

Jenny *et al.* then apply their theory to the determination of pH in colloidal suspensions of charged particles by regarding the suspensions as membranes. It is well known that the pH measured in such suspensions differs from that measured in the filtrates. This effect has been attributed to the influence on the reversible electrode of the ions in the swarm around the charged particles, and has been called the suspension effect by Wiegner and Pallmann (5). From the theory of Jenny *et al.* and their further experiments, two alternatives can be given: (1) There exists a suspension effect, and as a consequence of this no appreciable "membrane" or liquid junction potential can occur at the point of contact between the KCl bridge and the suspension. (2) There is no suspension effect; the difference in pH between the suspension and its filtrate is due to the liquid junction potential at the point of contact between the KCl bridge and the suspension.

They seem to prefer the second alternative which, however, is really disproved by their data on the transference number of Cl⁻ at different concentrations in the Ion-X exchanger membrane. From Fig. 1 in their paper it is seen that τ increases with increasing concentration of KCl.

According to the alternative theories presented here, the "membrane" potential at the point of contact between the KCl bridge and the suspension must be comparatively small (insignificant according to the Teorell-Meyer and Sievers theory), provided a concentrated solution of KCl is used in the bridge. Differences in the pH of the suspension and its filtrate must accordingly be attributed to a suspension effect, an explanation that is more satisfactory from a kinetic point of view.

The problem of the determination of ion activities in colloidal suspensions has recently been treated in a paper by the writer (6) and can be summarized briefly as follows: In any system of ions subjected to thermal motion, the electrochemical potential of an ion at equilibrium is the same at every point in the system. This is a thermodynamic principle from which the Donnan equation, for example, can be derived. The principle can be interpreted in this way: If, in a system of ions at equilibrium, the osmotic activity of an ion at point *a* differs from that at point *b*, then the electrical potential at *a* must differ from that at *b* in such a way that the work done in transporting an ion from *a* to *b* must be equal to the work gained in transporting the corresponding charges from *a* to *b*. The ratio of the osmotic activities of an ion at *a* and at *b* can then be calculated from the difference in the electrical potential between the points. From this it can be shown that, provided the liquid junction potential is negligible, the pH measured in a colloidal suspension of charged particles in the ordinary way represents the pH at the point of contact between the KCl bridge and the suspension, and not at the point of contact between the reversible electrode and the suspension.

Of course the practical importance of this con-

clusion rests on the assumption of a suspension effect, which has also been discussed by the writer (6). If the ions neutralizing the charges at the surfaces of the colloidal particles are subjected to thermal motion, thus forming a swarm, a suspension effect will occur, especially as the particles themselves are also subjected to thermal motion. There are many indications that a swarm, or a diffuse double layer, as it is also called, exists around charged particles. (This, of course, implies that the concept of matter is based on mass, charge, etc.). It is, for example, well known that most exchange reactions on colloidal particle surfaces take place rapidly. If, in addition to the electrical forces, the ions at the particle surfaces were also held by other and much stronger forces, their thermal motion would be practically zero and the exchange reactions very slow.

There are also many phenomena in colloid chemistry that have been successfully explained by theories based on the assumption of a diffuse swarm of ions around the individual particles. The stability of lyophobic colloidal suspensions, for example, is very difficult to explain without assuming the existence of a diffuse double layer that creates repelling forces between the particles (?). The negative adsorption of anions in clay mineral suspensions, treated by Schofield (8), and the relation between the water content and the "osmotic" pressure in a bentonite gel recently derived by the writer (9), are both experimentally verified theories based on the assumption of a diffuse double layer.

If, on the other hand, it is assumed that the thermal motion of the ions neutralizing the charges at the particle surfaces is insignificant—i.e., they do not influence the potential of a reversible electrode—it would be extremely difficult to explain the variation in the apparent transference number of Cl⁻ with the concentration of salt in the experiments by Jenny *et al.*

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Errata

Through an accident that occurred while the issue was on the press, in some copies of SCIENCE for March 30, page 361 is misnumbered 261. The article by R. J. Hickey and P. H. Hidy begins on this page.

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