Transport phenomena

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Experimental observations in biological membrane systems on concentration distribution, membrane potential, permeability and fluxes of ions, raise certain basic problems to be solved from our knowledge of theoretical electrochemistry, namely:

a) given that one has stationary state concentrations of permeant and nonpermeant ions of surrounding solutions, and electrical potential difference between adjacent aqueous solutions, can one compute theoretically, the fluxes of permeant ionic species, in agreement with experiments?
b) given boundary concentrations, required parameters about properties of the membrane and fluxes, can one compute the electrical potential difference, again in agreement with experiments?
c) given that one knows the values of stationary state fluxes and electrical potential difference, can one account for stationary state concentration distribution of ionic species on one side of the membrane, from the knowledge of the concentration on the other side?
d) In what manner is the permeability of a specified membrane to a specified ion dependent on electric potential difference, fluxes and concentration of other ionic species present in the system? Can one account for the observed influence of divalent cations, like calcium, on flux and permeability of univalent ions?
e) If active transport is to be interpreted as resulting from the influence of certain chemical reactions on magnitude and direction of fluxes of specified ions and molecules, can our knowledge of bioelectrochemistry shed light on the energetics and mechanisms of these processes?

Across their membranes, most living cells maintain a difference in electrical potential of about 50–100 mV, and large concentration gradients of inorganic ions. The ion distributions found in freshly dissected squid giant axons, and typical bathing solutions are summarized by Hurlbut (1970). In all cases listed by Hurlbut, the observed stationary state membrane potential, does not tally with the equilibrium potential as obtained from the Nernst equation, for the 3 permeant ions, sodium, chloride or potassium.

Concentrations of univalent ions in biological membrane systems are of the order of 0.5 moles per liter, a value too high for the activity coefficients of these ions to be regarded as unity. Fluxes observed using tracer methods are of the order 10^{-12} moles · cm^{-2} · s^{-1}. The membrane thickness is of the order 50–100 $\times 10^{-8}$ cm. Observed permeability coefficients are of the order of 10^{-8} cm/sec, for univalent ions. If one assumes the validity of Fick's law and linear concentration profile and identifies the permeability of ionic species, σ as $P_\sigma = (D_\sigma/h)$, where D_σ is the effective value of the diffusion coefficient, σ, in the membrane phase and h is the thickness of the membrane diffusion barrier, the diffusion coefficients of univalent ionic species in most membranes should be of the order of 10^{-14} cm^2/sec, a value to be compared with the values of the order of 10^{-5} cm^2/sec, usually obtained for diffusion coefficients of univalent ions in aqueous solution. Evidently, biological membrane systems offer high resistance for the motion of ions. It appears that Nature has buried the secret of the special and specified functions of biological membranes in their characteristic low thickness.

It is impossible to outline the partially satisfactory answers to the above mentioned basic questions, relevant to transport problems in biological membrane systems, within the short space of this review. However, it is pertinent to point out that any theory that attempts to explain membrane phenomena should take into account things we know for certain from experimental knowledge and theory. For example, physical conditions require that in small volume elements of solutions far removed from membrane solution interfaces, electroneutrality should be preserved. Conditions of zero net electric current must dictate the magnitude and direction of permeant ions, in the resting state of nerve axon systems. These considerations and the limitations of the equation of continuity, lead to the expression that the stationary state electric potential profile $\phi(x)$ is determined by the following set of equations:

$$
\begin{gathered}
\phi'(d)^2 - \phi'(o)^2 = [8\pi kT/\varepsilon](R + R_w) \\
(1 + \varkappa_2^2 \lambda^2)\ \phi'''(d) = \varkappa_2^2 \phi'(d) + (4\pi e/\varepsilon) ZR \\
(1 + \varkappa_0^2 \lambda^2) \phi'''(o) = \varkappa_0^2 \phi'(o) + (4\pi e/\varepsilon) ZR \\
\varkappa_2^2 = (4\pi e^2/\varepsilon kT) \sum_\sigma z_\sigma^2 c_\sigma(d) \\
\varkappa_0^2 = (4\pi e^2/\varepsilon kT) \sum_\sigma z_\sigma^2 c_\sigma(o) \\
ZR = \sum_\sigma Z_\sigma R_\sigma; \qquad R_\sigma = \sum_\sigma R_\sigma; \qquad R_w = (J_w r_w/kT) \\
R_\sigma = (J_\sigma r_\sigma/kT); \qquad \phi'(x) = (d\phi/dx) \\
\phi'''(x) = d^3\phi/dx^3. \qquad (1)
\end{gathered}
$$

In equation (1), $\varkappa_2^2$ and $\varkappa_0^2$ are the values of the Debye-Hückel parameter of solutions I and II, sandwiching the membrane. k is the Boltzmann constant and T is the temperature in degrees Kelvin. ε is the dielectric constant of the solutions. J_σ and J_w are respectively the fluxes of ionic species and water, expressed in moles cm^{-2} sec^{-1}. r_σ is the resistance offered by the membrane to species σ, for transport. R_σ has a dimension of the order of moles/cm^4, and approximately equals (J_σ/D_σ), where D_σ is the diffusion coefficient of σ in the membrane phase. z_σ is the valence charge number of species σ, and e is the protonic charge. λ^2 is a parameter independent of x, approximately equal to -8.33×10^{-14} cm^2 $\{-(\varkappa_2^2+\varkappa_0^2)/\varkappa_2^2\varkappa_0^2=\lambda^2\}$. Thus, if one has knowledge of stationary state fluxes of permeant species, knowledge of the composition of boundary solutions and resistance properties of the membrane, one can relate the derivatives of electrical potential profile to known quantities. d is the region of aqueous solutions and the membrane in which microscopic electroneutrality does not hold. Assuming a Taylor expansion form for electrical potential profile, enables one to compute the first few Taylor expansion coefficients and thereby compute the stationary state electrical potential difference, as a function of fluxes and known parameters of the system. Values of membrane potentials calculated in this manner yield values for all axon systems listed by Hurlbut in the right order of magnitude of observed membrane potentials. Thus, the answer to basic question b) can be assumed to be at least partially known. Partial answer to other questions raised may be found in the references listed at the end of this review.

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Photosynthesis

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The balance equation

$$6\,CO_2+6\,H_2O\xrightarrow{n\cdot h\nu}C_6H_{12}O_6+6\,O_2$$

characterizes photosynthesis as a reduction of CO_2 by water. It is difficult to understand how this strongly endergonic process might occur. The reaction obviously starts with a mixture of 2 molecular species, which undergo a catalytically enhanced interaction:

$$CO_2+3\,H_2O\rightleftharpoons HCO_3^-+H_3O^++H_2O\rightleftharpoons CO_3^{--}+2\,H_3O^+$$

It remains to be decided, which species of the equilibrium system has to be regarded as the precursor of the released molecular oxygen. Mass spectrometric experiments have not yet given convincing results[1].

The production of 1 mole of $C_6H_{12}O_6$ requires a free energy supply of ~2870 kJ. To transfer a single C atom from the oxidation state of CO_2 to that of carbohydrate we therefore need $2870/6\approx 480$ kJ. For a single molecule this corresponds to ~5 eV[2]. On the other hand, photosynthesis can be driven by the exclusive absorption of (red light) quanta with an energy content of 1.8 eV each. This simple comparison demonstrates that plant cells possess the capability of adding up the energies of several photons. Since the lifetime of the excited sensitizer (1-2 nsec) is orders of magnitude smaller than the average time interval between 2 photon absorption acts (~1 sec), there must be long-living 'intermediates' in the form of either chemical compounds, electric fields or energy-rich conformations.

If photosynthetically active cells are exposed to saturating light flashes, there is a remarkably small O_2 release: only 1 O_2 for 10^2–10^3 chlorophyll mole-