with opaque plant material, a large proportion of the incident energy is lost to the inactive opaque substances, and the photosynthetic efficiency is low.

When the opacity of the plant material is considered as a factor affecting the efficiency of photosynthesis, most chloroplast pigments must be regarded as effective, though not necessarily equally effective, in the process. The available evidence suggests that energy absorbed by pigments is utilized without concomitant chemical change of the pigments themselves.

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Concerning the Measurement of pH, Ion Activities, and Membrane Potentials in Colloidal Systems

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IN THE FIELDS of biology and agriculture and in many industrial laboratories, pH measurement of colloidal systems, such as gels and thick suspensions, plays a prominent role in research and testing activities.

Measurement of pH with H_2-, quinhydrone-, and glass-electrodes, and of cation activity with various charged membranes, always involves a liquid junction, usually at a KCl bridge. In measurements made in true solutions the liquid junction potential probably is negligible, but this is not necessarily true for systems containing a great number of electrically charged particles of extremely high valencies, such as those represented by large clay and resin particles.

We are proposing a theory, supported by experimental data, showing that in certain colloidal systems liquid junction potentials may assume considerable magnitudes.

Consider microscopic particles of cation exchange material (e.g., resin) bathed in a dilute solution of KCl. Let ionic equilibrium be established. When a salt bridge containing saturated KCl is inserted into such a system, a junction between solutions having two different KCl concentrations within the matrix of the negatively charged particles results. If the negatively charged particles affect the relative diffusion rates of K^+ and Cl^-, a potential will arise at the interface of bridge and assemblage of particles, which we shall describe in terms of the activities of KCl in the liquid between the particles and in the bridge and the transference numbers of K^+ and Cl^- in the interface.

Transference numbers of K^+ and Cl^- in systems comprising KCl solution and cation exchanger material were determined by a modification of the Hittorf method. An 8-mm layer of the cation exchange material was interposed between the anode and cathode compartments of a Bradfield cell so that ions trans-

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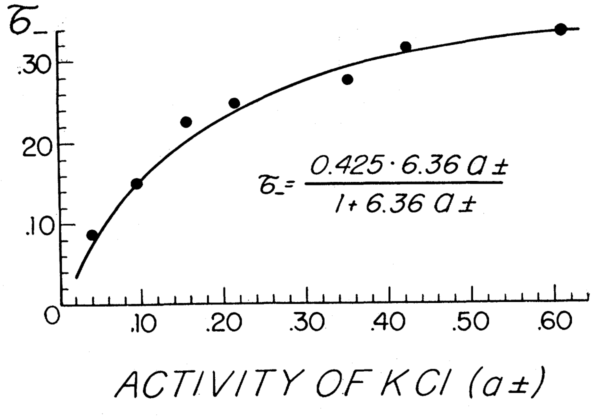

FIG. 1. Transference numbers of Cl in the system K-Ion-X + KCl.

porting current had to pass through the exchange material. The two membranes were prepared from uncharged Visking cellulose casings. Transference numbers ($\tau -$) so determined in systems containing a variety of cation exchange materials are presented in Fig. 1 and in Table 1. It is apparent that the negatively charged particles seriously affect the relative movements of Cl^- and K^+. The higher the charge density of the solid phase, as reflected by cation exchange capacity, the smaller is τCl^-. As seen in Fig. 1, the influence of the ion exchanger on $\tau -$ is greater at low than at high electrolyte concentrations.

Potentials developed across a layer of cation exchanger material in equilibrium with KCl solution of a given concentration C_1, and separating this first solution from a second KCl solution of a different concentration C_2, were measured (Table 1). The cell was:

$$\mathrm{Hg}\,\Big|\,\mathrm{Hg_2Cl_2}\,\Big|\,\mathrm{KCl\ (sat)}\,\Big|\,\begin{matrix}\mathrm{KCl}\ (a=a_2)\\(C_2)\end{matrix}\,\underset{X}{\Big|}\,\begin{matrix}\text{cation exchanger}\\+\,\mathrm{KCl}\ (C_1)\end{matrix}\,\underset{Y}{\Big|}$$

$$\begin{matrix}\mathrm{KCl}\ (a=a_1)\\(C_1)\end{matrix}\,\Big|\,\mathrm{KCl\ (sat)}\,\Big|\,\mathrm{Hg_2Cl_2}\,\Big|\,\mathrm{Hg}\quad \text{Cell A}$$

Either calomel electrode can be replaced by a glass electrode without affecting changes in emf observed when a_2 is changed. As will be discussed later, the equality of the Cl concentration (C_1) on both sides of the membrane Y was verified experimentally.

The general form of the equation for the liquid junction potential between two solutions I and II, is:

$$E_L = \frac{RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} \Sigma_i \frac{\tau_i}{z_i}\,\mathrm{dln}\,a_i \qquad (1)$$

where τ_i, z_i, a_i represent transference number, valency, and activity of a given ion species. For the case of KCl, using the τ-a-function depicted in Fig. 1 and assuming that the activity, if KCl is not affected by the cation exchanger, $a_+ = a_- = a_\pm$, the integrated equation assumes the form:

$$E_L = \frac{RT}{F}\left[\ln\frac{a_2}{a_1} - 0.85\ln\frac{1+6.36\,a_2}{1+6.36\,a_1}\right] \qquad (2)$$

where a_1 and a_2 refer to mean activities of KCl. When a_1 and a_2 do not differ greatly, so that τ_i may be considered to a first approximation to be independent of concentration, equation (1) becomes:

$$E_L = (\tau_+ - \tau_-)\frac{RT}{F}\ln\frac{a_2}{a_1} \qquad (3)$$

According to Table 1, the agreement between measured emf and calculated emf (equation 2) is satisfactory, even for fairly large concentration differences. Although the boundary conditions at the KCl junction (X) are undoubtedly more complicated than is assumed in equation (1), the order of magnitudes of the high potentials ~~observed~~ (Table 1) are predictable on the basis of a liquid junction potential.

TABLE 1

JUNCTION POTENTIALS IN COLLOIDAL SYSTEMS

Exchanger	Cation exchange capacity me per 100 gm	Mean activity of KCl solution		Junction potential millivolts		
		a_1	a_2	Measured*	Calculated eq.2	Calculated eq.3†
Ion—X Dow Chemical Corp.	370	0.00463	0.00902	18.0	17.7	17.0
		"	0.0441	53.7	53.7	57.8
		"	0.296	91.7	85.2	106.8
		"	0.432	96.5	89.3	116.3
		"	2.323	113.0	102.0	159.5
IR—100 Resinous Products Co.	173	0.0408	0.0746	11.0	....	10.0
		"	0.462	38.2	....	40.0
Bentonite Utah	100	0.0408	0.0751	5.9	....	5.0
		"	0.454	20.4	....	21.0

* Measured with Cell A.

† Using the experimentally determined value of τ_i referring to a_1. For $a_{\mathrm{KCl}} = 0.0408$; $\tau -$ for IR − 100 = 0.180; $\tau -$ for bentonite = 0.327.

The interpretation presented is at variance with the customary explanation of the emf measured with Cell A. It is often assumed that the seat of the emf is not at the junction X but at the boundary Y, which is said to act as a membrane of the Donnan type. Thus the emf observed is attributed to a Donnan membrane potential at Y, rather than a junction potential at X. The latter is considered to be negligible, especially if the KCl solution (C_2) is saturated. At present it is impossible to distinguish by direct emf observation between the two theories, because any emf measurement includes both potentials. Both potentials have the same sign.

Our investigation on transference numbers indicates that the potential difference at the junction X may be appreciable, at least for the systems under consideration (amberlite, Dowex, clays, soils). Moreover, our theory predicts the correct order of magnitude for the emf, provided the potential difference at Y is considered to be very small. It is important to note that, if one wishes to adhere to the theory of membrane potential at Y, it is necessary to conclude that its magnitude depends on the KCl concentration in the salt bridge as indicated by C_2 in Cell A, and a_2 in equation (2).

In ordinary potentiametric pH determinations, the usual cell is:

$$\begin{array}{c|c|c|l|c|c|c} \mathrm{Ag} & \mathrm{AgCl,\ HCl} & \mathrm{Glass} & \begin{array}{l}\text{Test}\\ \text{solution}\\ \mathrm{KCl},\ a=a_1\\ \mathrm{H},\ a=x\end{array} & \begin{array}{c}\mathrm{KCl\ (sat)}\\ a_2\end{array} & \mathrm{Hg_2Cl_2} & \mathrm{Hg} \end{array}$$

$$X$$

It is generally assumed that the liquid junction potential, test solution KCl a_1|KCl (sat), at X, is negligible, and that only the emf across the glass membrane is measured. If, however, the solution contains many suspended or sedimented electrically charged particles of high valency, this system corresponds to that depicted in Cell A. The emf measured includes both the potential across the glass and the potential arising at the junction between the KCl bridge and the system containing particles. The latter emf may be estimated on the basis of unequal transference of K^+ and Cl^- ions in the test system, in contrast to equal transference of these two ions in true solution, and to differences in KCl concentration between the salt bridge and the intermicellar liquid.

Generally speaking, the junction potential operates in the direction of making the pH of suspensions, or particularly of pastes, appear lower than is attributable to the H ion activity of the system. The following striking examples are presented: a K-Ion-X containing no exchangeable H ions (with $\frac{n}{1}$ KCl leaching) will, when immersed in water, give a pH of 2.8 when the electrode pair of a Beckman assembly is pushed into the coarse sediment. A K-bentonite having a pH of 9.2 in a 10 percent suspension will give a pH of 5.8–5.9 if the electrode pair is inserted into a paste consisting of equal volumes of bentonite and water.

The simple case that has been developed in equation (1) and Table 1 involves an ion exchanger KCl solution system at pH 7, so that KCl is the only electrolyte to be considered in the calculation of the emf expression. For more complex systems, additional terms must be inserted in the emf equation to account for the contribution of other ion species to the junction potential.

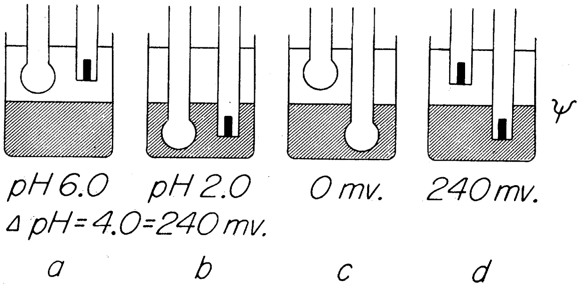

FIG. 2. Illustration of suspension effect (Δ pH) and "membrane potential." Glass electrode symbolized by sphere, calomel electrode by rectangle with a black bar representing the KCl-bridge.

The theory that has been briefly developed here sheds interesting light on some important observations relating to the *suspension effect,* viz., the difference in pH of a colloidal system (suspension, gel) and its filtrate, supernatant liquid or intermicellar liquid. It has long been observed that, in a sediment of acid soil in equilibrium with its supernatant liquid, the pH of the sediment is considerably lower than that of the supernatant liquid.

Du Rietz (*3*) and Davis (*2*), among others, have found that the pH of such a two-phase system depends not at all on the position of the glass electrode in the system. However, the position of the salt bridge leading to the calomel electrode, whether in the sediment or in the supernatant liquid, has a profound effect on the pH values obtained. An extreme example of this phenomenon may be obtained with the H-resin Ion-X dispersed in water. A supernatant liquid with a pH of 6.0 in equilibrium with a sediment of pH 0.5 may be found. The difference, Δ pH, corresponds to the very large emf of 325 millivolts.

Experiments in this laboratory have shown that variations in the KCl concentration of the salt bridge or variations in the electrolyte concentration of the suspension result in systematic changes in the pH difference between sediment and supernatant liquid. The emf values obtained may be related to electrolyte concentrations in the bridge and in the suspension by equations similar to equation (1). In all such systems, the magnitude of the suspension effect (Δ pH) corresponds exactly to the potential across two calomel electrodes with KCl salt bridges, one immersed in each phase (Fig. 2 *d*).

If, on the other hand, electrodes reversible to hydrogen ions are inserted in the supernatant liquid and in the sediment, and connected to a voltmeter, no emf results (Fig. 2 *c*). Its absence is usually explained by a Donnan membrane potential "without membrane" existing at the boundary of sediment and supernatant liquid. The magnitude of the "membrane" potential is said to be equal and opposite to the suspension effect. According to Brönsted (*1*), "the membrane potential is measurable as the difference between the electromotive potentials of two standard electrodes (e.g., calomel electrodes) in contact with the solutions on the two sides of the membrane, the junction potential being eliminated." Following Loeb (*4*), the membrane potential is often calculated from the difference of the pH values observed potentiometrically between "inside" (sediment) and "outside" solution.

With numerous resin and clay systems we have verified the identity of the "membrane" potential and the Δ pH values (suspension effect). However, our explanation is different. According to our picture we have merely measured the same junction potential twice, once when measuring pH and once when measuring the "membrane" potential (Fig. 2, *a, b, d*).

It is important to note that in our systems

$$\begin{array}{r|l} \text{KCl} & \text{K-cation exchanger} \\ & \\ C_1 & \text{KCl} \\ \multicolumn{2}{c}{Y} \end{array}$$

no Donnan distribution across the interface, *Y*, could be observed. Even after long standing, the Cl^- concentration of solution removed by rapid filtration from the right-hand compartment was identical with that of the solution in the left-hand compartment. Likewise, if colloidal H-resin particles are added to one side of a two-compartment cell containing equal amounts of HCl on both sides, no redistribution of HCl takes place. This suggests that *Y* is not a phase boundary in the usual sense, and that the solution phase KCl (C_1) exists on both sides of *Y*. No membrane potential in the Donnan sense is expected to exist. Yet, by inserting two calomel electrodes with salt bridges, large emf values are obtained. These we attribute to the junction potential.

The following question still remains: If the boundary of supernatant liquid|sediment is not the chief seat of the potential difference observed between two calomel electrodes (Fig. 2 *d*), how is the absence of an emf between two glass electrodes (Fig. 2 *c*) to be explained? Two explanations come to mind. First, the activities of the H ions are identical in the supernatant liquid and in the sediment; this would imply that the H ions of the ion swarm of the particles have the same activity as those of the intermicellar liquid. Second, the adsorbed H ions (swarm) do not affect the glass electrode. Only the diffusable H ions of the intermicellar liquid are recorded by the electrode.

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Technical Papers

Chemical Composition of the Vitelline Membrane of *Ascaris lumbricoides* var. *suis*[1]

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A large number of living female *Ascaris lumbricoides* var. *suis* were slit open and the uteri dissected out. The edge of a glass slide was rubbed gently along the uteri to force the eggs out on a glass plate. The eggs at the distal end of the uteri were frequently checked under the microscope to make certain that they were fertilized. Immediately after collection the eggs were placed in a 0.2% solution of concentrated CP hydrochloric acid to dissolve the outer mucoid coat. The material was allowed to stand overnight at room temperature and was then centrifuged, and the supernatant fluid was stored in the refrigerator for further testing. The eggs were washed three times in distilled water and then exposed to artificial gastric juice at 37° C. This step was to eliminate any remnants of the mucoid layer. The supernatant fluid after this procedure showed no quantitative or qualitative differences from artificial gastric juice. This indicates that the previous hydrochloric acid extraction was complete.

The eggs were then rinsed and placed in a large test tube in a water bath and the temperature was held between 72° and 74° C in a warming oven. The vitelline membrane melted at this temperature and gathered in large globules, usually at one end of the egg. The eggs were allowed to cool and an acetone extraction for fats and fatty acids was made at room temperature. The supernatant fluid was filtered off, and the extraction was repeated three times. On chilling, this supernatant fluid showed a white flocculent precipitate. Later tests with heated beeswax in acetone showed a similar precipitate on chilling. The nature of the precipitate in our acetonic

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[1] This work was carried out under the guidance of B. G. Chitwood.