Concerning iron transport in plant systems, however, this study shows that iron absorbed from a ferric chelate moves up the stem and is held in the exudate in other chelated forms, the principal one being iron malate. The presence of iron chelates in the exudate of plants would account for the solubility of iron at the relatively high pH's of these systems and at the same time suggests that chelated iron is the form being translocated in intact plants.

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Electrochemical Diffusion

Abstract. The methods of irreversible thermodynamics, applied to the problem of steady-state linear diffusion, lead to the conclusion that the flux across any system of parallel membranes or phase boundaries can be expressed as a linear function of the differences in electrochemical potential across the system. The presence of fixed charges, polarizable molecules, or electric fields does not alter the flux-force relation.

The classical approach to diffusion problems is that of Fick (*1*). His treatment has been extended to the problem of diffusion of electrolytes by Nernst (*2*), Planck (*3*), and Teorell (*4*), but only the relatively simple Nernst formulation has found wide use in chemistry or biology. Goldman (*5*) and Hodgkin and Katz (*6*) introduced concepts from electrostatics in the effort to obtain equations applicable to bioelectric potentials, but their differential equations, like those of Teorell, can be integrated only for special cases and

with the aid of a number of assumptions of uncertain validity.

Prigogine, Mazur and Defay (*7*) have provided the basis for a new approach to the problem by demonstrating theoretically that, in any microscopic portion of a system at constant uniform temperature and pressure the diffusion affinity A_i of any molecular species i is

$$A_i = -\text{grad } \mu^*_i \qquad (1)$$

The electrochemical potential μ^*_i is

$$\mu^*_i = \mu'_i - \frac{E^2}{8\pi}\delta_i + z_iF\phi = \mu_i + z_iF\phi \quad (2)$$

where μ_i is the chemical potential, μ'_i is the chemical potential in the absence of an electric field (hence, $RT \ln f_iC_i$), E is the electric field strength, δ_i is the dielectric increment dD/dC_i, z_i is the electrochemical valence, F is the Faraday, and ϕ is the electric potential.

Suppose that two parallel planes, located in a rectangular coordinate system at $x = \alpha$ and $x = \eta$, and normal to the x-axis, bound an aqueous system, made up of molecular species a,b,...i,j,...n, which is homogeneous with respect to the y- and z-axes. The flux of any constituent $\mathbf{J}_i$ across unit area of any plane parallel to the bounding planes is

$$\mathbf{J}_i = \sum_j L_{ij}\mathbf{A}_j \qquad (3)$$

In this and subsequent equations, symbols in bold-face indicate vectorial components along the x-axis only, and the L_{ij} are linear phenomenological coefficients (*8–10*). In the steady state,

$$\mathbf{J}_i = \frac{1}{\lambda} \int_{x=\alpha}^{x=\eta} \left(\sum_{j=a}^{j=n} L_{ij}\mathbf{A}_j \, dx \right) \quad (4)$$

where λ is the distance between α and η. The diffusion affinity $\mathbf{A}_j$ will be a continuous function of x, hence the diffusion affinity $\mathbf{A}_j^d$ across the system will be

$$\mathbf{A}_j^d = \int_{x=\alpha}^{x=\eta} \mathbf{A}_j \, dx \qquad (5)$$

If we define a set of mean linear coefficients by

$$L'_{ij} = \frac{\dfrac{1}{\lambda} \int_\alpha^\eta \sum_j L_{ij}\mathbf{A}_j \, dx}{\int_\alpha^\eta \mathbf{A}_j \, dx} \qquad (6)$$

we have

$$\mathbf{J}_i = \sum_j L'_{ij}\mathbf{A}_j^d \qquad (7)$$

The expanded differential equation for $\mathbf{A}_j$ in any plane is

$$\mathbf{A}_j = -\frac{d\mu'_j}{dx} + \frac{E^2}{8\pi}\frac{d\delta_j}{dx} + \frac{\rho\delta_j}{D}\frac{d\phi}{dx} - z_iF\frac{d\phi}{dx} \qquad (8)$$

The equation therefore includes explicitly the electric field strength, the dielectric increment and dielectric constant, which are related to the presence in the system of polarizable molecules, and implicitly from Poisson's relation

$$\nabla^2\phi = -\frac{4\pi\rho}{D} \qquad (9)$$

the charge density ρ, which will include any fixed charges in the structure of the system. With the above and the electrostatic equation for field strength

$$E = -\text{grad } \phi \qquad (10)$$

we can readily integrate Eq. 5 to

$$\mathbf{A}_j^d = (\mu^*_j)\alpha - (\mu^*_j)\eta = \Delta\mu^*_j \quad (11)$$

and the flux Eq. 7 becomes

$$\mathbf{J}_i = \sum_j L'_{ij} (\Delta\mu_j + z_jF\Psi) \qquad (12)$$

where Ψ is the electrical potential difference between α and η. This relation will be valid for linear diffusion in any continuous aqueous system in which the linear phenomenological relations hold.

Equation 12 may readily be extended to include discontinuities such as phase boundaries or membranes of infinitesimal thickness; finite membranes can be treated as aqueous systems. Assume that the planes at $x = \alpha$ and $x = \eta$ are phase boundaries separating an internal phase from two infinite external phases I and II. Let $\mathbf{J}_i^\alpha$, L^α_{ij}, and $\mathbf{A}_i^\alpha$ represent the flux, linear coefficients, and diffusion affinities across α, and $\mathbf{J}_i^\eta$ and so on those for η. Define another set of coefficients

$$L''_{ij} = \frac{\dfrac{1}{3}\left(\sum_j L_{ij}^\alpha\mathbf{A}_j^\alpha + \sum_j L'_{ij}\mathbf{A}_j^d + \sum_j L\eta_{ij}\mathbf{A}_j^\eta \right)}{\sum_j (\mathbf{A}_j^\alpha + \mathbf{A}_j^d + \mathbf{A}_j^\eta)}$$

$$(13)$$

Then the flux from I to II becomes

$$\mathbf{J}_i = \sum_j (L''_{ij}\Delta\mu_j + Z_jFE) \qquad (14)$$

where $\Delta\mu_j$ and E are now the differences respectively in chemical and electrical potential between I and II, and these quantities can in general be measured experimentally.

In a more detailed paper, I have

carried out the full derivation of Eq. 14, and used the method of Staverman (8) to derive an equation relating electric current flux $\mathbf{I}$ to potential difference E for a membrane system in which active transport processes occur (10). This relation, which can now readily be shown to apply to any system of parallel phases and boundaries, is

$$\mathbf{I} = L_E E + \sum_j t'_j \Delta \mu_j + \sum_j z_j F \mathbf{J}_j{}^A \quad (15)$$

Here L_E is the electric permeability or conductance, t'_j the reduced transference numbers (8), and $\mathbf{J}_j{}^A$ the active components of the flux.

Equation 15 is now seen to be quite general, applicable to any system of parallel membranes and phases regardless of the occurrence within the system of electric fields, fixed charges, polarizable molecules, or active transport processes. The equation takes on classical forms in simple cases. It reduces to Ohm's law when there are no chemical potential differences or active transport processes. When no current flows, in the absence of active transport, and with the same uni-univalent electrolyte on both sides of the membrane, it yields the Nernst liquid junction potential equation (2). When the chemical and electrical potential differences are zero, in the presence of active transport, the current flux is equal to the active transport current, as Ussing has shown for frog skin (11). For the more complicated situation across the membrane of the nerve axon, Eq. 15 readily yields the Hodgkin and Huxley equation for the resting current-voltage relation when the net active transport current is zero (12). Equation 15 is not readily reduced to the complex liquid junction equation of Planck (3), nor to the membrane equations of Teorell (4), Goldman (5), or Hodgkin and Katz (6). All of these use concentrations instead of chemical potentials, and the membrane equations utilize a number of assumptions about the membrane field and the concentration relations between the membrane and the external solutions. The constants in the resulting equations are consequently not comparable to the constants in Eq. 15, which are directly and simply related to the phenomenological coefficients.

In a previous report, I have noted the fact that for several types of biological membrane system, the resting current-voltage relation is linear, as Eq. 15 predicts (10). The equation is derived from thermodynamic considerations, and consequently is not related

to any mechanism of active transport; it cannot, therefore, be used by itself to test the validity of any such mechanism. It is not applicable in conditions which depart from the steady state, as in the excited nerve membrane. It should, however, have considerable value in the experimental study of diffusion, liquid junction potentials, and the important related phenomena in living membranes.

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Temporal Discrimination in Pigeons

Abstract. Pigeons trained to peck a lighted key were presented with a key that was alternately dark and lighted. The key was dark for intervals of from 3 to 30 seconds. Pecking of the lighted key was reinforced only after the shortest or, in a second experiment, the longest interval that the key was dark. The pigeons were able to discriminate the duration of the dark interval.

Previous studies (1) have shown that organisms can discriminate the duration of a stimulus. In a fixed-interval schedule of reinforcement (2), for example, a response is reinforced only after a fixed interval of time has elapsed since the previous reinforcement. The frequency of responding generally increases throughout the interval between two reinforcements, indicating that the organisms are to some extent sensitive to the passage of time.

Our procedure (3) was a modification of a standard procedure for the simultaneous study of stimulus discrimination

and generalization (4). In the standard procedure as applied to pigeons, several different stimuli, lights of different wavelength, for example, are successively presented to the pigeon. Pecks are reinforced with food in the presence of one wavelength and not in the presence of the other wavelengths. The frequency of pecking plotted against wavelength reveals both discrimination of the wavelength associated with reinforcement and generalization to wavelengths adjacent to it on the continuum. This procedure was modified in our work to accommodate a peculiarity of the continuum of duration, namely, that the duration of a stimulus does not have a single, unchanging value until the stimulus has terminated. Accordingly, in order precisely to define the durations to which our pigeons responded, we exposed them to various durations of a stimulus and allowed them to peck after, rather than during, the presentation of each duration. Pecking was reinforced after one duration and was not reinforced after the other durations.

The experiments were conducted in a standard pigeon chamber containing a feeder for delivering grain to the pigeon and a circular plastic key that could be illuminated with orange light. For observing the birds, there was dim overhead illumination throughout each session. The pigeons were maintained at 80 percent of free-feeding weight and had previously been trained to peck a lighted key.

In each daily session, intervals of various durations during which the key was dark were each followed by a 30-second interval during which the key was lighted. The dark-key intervals ranged from 3 to 30 seconds in steps of 3 seconds. They were presented in an irregular order (5). Each duration occurred 12 times per session. In the first experiment, pecks on the lighted key were reinforced only after a dark-key interval of 3 seconds, and were not reinforced after longer dark-key intervals. In the second experiment, pecks on the lighted key were reinforced only after a dark-key interval of 30 seconds, and were not reinforced after shorter dark-key intervals. Reinforcement was a presentation of grain for 3 seconds, according to a variable-interval schedule with an average interreinforcement interval of 20 seconds.

Figure 1 shows the results of the two experiments for each of four pigeons. The median number of pecks on the lighted key during the last five sessions