nonvolume work thermodynamics thus constructed is applied for description of the equilibrium that an electrolyte solution attains at a membrane permeable to cations only. The detailed mechanical equilibrium condition requires the gradient of cation's electrochemical potential be zero, while for description of the anion's equilibrium the augmented electrochemical potential is needed. The electrical effect in the form of the Nernst equilibrium potential and the Donnan potential are then consistently described and their mechanism elucidated. Also the osmotic effect appears quite naturally in the situations considered.

Thermodynamic equilibrium has small relevance to the living cell's electric potential. So we consider the electric effects on the membrane when steady flows of ions across the membrane occur, in the third section of the report. Owing to the ion-specific channels in biological membranes, the ionic fluxes are not coupled to each other directly and thanks to that we can describe the steady-state flow of an electrolyte across such a membrane using a very simple equivalent electric circuit. Chemical potential differences of the ions on the membrane are represented as electromotive forces in the circuit. The electric potential difference at the membrane that arises in such a situation couples the fluxes of positive and negative ions. The nearer to thermodynamic equilibrium is one of the two ions, the more the flux of the other ion is enhanced by the membrane electric

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potential. When ions of one valency are at equilibrium and are moving without friction across membrane channels, the work they do against the electric potential difference, at the expense of the electrolyte's free energy, is totally spent on dissipation (or useful work) by the opposite-valency ions driven through the membrane by the electric force, provided the latter ion's augmented chemical potential difference at the membrane is equal to zero. Aside from the biological membrane, this situation is realized in the electrochemical concentration cell, which is the subject of the last section. Again, due to momentum balance added to the thermodynamic description, the electric coupling and energy conversion in the concentration cell is elucidated and the known expression for the cell's EMF is derived easily.

The mechanism of energy conversion on an ion-selective membrane and in a concentration cell presented here applies to any galvanic cell. While in the concentration cell the free energy of dilution is the source of energy, in a galvanic cell the energy comes from the cell's redox reaction free energy ΔG_r. Even under normal operation conditions the cell's reaction goes on quite near equilibrium if only the electrode surfaces are large enough. Otherwise, the equalities $\Delta G_r = \nu_e FE$ and $E = I(R_{ext} + R_{int})$ could not be satisfied simultaneously.

II. Thermodynamics of Nonvolume Work

The membrane is understood, in this report, as a partition between two electrolyte or nonelectrolyte aqueous solutions. However, it does not separate the solutions completely, allowing exchange of matter and energy between them. For that it has to be porous and selective. The porosity must be such that passage of solvent but not that of solute is allowed. The membrane may have ion selective channels that pass water and particular ions, e.g. cations but not anions or vice versa. Such a membrane allows a solute to diffuse through without leaving its water environment, being, however, in very close contact with the membrane also. So that solute−membrane interaction is present in the form of friction and/or potential interaction. At thermodynamic equilibrium only the latter interaction remains and the solute perceives the membrane as an energy barrier. Thus, from the physical point of view, the membrane constitutes a thin region (of thickness much smaller than the area of its contact with the solution) where external forces can be transmitted to the solution, both frictional and/or potential. On the other hand, the membrane pores must be continuous and thermodynamically viable volumes of solution.

In the above-described membrane−solution system may occur mechanical and electrical phenomena in the form of osmotic pressure and/or flow and membrane electric potential, with possible energy conversion. Since they occur in an aqueous solution where compression or expansion cannot take place, the volume work thermodynamics commonly found in the textbooks cannot be a sufficient tool here.

A need, therefore, arises for a nonvolume work thermodynamics, which we construct here following the scheme of irreversible thermodynamics, i.e., the basic Gibbs equation plus balance equations of energy, momentum, and entropy. Thus, the first law is employed to construct the so-called basic Gibbs equation:

$$dU = TdS - pdV + \Sigma\mu_i dn_i \qquad (1)$$

Since the state function $U(S,V,n_i)$ is a homogeneous function of the first order, the Euler theorem allows us to write

$$U = TS - pV + \Sigma\mu_i n_i \qquad (2)$$

Comparing the differential of this equation with that given by eq 1, we get

$$SdT - Vdp + \Sigma n_i d\mu_i = 0 \qquad (3)$$

For isothermal conditions, and upon division by V and dx, this equation results in

$$\nabla p = \Sigma c_i \nabla\mu_i \qquad (4)$$

which is known as the Gibbs−Duhem equation. At thermodynamic equilibrium, chemical potential gradients, $\nabla\mu_i$, of all components must be equal to zero and we would get an isobaric system, with the same pressure throughout, and no mechanical effect on the membrane. Besides, since $\mu_i = \mu_i^o + V_i p + \mu_i^c$, eq 4 also gives $\Sigma c_i \nabla\mu_i^c = 0$; meaning that internal forces sum up to zero, and thus volume work thermodynamics is unable to describe systems with pressure gradients present. And this could be expected, because such thermodynamics contains only the energy conservation principle for homogeneous systems. It needs to be supplemented with the momentum conservation principle, which for systems with no viscous flow possible assumes the simple form of the mechanical equilibrium equation:

$$\nabla p = \Sigma c_i f_i^{ext.p} \qquad (5)$$

where $f_i^{ext.p} \equiv -\nabla\mu_i^E$ is an external force of potential character on 1 mol of the ith component, which is by definition equal to the negative gradient of an excess part of chemical potential of the component. Combining eqs 4 and 5, we get

$$\Sigma c_i \nabla\mu_i(x) = 0 \qquad (6)$$

where $\mu_i(x) = \mu_i + \mu_i^E$ is an augmented chemical potential, called also mechanochemical potential.[1]

Now a thermodynamic definition of the augmented chemical potential can be given. For that we divide eq 2 by volume V, getting

$$u = Ts - p + \Sigma\mu_i c_i \qquad (7)$$

where u, s, and c_i are volume densities of internal energy, entropy, and number of moles, respectively. With the new potential $\mu_i(x)$

$$u = Ts - p + \Sigma\mu_i(x)c_i + const \qquad (8)$$

Hence

$$u + p - Ts \equiv g = \Sigma\mu_i(x)c_i + const \qquad (9)$$

while from eq 7 $g = \Sigma\mu_i c_i$. Comparing the two expressions for g, we obtain $\Sigma\mu_i^E c_i + const = 0$ and hence $d\Sigma\mu^E c_i = 0$.
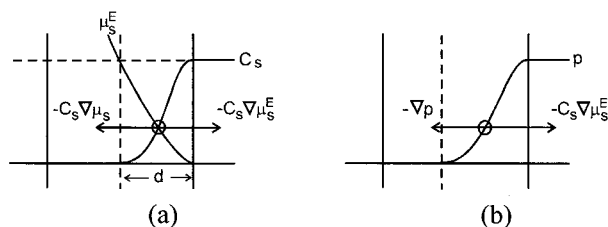
Using eq 9, we get $dg = d\Sigma\mu_i(x)c_i = \Sigma\mu_i(x)\,dc_i + \Sigma c_i d\mu_i(x) = \Sigma\mu_i(x)dc_i$, because at equilibrium $d\mu_i(x) = 0$; i.e., gradients of all the potentials must vanish.

From the obtained expression for dg it follows that

$$\mu_i(x) = \left(\frac{\partial g}{\partial c_i}\right)_T = \left(\frac{\partial G}{\partial n_i}\right)_T \qquad (10)$$

Thus, the augmented potential is defined like the normal potential save for the absence of the $p = const$ condition.

Now, since $dg = -sdT + dp + \Sigma\mu_i dc_i$, we obtain $(dg/dc_i)_T = (dp/dc_i)_T + \mu_i$, and hence, $\mu_i^E = (dp/dc_i)_T = (de_{mech}/dc_i)_T$, as $\mu_i(x) = \mu_i + \mu_i^E$. Thus, the excess of the chemical potential is

Electrical Effects and Energy Conversion on Membranes

J. Phys. Chem. B, Vol. 104, No. 7, 2000 **1619**

Figure 1. (a) Profiles of concentration and chemical potential excess due to potential interaction of a solution component with the membrane and force on the component, in a membrane−water physical interphase of thickness d. (b) Pressure profile in a membrane−water physical interphase and its gradient balanced by solute−membrane interaction.

Figure 2. Balance of forces on an electrolyte in a membrane impermeable to the anion. The forces are explained in the text.

$c_+ z_+ F(-\nabla\psi) - c_+ \nabla\mu_+ = 0$. This equation implies that $\nabla(\mu_+ + z_+ F\psi) = \nabla\tilde{\mu}_+ = 0$, where $\tilde{\mu}_+ = \mu_+ + z_+ F\psi$ is the electrochemical potential of the ion. Equation $\nabla\tilde{\mu}_+ = 0$ corresponds to the equation $\nabla\mu_s(x) = 0$ for nonelectrolyte solution. Hence also $z_+ F\psi = \mu_+^E$ corresponds to μ_s^E and represents the excess potential from the ion−membrane interaction.

As seen in Figure 2, equilibrium of the negative ion implies the existence of a direct, nonelectrostatic membrane-anion force that keeps the electrolyte from moving and contributes an excess potential $\mu_-^E(m)$ to the anion's electrochemical potential, so that for the anion $\mu_-(x) = \mu_- + z_- F\psi + \mu_-^E(m)$. The equilibrium of forces on the anion yields the equation: $\bar{F}_-^{el} + \bar{F}_-^{chem} + \bar{F}_m = 0$, where F_m is the force that keeps the electrolyte from moving across the membrane, i.e., $\bar{F}_m = c_e\Delta\mu_e$, with c_e being electrolyte concentration and μ_e its chemical potential. From this force balance since $\bar{F}_-^{el} = -\bar{F}_+^{el} = \bar{F}_+^{chem} = -c_+\nabla\mu_+$, we get

$$-c_+\nabla\mu_+ - c_-\nabla\mu_- - c_-\nabla\mu_-^E(m) = 0 \qquad (11)$$

Hence, $\nu_+\nabla\mu_+ + \nu_-\nabla\mu_- \equiv \nabla\mu_e = -\nu_-\nabla\mu_-^E(m)$, where the chemical potential of an electrolyte has the usual definition: $\mu_e = \nu_+\nabla\mu_+ + \nu_-\nabla\mu_-$. From before-the-last equality we gather that the electrolyte is kept fixed on the membrane by the excess of the anion's chemical potential $\mu_-^E(m)$. Alternatively, eq 11 can be obtained by applying our basic eq 6 and the local electroneutrality $c_+ z_+ + c_- z_- = 0$.

Now, using the equations $d\Sigma\mu_i^E c_i = 0$, $\nabla\mu_i^E = -f_i^{ext}$, and eq 5, we obtain $dp = \Sigma\mu_i^E dc_i$. With this $dp = (z_+ F\psi)dc_+ + (z_- F\psi + \mu_-^E(m))dc_-$. Hence follows the thermodynamic definition of the excess part of the chemical potential of ions:

$$\left(\frac{dp}{dc_+}\right)_{c_-} = z_+ F\psi \qquad \left(\frac{dp}{dc_-}\right)_{c_+} = z_- F\psi + \mu_-^E(m) \qquad (12)$$

From the above definitions it follows that the electric part of the electrochemical potential of an ion represents the mechanical energy contribution on addition of 1 mol of the ion to a given place in a solution due to electric interaction, and not an electric energy contribution as the expression $zF\psi$ suggests.

Thus, the mechano-chemical potentials of the components of the system we describe have to be expressed as follows: $\mu_+(x) = \mu_+^o + V_+ p + \mu_+^c + z_+ F\psi$, $\mu_-(x) = \mu_-^o + V_- p + \mu_-^c + z_- F\psi + \mu_-^E(m)$, and $\mu_w(x) = \mu_w^o + V_w p + \mu_w^c$ (no μ_w^E here because there is no membrane energy barrier for water, or if there is, it is symmetrical[2]). Using these expressions in eq 6, as well as $\Sigma c_i\nabla\mu_i^c = 0$ and $c_+V_+ + c_-V_- + c_wV_w = 1$ and the electroneutrality condition $c_+ z_+ + c_- z_- = 0$, we obtain $\nabla p + c_-\nabla\mu_-^E(m) = 0$—an equation that describes the osmotic effect of the electrolyte. With eq 11, this can be cast into the more transparent form $\nabla p = c_e\nabla\mu_e$.

Thus, also when an electrolyte is stopped by a membrane an osmotic pressure arises of magnitude determined by the electrolyte concentration difference on the membrane.

Besides that, an electric effect takes place in the form of an electric potential difference on the membrane. Its magnitude can be found from the detailed equilibrium condition $\nabla\tilde{\mu}_+ = 0$, which after integration yields $\Delta\psi = (V_+/z_+ F)\Delta p + (RT/z_+ F)$

equal to the derivative of mechanical energy with respect to concentration.

So far we have not yet used the energy conservation principle for our nonisobaric system. The first law of thermodynamics was employed at the beginning only to construct the basic Gibbs equation and thus the state functions for homogeneous systems. For the nonisobaric, nonhomogeneous system we describe the energy balance equation states that $du = Tds - dw$. The work differential has a minus sign because work is done by the system. Substituting this equation and $dp = fdx = dw$ into the expression $dg = du + dp - Tds$, we get $dg = 0$ for thermodynamic equilibrium or $dg \leq 0$ after employing also the second law. This result tells us that the free energy density is the same throughout the system at thermodynamic equilibrium and that dissipation is covered by a free energy decrease if a spontaneous process occurs.

From $g = \Sigma c_i\mu_i$ we have $\Sigma c_i d\mu_i = -\Sigma\mu_i dc_i$, which on substitution into $dp = \Sigma c_i d\mu_i$ gives $dp = -\Sigma\mu_i dc_i = dw$, or $dw \leq -\Sigma\mu_i dc_i$, with first and second laws employed. And, indeed, the term $\Sigma\mu_i dn_i$ in eq 1 is meant to represent nonvolume work.

Summing up the energy considerations, we can say that the nonvolume work done on virtual, infinitesimal displacement by an osmotic system is due to concentration changes on the displacement.

III. Thermodynamic Equilibria of Solutions on Membranes

Thermodynamic equilibrium of a solution within a membrane implies equilibria of all the components of the solution. Thus, in case the membrane is permeable to solvent and not to solute, the latter will experience forces within the membrane as shown in Figure 1a,b.

At the membrane−solution interface of thickness d the force originating from chemical potential gradient of the solute $(-c_s\nabla\mu_s)$ is balanced by the membrane energy barrier force $(-c_s\nabla\mu_s^E)$. Since the latter force is external and the solute is in close contact with the solvent, that force is transmitted to the solvent and a pressure gradient arises of magnitude $\nabla p = -c_s\nabla\mu_s^E$ (Figure 1b). The pressure thus arising is the osmotic pressure. If there are many impermeant solutes in a solution, for each one the equation must hold: $\nabla\mu_s + \nabla\mu_s^E = \nabla\mu_s(x) = 0$. Hence, also $\Sigma c_i\nabla\mu_i(x) = 0$, as stated by eq 6. This inference cannot be drawn from eq 6 alone because c_i are not independent.

In the case of an electrolyte solution and a membrane impermeable to the anion the electrolyte will not flow across, because the passage of the cation will also be stopped by the arising electric potential difference on the membrane, as shown in Figure 2. The electric force that keeps the cations from moving $F_+^{el} = qE = c_+ z_+ F(-\nabla\psi)$. This force is balanced by the one coming from the chemical potential gradient of the cation: $F_+^{chem} = -c_+\nabla\mu_+$, according to the equation

$\ln(a_+'/a_+'')$. With the pressure-dependent term neglected, this formula is known in the biophysical literature as the Nernst equilibrium potential of an ion on a membrane, where a_+ stands for the activity of the ion. A biological situation may involve not one but many different ions staying in thermodynamic equilibrium on a cell membrane. Then for each ion one can write the equation $\nabla\tilde{\mu}_i = 0$, and obtain $\Delta\psi$ expressed by the activity ratio of the ion on both sides of the membrane. Such a description leaves open the question about the mechanism of electric potential generation; whether a particular ion generates the potential or just distributes according to the potential.

The answer to such a question can be obtained only when we take into account not only the energetic equation $\nabla\tilde{\mu}_i = 0$ but also the momentum balance equation $\nabla p = \Sigma c_i f_i^{\text{ext,p}}$, i.e., eq 6. Then the negative charge in Figure 2 represents not one ion's volume density of charge but the volume density of all negative charges that cannot flow, either those for which the membrane is impermeable or which are fixed within the membrane or both. The positive charge in the figure then represents the net charge of all ions that are free to move across the membrane, and these ions taken together now constitute the electrolyte whose equilibrium we want to describe. Since the negative charges are fixed within the membrane, the force F_-^{chem} does not exist here and Figure 2 then represents the momentum balance of the so-called Donnan equilibrium.

We may now apply eq 6 to the mobile electrolyte within the membrane. The summation may not include water as we are not interested in the possible pressure effect. The permeant electrolyte constitutes the thermodynamic system we describe, which may thus be viewed as a gas of ions, so that $\tilde{\mu}_i = \mu_i^o + \mu_i^c + z_iF\psi$. The electroneutrality condition has the form $\Sigma c_iz_i = -c_nz_n = (R^-)$, putting $z_n = -1$ for the fixed charge of concentration (R^-). On the other hand, the sum $\Sigma c_iz_i = k\Sigma c_i = (R^-)$, and hence $\Sigma c_i = (R^-)/k$, where k is a constant determined by the valences of the mobile ions. We also assuming that activity coefficients of all the ions are equal, i.e., $\gamma_i = \gamma$. Under the above conditions eq 6 yields

$$\Delta\psi = -\frac{RT}{kF}\left[\ln\frac{(R^-)_o}{(R^-)_i} + \ln\frac{\gamma_o}{\gamma_i}\right] \tag{13}$$

This result says that the Donnan potential is determined by the fixed charge distribution, depending also on activity coefficient ratio of the mobile ions and on the electrolyte net charge coefficient k within the membrane.

When there is one permeant ion, say potassium, then $(R^-) = K^+$ and from eq 13 we get $\Delta\psi = RT/F \ln(a_K^i/a_K^o)$, i.e., the Nernst equilibrium equation for the potassium ion.

IV. Steady-State Electric Effects on Membranes

The living cell much depends on the ability of its plasma membrane to control the passage of ions across it. The membrane is highly selective toward the respective ions, allowing easy passage for some ions via ion-specific channels, transporting ions via specialized pores with the use of coupling between ionic fluxes or pumping some ions up their electrochemical potentials using membrane-incorporated enzymes and energy from hydrolysis of ATP. The steady state that the living cell maintains involves the existence of a resting membrane electric potential difference across the plasma membrane.

So the simplest biologically relevant situation is a membrane with separate channels for cations and anions between two solutions of different concentrations. An electrical representation of this situation is a circuit shown in Figure 3, where $I_1 = z_1FJ_1$
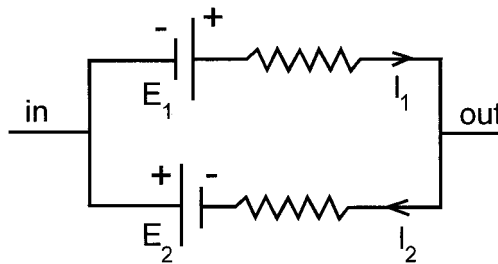

Figure 3. Equivalent electric circuit for an electrolyte diffusing through a membrane with separate channels for the cation and anion.
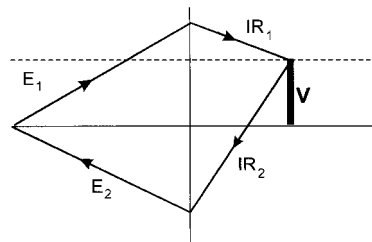

Figure 4. Electric energy diagram for the circuit of Figure 3.

is the current carried by cations and $I_2 = |z_2|FJ_2$ that by anions. Since the diffusing electrolyte carries no electric current, we have $I_1 = I_2 = I$.

The circuit of Figure 3 has to be both topologically and energetically equivalent to our physical situation. The energetic equivalence can be established by using the dissipation function of irreversible thermodynamics, i.e., $\sigma T = \bar{X}_1\bar{J}_1 + \bar{X}_2\bar{J}_2 \geq 0$, where $\bar{X}_i = -\nabla\tilde{\mu}_i$. Since the two fluxes are positive and downhill the respective electrochemical potentials, both terms in the dissipation function are positive and equal to the work dissipated in each of the resistors:
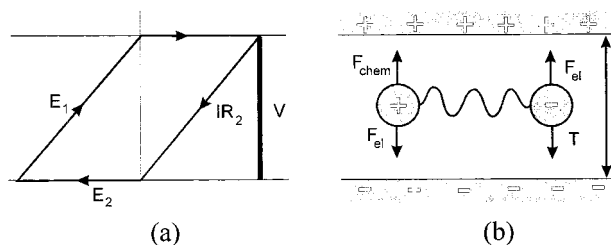
$$-\nabla\tilde{\mu}_iJ_1 = I_1(E_1 - V) > 0 \tag{14}$$

$$-\nabla\tilde{\mu}_iJ_2 = I_2(E_2 + V) > 0 \tag{15}$$

Now, using the expression $\tilde{\mu}_i = \mu_i^o + \mu_i^c + z_iF\psi$ and taking into account that $I_1 = z_1FJ_1 > 0$ and $I_1 = |z_2|FJ_2 > 0$ and $\Delta\tilde{\mu}_i = \tilde{\mu}_i^{\text{out}} - \tilde{\mu}_i^{\text{in}} < 0$, we can solve the above equations for E_1 and E_2, obtaining $E_1 = |\Delta\mu_1^c|/z_1F$ and $E_2 = |\Delta\mu_2^c/z_2F|$. Thus, the EMFs in the equivalent circuit are expressed by chemical potential differences of the respective ions.

Though the two ions of an electrolyte diffusing through a membrane move along separate channels and thus do not interact by way of friction, they are, however, electrically coupled. That coupling is conspicuously revealed by the energy diagram of Figure 4. The common factor for the fluxes of the two ions is the potential V. Thus, the coupling can be expressed by the equation that obviously follows from the diagram: $E_1 - IR_1 = V = IR_2 - E_2$. Hence $E_1 = IR_1 + V = IR_1 + IR_2 - E_2 = IR_w + IR_z$, where $R_w = R_1$ and $IR_z = IR_2 - E_2 = V$; i.e., the resistance cations encounter within the membrane can be regarded as internal resistance and the voltage drop on the membrane due to anion flow equal to V can be regarded as the voltage drop on an external resistance.

The resulting textbook formula $E_1 = I(R_w + R_z)$ clearly shows that the diagram of Figure 1 represents the operation of an electrochemical cell. Not only is the driving force $E_1 = \Delta\mu_1/F$ (assuming $z_1 = |z_2| = 1$ and $\Delta\mu_1 > 0$, for simplicity of notation) seen to be performing work on the passage of cations across the membrane, but also the flow of anions is going on partly at the expense of E_1. This electric coupling is at a maximum when $V = E_1$ and $E_2 = 0$. Then the electric energy diagram assumes

Electrical Effects and Energy Conversion on Membranes

J. Phys. Chem. B, Vol. 104, No. 7, 2000 **1621**

Figure 5. (a) Electric energy diagram for cations moving uphill the electric potential V and doing work on transport of anions toward higher potential. (b) Visualization of the electric coupling between cations and anions within membrane of thickness Δx. The forces are explained in the text.
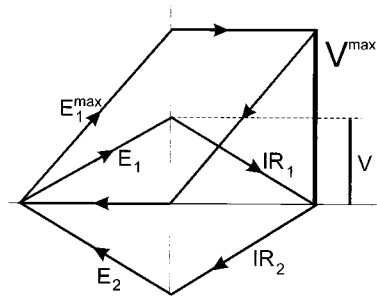
Figure 6. Electric energy diagram explaining why the EMF of the enhanced transport on membrane and that of the concentration cell is equal to the electrolyte chemical potential difference over Faraday constant F. Explanation in the text.

the form shown in Figure 5a, which is identical with what one would draw for the operation of a genuine electrochemical cell. Now the work done by the electromotive force E_1 is totally spent on dissipation by the anions when they move across the membrane driven by the electric force up the electric potential. This is the principle of galvanic cell operation, with E_1 representing electric potential elevation effected by the cell redox reaction at the electrode−solution interface of both electrodes and IR_2 the potential drop on external resistance effected by the flowing electrons. The principle is visualized in Figure 5b, where the force $F_{chem} = E_1/\Delta x = \Delta\mu_e/F\Delta x$ pushes cations up the electric potential V. That force is transmitted via an electric field to the anion, moving it across the membrane against the opposite force of friction T.

A necessary condition for the situation depicted in Figure 5 is frictionless movement of cations across the membrane. This is possible when membrane channels are open for cations and they remain at thermodynamic equilibrium, because only then is the balance $F_{chem} = F_{el}$ possible.

Another necessary condition is zero driving force on the anions originating from the chemical potential difference of the electrolyte. This can be realized when the membrane exerts a nonelectrical potential force on the anions, described by an excess part $\mu_2^E(m)$ of its chemical potential so that $E_2 = \Delta\mu_2/F = (\Delta\mu_2^c + \Delta\mu_2^E(m))/F = 0$.

When the chemical potential difference of one of the ions is made equal to zero, the chemical potential difference of the other ion becomes equal to the chemical potential difference of the electrolyte. This can be easily substantiated and understood by considering the energy diagram shown in Figure 6 as follows:

Taking an electrolyte with equal chemical potential differences of the two ions, $E_1° = E_2°$, and equal mobilities inside the membrane, $R_1 = R_2$, we obviously get a zero diffusion potential. Now, making the passage of the anion more and that of the cation less difficult, we get positive diffusion potentials
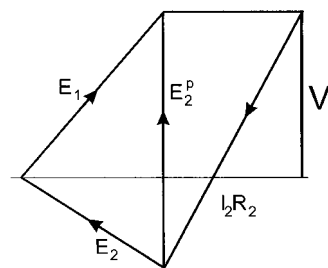
Figure 7. Electric energy diagram for the operation of the Na,K-ATPase of a living cell, with potassium ions kept at thermodynamic equilibrium by sodium pump EMF $= E_2^p$.

of magnitude $V' < V$, with V being the Nernst equilibrium potential of the cation, i.e., $V = E_1°$, obtainable when $R_1 = 0$. The dissipation that then obtains, IR_2', is covered jointly by E_1' and E_2'. But now we can exclude the anion from doing work on dissipation by switching on a membrane−solute, potential interaction force represented by the excess part of the solute's chemical potential. Thus, we may have $\Delta\mu_2 = \Delta\mu_2^c + \Delta\mu_2^E(m) = 0$, meaning that $E_2 = \Delta\mu_2/F = 0$. However, the electrolyte chemical potential difference on the membrane must remain unchanged, i.e., $E_1' + E_2' = \Delta\mu_e/F = E_1^{max} + 0 = E_1^{max}$, this resulting in membrane potential of magnitude $2V$ and $E_1^{max} = 2\Delta\mu_1/F$, as confirmed by the diagram of Figure 6.

The membrane potential obtained in such a way is not just membrane potential but an electromotive force, as it performs work on moving the anions against the force of friction, i.e., on their dissipation, at the expense of chemical potential difference of the electrolyte. And this is exactly what happens in an electrochemical concentration cell.

Such electric potential generation is also employed by the living cell to create the cell resting potential and regulate the movement of ions across its membrane. For its steady operation the cell has to maintain a constant concentration of its principal ions, and this is done by ionic pumps that are known to operate within a biological membrane. Sodium−potassium ATPaze is the best known pump, which is an enzyme that drives potassium ions in and sodium ions out of a cell at the expense of ATP hydrolysis. The electric equivalent circuit that makes allowance for such a pump is obtained when we install two additional electromotive forces into it, one for potassium and one for sodium.[3] When the sodium pump EMF $= E_2^p$ is large enough, i.e., $E_2^p = E_1 + E_2$, and the potassium channels are open, an equilibrium for potassium can be established, i.e., $V = -E_K = (RT/F) \ln\{(K^+)_i/(K^+)_o\}$, whose very existence depends, however, on continued operation of the sodium pump, as seen in the energy diagram of Figure 7. Assuming adequate flexibility of the sodium pump, we can predict that the cell potential will respond to potassium concentration in the medium as a potassium electrode. And, in fact, such a behavior is observed.[4] The cell hyperpolarizes with decreasing potassium concentration following a slope of 55 mV/decade, but to a certain limit where the so-called switch-off occurs, when the strain on the sodium pump is too great to sustain. Thus, though the cell potential can be calculated from the potassium ion equilibrium distribution, it is, in fact, maintained by sodium pump operation and should be treated as an EMF of an electrochemical cell.[3]

V. Concentration Cell with Transference

An electrochemical concentration cell, as shown in Figure 8, consists of two beakers filled with, e.g., $AgNO_3$ solution with immersed silver electrodes that can be connected with a wire, and a salt bridge containing NH_4NO_3 that connects the solutions.
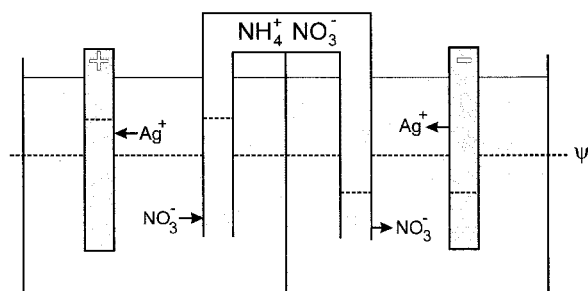
Figure 8. Electrochemical concentration cell operation, with electric potential profile and ion movement indicated.
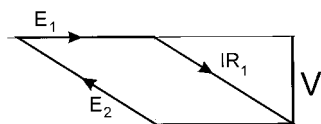
Figure 9. Electric energy diagram for the concentration cell of Figure 8.

Assuming that the electrolyte concentration is higher in the left beaker, the electric situation obtained is shown in Figure 9. The bridge functions as membrane channel open for the NO_3^- ion. That allows the ion to diffuse down its chemical potential gradient as long as it can be neutralized electrically by Ag^+ ions leaving the right electrode and entering the left one. But soon the potentials developing on the electrodes put a stop to that process and a thermodynamic equilibrium is reached (provided NH_4^+ ions have zero mobility), meaning that $2\Delta\mu_-/F = \Delta\mu_e/F = E_2 = V$; i.e., the electrolyte chemical potential difference is balanced by the potential V that arises between the two electrodes. The electric potentials at the ends of the bridge are equal to the respective potentials on the electrodes, as shown in Figure 8. This is necessary because Ag^+ ions must remain at equilibrium with both the electrodes and the salt bridge. Otherwise they would move from an electrode to the bridge or in reverse, allowing electric current to flow across the bridge. That is, however, impossible as long as the electrodes are not connected with a wire. When the connection is made with a wire whose resistance is much greater than that encountered by NO_3^- ions along the bridge ($R_2 \ll R_1$), the anions move from the left to the right beaker doing work against the electric potential V and that work is expended on dissipation by electrons moving from the right to left electrode along the connecting wire. The condition ($R_2 \ll R_1$) ensures that the anions remain practically at thermodynamic equilibrium and do electric work at the expense of the electrolyte free energy without dissipating it themselves.

The principle of operation of the concentration cell can thus be summerized by the energy diagram of Figure 9, which results from the one shown in Figure 5a when $E_1 = 0$ and $E_2 = V$.

The condition $E_1 = 0$, corresponding to the previous $E_2 = (\Delta\mu_2^c + \Delta\mu_2^E(m)) = 0$, means that the chemical potential difference of Ag^+ is balanced by the two electric potential jumps at the solution−electrode interfaces.

However, in practice, the electromotive force of the cell just discussed is not equal to $E_2 = \Delta\mu_e/F = RT/F \ln(a'/a'')_e$, because of the nonzero mobility of the NH_4^+ ions in the salt bridge. These cations will diffuse down the electric potential created by NO_3^- ions, enabling the latter to diffuse also. Thus, a flow of the electrolyte develops in the bridge and forces of friction T_- and T_+ have to be allowed for in the balance of forces on the ions in the bridge, as shown in Figure 10.

Because of the presence of the forces of friction, the electric field E in the bridge must be smaller than the equilibrium value
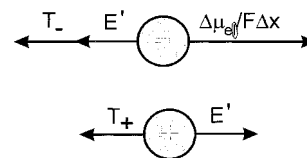
Figure 10. Force balance for ions within the salt bridge of a concentration cell. The forces are explained in the text.

$E = \Delta\mu_e/F\Delta x$. The two force balances of Figure 10 plus the zero current condition for diffusion of the electrolyte, $j_+ + j_- = 0$, are the three equations that can be used for calculating the potential difference $V' = \Delta x E'$.

Thus, $j_+ = u_+ z_+ n_+ e E' = u_+ ecA E'$, where u_+ is the mobility, z_+ is the valency, n_+ is the number of ions in unit volume, e is the electronic charge, and c is the electrolyte molar concentration, and A is Avogadro's number, while $j_- = u_- z_- n_- e E_r = -u_- ecA E_r$, where $E_r = \Delta\mu_e/F\Delta x - E'$ is the resultant active force on the anion. Substituting the specified expressions for the ionic currents into the equation $j_+ + j_- = 0$, we obtain the result $V' = t_- \Delta\mu_e/F$, where $t_- = u_-/(u_+ + u_-)$ is the anion transference number.

The obtained expression, $E = t_- \Delta\mu_e/F$, for the electromotive force of an electrochemical concentration cell is reputed to be correct.[5] It says that the conversion of free energy of an electrolyte diffusing down its chemical potential is less than perfect ($t_- < 1$), because part of the energy dissipates within the salt bridge. The decrease in the cell EMF that that induces is not, however, brought about by a diffusion potential, as commonly stated, because for equal transference numbers of cations and anions the genuine diffusion potential disappears, while the obtained formula says that the EMF is then by half smaller than the maximum possible value for $t_- = 1$.

VI. General Conclusions

Since in the respective sections of the report the considerations are brought to clear-cut conclusions, we will not recapitulate them here, except for saying that they indicate at the usefulness of the approach presented. So the following are some general conclusions only.

The electric and mechanical effects on membranes can be consistently described using thermostatics, but only when it is supplemented with the momentum conservation principle, because thermostatics, as such, contains only the energy conservation and entropy principles. Doing so, we obtain a nonvolume work thermostatics, which is what results from irreversible thermodynamics in the limit of zero dissipation.[6] The long-standing problems with osmotic pressure and the cell resting potential could perhaps be overcome when approached in the way presented here. Some tough to interpret results of electrophysiological experiments have been successfully treated in this way.[3] The electric coupling between ionic fluxes in biological membranes, which could be elucidated here only after all the forces present are taken into account, realizes an enhanced transport, which is a form of active transport so important in the living cell.

Open membrane channels for one type of ion and gradient of the augmented chemical potential equal to zero for another type of ion is a situation realized in electrochemical cells, and it constitutes the basic condition for their operation as energy converters. Under such conditions external forces can do useful work at the expense of the system's free energy with near 100% efficiency. With the momentum conservation principle applied, the electrochemical sources of electric energy can be described and understood better than is possible when merely electric work

Electrical Effects and Energy Conversion on Membranes

J. Phys. Chem. B, Vol. 104, No. 7, 2000 **1623**

is compared with the free energy decrease and the cell's redox reaction is written down.

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