3. The magnetic susceptibility of each of two of the allotropic forms of manganous sulfide has been confirmed.

4. A possible theoretical explanation of the defect observed in the magnetic susceptibility of certain compounds of manganese has been advanced.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Poisson-Boltzmann Equation Derived from the Transfer of Momentum

BY ALBERT SPRAGUE COOLIDGE AND WALTER JUDA

The modern treatment of equilibrium states of electrolytic solutions is based on the Poisson–Boltzmann equation

$$\nabla^2\bar{\psi} = -\frac{4\pi}{D}\Sigma_i n_i^0 \epsilon_i e^{-\epsilon_i\bar{\psi}/kT} \qquad (1)$$

Here n_i^0 is the stoichiometric concentration (assuming complete dissociation) of ions of the species i with charge ϵ_i, and $\bar{\psi}$ is the time average of the electrostatic potential. This is a continuous point-function, having the value zero at all ordinary points in the solution, but differing from zero at special points in the neighborhood of some permanent feature such as a phase-boundary or fixed charge. It may also differ from zero at an ordinary point if the average is taken, not over all time intervals, but only over those during which some specified configuration of ions happens to prevail in the neighborhood—this may be loosely called the average at a special point near the given configuration, and in the ensuing discussion, the term "special point" will be understood to include this interpretation. D is the dielectric constant of the solvent.

The theoretical foundations of (1) have been clearly discussed by Fowler and Guggenheim[1] and by Onsager.[2] The rigorous form of the Boltzmann equation is

$$\bar{n}_i = n_i^0 e^{-W_i/kT} \qquad (2)$$

where $\bar{n}_i$ is the time average concentration of the ionic species i at any special point, and W_i is the potential of the average force acting on an i ion whenever it happens to be at the special point, this force itself being $-\nabla W_i$. In other words, W_i is the work which would be required to carry an i ion from an ordinary point to the special point, if at every point in the path it were subjected to just the average force associated with the proximity of the special feature or configuration involved, this latter being held constant. The Poisson equation takes the form

$$\nabla^2\bar{\psi} = -4\pi\bar{\rho}/D = -\frac{4\pi}{D}\Sigma_i \bar{n}_i \epsilon_i \qquad (3)$$

where $\bar{\rho}$ is the average charge density. It is not immediately obvious that this equation is correct, for if the ions are true point charges the instantaneous value of ρ is always either zero or infinity and cannot be averaged directly, while if the ions have a finite extension and the $\bar{n}_i$ are the distribution functions for their centers of mass, then $\bar{\rho}$ at each point will depend on the $\bar{n}_i$ averaged over a corresponding extension in the neighborhood of that point. We shall show later that (3) holds in the limit as the extension approaches zero. In order to obtain (1) it is now necessary to assume that

$$W_i = \epsilon_i\bar{\psi} \qquad (4)$$

This assumption can be justified only *a posteriori* by the self-consistency of the results to which it leads. It implies that on the average, the force acting on any ion which happens to be present at a special point can be computed from the average field that prevails there whether or not an ion is present. Since this force is due to the field of the other ions in the neighborhood, the assumption is essentially that there is no correlation between the presence or absence of an ion at the given point and the fluctuations of the field arising from the neighboring ions.

Onsager[2] has considered the conditions under which (4) is valid. So long as $\epsilon_i\bar{\psi} << kT$, (1) reduces to the familiar linear approximation of Debye and Hückel, and its solutions give distribution functions in the form of superposable ionic atmospheres. At least in the interior of the solution, the atmosphere of each ion is spherically symmetrical and exerts no force upon the ion at its center, which therefore experiences only the forces due to the distribution of other ions with their atmospheres which would exist, under the given circumstances, if the central ion were not there. Assumption (4) is therefore vindicated in the usual theory of ionic interaction. At points near a phase boundary this reasoning fails; even though superposable, the atmospheres of the ions are distorted and exert forces on the "central" ions, usually away from the boundary, which cannot be calculated from the average potential. Thus, Langmuir's[3] theory of forces on walls needs examination to determine the errors produced by overlooking this effect. In the remainder of this

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(1) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, 1939, p. 405.

(2) L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

(3) I. Langmuir, *Science*, **88**, 430 (1938); *J. Chem. Phys.*, **6**, 873 (1938).

paper we shall ignore such inconsistencies and retain assumption (4).

An alternative derivation of equation (1) may be obtained in a way which perhaps yields a clearer visualization of the mechanism of the ionic equilibrium, by postulating that the electrostatic forces on the ions in any portion of the solution must be, on the average, balanced by the fictitious thermal forces produced by the Brownian movement.

By considering the average force acting upon the contents of any fixed portion of space, dividing by the volume, and passing to the limit as the volume is made infinitesimal, we may define the "force density" as a continuous point function. The average force density arising from the electrostatic forces upon the ions of a given kind at a point is evidently $-\bar{n}_i\nabla W_i$. Now the average kinetic energy of the ions is independent of their distribution and of all real forces, so that the Brownian movement carries an average momentum $kT\bar{n}_i$ in unit time across every plane of unit area, thus simulating a pressure $kT\bar{n}_i$ and producing a thermal force density $-kT\nabla\bar{n}_i$. For equilibrium

$$\bar{n}_i\nabla W_i = -\,kT\nabla\bar{n}_i \tag{5}$$

In connection with (4) this becomes

$$\bar{n}_i\epsilon_i\nabla\bar{\psi} = -\,kT\nabla\bar{n}_i \tag{6}$$

which integrates to

$$\bar{n}_i = n_i^0 e^{-\epsilon_i\bar{\psi}/kT} \tag{7}$$

n_i^0 entering as an integration constant. Summing over i and using (3) gives

$$\frac{D}{4\pi}\nabla^2\bar{\psi}\nabla\bar{\psi} = kT\Sigma_i\nabla\bar{n}_i = -\Sigma_i n_i^0\epsilon_i e^{-\epsilon_i\bar{\psi}/kT}\nabla\bar{\psi} \tag{8}$$

which reduces to (1) on cancelling $\nabla\bar{\psi}$. The left side represents the electrostatic force density, and the right the negative of the thermal force density. Since (2) is simply the integral form of (5), it is clear that the two procedures are theoretically equivalent.

The left-hand member of (8) can be written in various forms

$$\frac{D}{4\pi}\nabla^2\bar{\psi}\nabla\bar{\psi} = \frac{D}{4\pi}\bar{\mathbf{E}}\nabla\cdot\bar{\mathbf{E}} = \bar{\rho}\bar{\mathbf{E}} = \nabla\cdot\bar{\bar{\Phi}} \tag{8$'$}$$

where $\bar{\mathbf{E}}$ is the average field intensity and $\bar{\bar{\Phi}}$ is the tensor $\frac{D}{8\pi}(2\bar{\mathbf{E}}\bar{\mathbf{E}} - \bar{E}^2\mathbf{I})$, $\mathbf{I}$ being the idemfactor. If $\bar{\mathbf{E}}$ is resolved into components $\bar{X}$, $\bar{Y}$, $\bar{Z}$ along a set of perpendicular axes, then the matrix of $\bar{\bar{\Phi}}$ is

$$\frac{D}{8\pi}\left\{\begin{matrix} \bar{X}^2 - \bar{Y}^2 - \bar{Z}^2 & 2\bar{X}\bar{Y} & 2\bar{X}\bar{Z} \\ 2\bar{X}\bar{Y} & \bar{Y}^2 - \bar{Z}^2 - \bar{X}^2 & 2\bar{Y}\bar{Z} \\ 2\bar{X}\bar{Z} & 2\bar{Y}\bar{Z} & \bar{Z}^2 - \bar{X}^2 - \bar{Y}^2 \end{matrix}\right\}$$

Except for the average signs, this tensor has the same form as the familiar electrostatic stress tensor $\Phi = (D/8\pi)(2\mathbf{EE} - E^2\mathbf{I})$ which describes the force system in a static continuous charge distribution. In the static case, the forces on the charge itself, as distinguished from those acting on the medium, produce everywhere a force density $\nabla\cdot\Phi = \rho\mathbf{E}$. From this it follows that the time average force density must be $\nabla\cdot\bar{\Phi} = \overline{\rho\mathbf{E}}$, a quantity which differs from that occurring in (8′), since it involves the average of a product instead of the product of two averages. The difference is due to the fact that $\overline{\rho\mathbf{E}}$ contains contributions arising from the electrostatic interaction of different parts of the same ions.

In order to demonstrate this, it is necessary to follow through a limiting process in which the ions are first regarded as having a finite extension, which is then allowed to shrink to a point. For definiteness, the ions of one kind can be regarded as spheres of radius a, with their charges uniformly distributed throughout their volumes. The dielectric constant will be assumed to have the same value in the interior of the ions as outside, but the general nature of the result does not depend on this assumption. Finally, it will be supposed that the centers of the ions have a distribution function $\bar{n}_i$ which can, in the neighborhood of the point of interest, be expanded in series form:

$$\bar{n}_i = n_0 + n_1x + n_2x^2 + \ldots$$

where x is measured from the given point as origin in the direction of most rapid increase of $\bar{n}_i$. This assumption, though not the most general, will serve to illustrate the point under discussion. The instantaneous field is finite at every point; at a point not lying inside any ion it has the value $\mathbf{E}_0$ due to neighboring ions and is the same as though their charges were concentrated at their centers. At a point inside an ion at a distance r from its center, there is an additional field $\mathbf{E}_i$ of magnitude $\epsilon_i r/Da^3$. Because of the assumed independence of $\bar{n}_i$ on y and z, only the x-components of $\mathbf{E}_0$ and $\mathbf{E}_i$ need be considered, the others averaging to zero.

If there is an ion with its center at $-x$, $-y$, $-z$, with $x^2 + y^2 + z^2 < a^2$, it will produce at the origin an internal field with x component $\epsilon_i x/Da^3$. The average value of this contribution will be

$$\bar{X}_i = \frac{\epsilon_i}{Da^3}\int\!\!\int\!\!\int dv(n_0x + n_1x^2 + \ldots)$$

the integral extending throughout the range specified. The first term vanishes by symmetry; but even if the ion were unsymmetrical it is clear that the integral would be of the order of magnitude of n_0 times the fourth power of the linear dimensions of the ion, so that $\bar{X}_i$ goes to zero as these dimensions become infinitesimal. The instantaneous value of ρ_i is $3\epsilon_i/4\pi a^3$ and its average is

$$\bar{\rho}_i = \frac{3\epsilon_i}{4\pi a^3}\int\!\!\int\!\!\int dv(n_0 + n_1x + \ldots)$$

In the limit this obviously reduces to $\bar{\rho}_i = \epsilon_i n_0 = \epsilon_i\bar{n}_i$, thus confirming (3). The instantaneous value of the force density due to the interna field has the x-component $\rho_i \ X_i = 3 \ \epsilon_i^2 x/4\pi Da^6$. Upon integration this gives the average value

$$\overline{\rho_i X_i} = \frac{3\epsilon_i^2}{4\pi Da^6} \int\int\int \mathrm{d}v(n_0 x + n_1 x^2 + \ldots) \ .$$

Even if the first term vanishes by symmetry, the second term in the integral is proportional only to the fifth power of a, so that the internal field makes a contribution to the force density which becomes infinite for the point-charge model. This may also be seen as follows. For ions of finite volume, the force acting on the contents of any fixed cell in space will include internal repulsion whenever an ion happens to overlap the boundary of the cell, and there will be a corresponding term in the average force. If the ions are made smaller, the time spent in crossing the boundary will be reduced in proportion to a linear dimension, but the force acting when a given fraction of the ion has crossed will increase in proportion to the square of a linear dimension, so that the average effect increases without limit as the ions approach point charges.

Since the ions are assumed internally stable, it is clear that the term $\rho_i\mathbf{E}_i$ must be balanced, both instantaneously and on the average, by some cohesive force the nature of which need not be specified further, and that the force density to be balanced by the thermal pressure is $\overline{\rho\mathbf{E}} - \Sigma_i\overline{\rho_i\mathbf{E}_i} = \overline{\rho\mathbf{E}_0}$. Now, the assumption underlying (4), if translated into terms applying to the finite radius model, is simply that there is no correlation between the fluctuations in ρ and those in $\mathbf{E}_0$, so that $\overline{\rho\mathbf{E}_0} = \bar{\rho}\bar{\mathbf{E}}_0$. But $\bar{\mathbf{E}}_0 = \bar{\mathbf{E}} - \Sigma_i\bar{\mathbf{E}}_i$, and we have seen that the last term vanishes for point charges. Hence, so long as (4) is justified, we may replace $\overline{\rho\mathbf{E}_0}$ by $\bar{\rho}\bar{\mathbf{E}}$. (8) can then be written in the simple form

$$\nabla \cdot \bar{\bar{\Phi}} = \nabla p, \quad p = kT\Sigma_i\bar{n}_i \qquad (9)$$

If (4) cannot be used, there does not seem to be any way to derive the interionic part of the electrostatic force from a stress tensor.

It is interesting to see how it can happen that a force system derived from a second-rank tensor, $\bar{\bar{\Phi}}$, can be in equilibrium with one derived from a pure scalar p. In order that a vector, $\nabla \cdot \Phi$, may be represented as the gradient of a scalar, it is a necessary and sufficient condition that the curl of the vector vanish. Hence $\nabla \times \nabla \cdot \bar{\bar{\Phi}} = 0$. Giving $\nabla \cdot \bar{\bar{\Phi}}$ its value in terms of $\bar{\psi}$ leads to

$$0 = \nabla \times (\nabla\bar{\psi}\nabla^2\bar{\psi}) = \nabla\nabla^2\bar{\psi} \times \nabla\bar{\psi} + \nabla^2\bar{\psi}\,\nabla \times \nabla\bar{\psi}$$

The second term vanishes identically because the field is irrotational. Now, $\nabla^2\bar{\psi}$ is proportional to the charge density. The vanishing of the first term therefore means that the gradient of the charge density has no component perpendicular to the field, and the charge density is a function of $\bar{\psi}$ only. By a similar argument, the relation $\nabla p = \frac{D}{4\pi}\Delta\bar{\psi}\nabla^2\bar{\psi}$ implies that p is a function of $\bar{\psi}$ only. These conditions can evidently be met in the case of any fluid medium, *i. e.*, one in which the only stresses of other than electrostatic origin, when the medium is at rest, constitute a pure hydrostatic pressure which is at each point some function of the density and composition of the medium only. In a state of thermodynamic equilibrium, the density and composition depend only on $\bar{\psi}$, so that the pressure depends only on $\bar{\psi}$, say $p = f(\bar{\psi})$, and the electric density depends only on $\bar{\psi}$, say $\frac{D}{4\pi}\nabla^2\bar{\psi} = g(\bar{\psi})$. The stresses will balance if

$$\nabla f(\bar{\psi}) = g(\bar{\psi})\nabla\bar{\psi}$$

whence

$$g(\bar{\psi}) = \mathrm{d}f(\bar{\psi})/\mathrm{d}\bar{\psi}$$

In the special case of a unidirectional field a different procedure is possible, leading to a first-order differential equation for $\bar{\psi}$. Let the potential and the densities be functions of x only, so that $\bar{Y} = \bar{Z} = 0$. Then in (9) we need consider only the x-components of the vectors. Since $\bar{\bar{\Phi}}$ is diagonal, (9) reduces to

$$\mathrm{d}\ \Phi_{xx}/\mathrm{d}x = \mathrm{d}p/\mathrm{d}x$$

and on giving Φ_{xx} its value $\frac{D}{8\pi}\bar{X}^2$ and integrating with respect to x we obtain

$$p = \frac{D}{8\pi}\bar{X}^2 + p_0$$

where p_0 is the thermal pressure at any point where the field is zero. This gives a particularly simple physical picture—the thermal pressure is equal, except for an additive constant, to the familiar electrostatic tension which acts across the equipotential surfaces.[4] On giving p and $\bar{X}$ their values in terms of $\bar{\psi}$ we obtain

$$(\mathrm{d}\bar{\psi}/\mathrm{d}x)^2 = (8\pi kT/D)\Sigma_i n_i^0 \exp(-\epsilon_i\bar{\psi}/kT) - \text{const} \quad (10)$$

where the constant is equal to $8\pi p_0/D$. An interesting example of a unidirectional field is the case of a solution extending from a uniformly charged wall to infinity (a few mm. may be taken as infinity in this case). The direction x of the field is normal to the wall. Specializing equation (10) for a uni-univalent salt and determining the constant from the boundary condition $(\mathrm{d}\bar{\psi}/\mathrm{d}x)_{x=\infty} = 0$ and $(\bar{\psi})_{x=\infty} = 0$ gives

$$(\mathrm{d}\bar{\psi}/\mathrm{d}x) = \pm (2kT\kappa/\epsilon) \sinh \epsilon\bar{\psi}/2kT$$

where $\kappa = (8\pi n^0\epsilon^2/DkT)^{1/2}$. The same result is, of course, obtained by integrating the Debye–Hückel equation.[5]

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(4) In directions at right angles to the field the electrostatic stress is a pressure, which is superposed upon the thermal pressure; but, being uniform each term is separately in equilibrium and no mutual compensation is required.

(5) W. Horwitz, *J. Chem. Ed.*, **16**, 519 (1939).

For fields varying in direction this reduction fails. For example in a radial field we have potential and ion densities functions of r only. Let the radial component of $\overline{E}$ be $\overline{R}(r)$, the others vanishing. Then it can be shown that the radial component of (5) reduces to

$$\frac{D}{8\pi r^4}\frac{\mathrm{d}}{\mathrm{d}r}(r^2\overline{R})^2 = \frac{\mathrm{d}p}{\mathrm{d}r}$$

This relation between p and $\overline{R}$ cannot be integrated without knowledge of the manner in which one of them depends upon r.

Summary

The Poisson-Boltzmann equation for solutions of electrolytes is derived by postulating a state of balance between the electrostatic forces and the thermal pressure due to the Brownian movement of the ions. The same assumption is required as in the usual derivation, namely, that the average force on any ion can be calculated from the average field. Using this approximation, the average interionic force on the contents of any specified volume can be derived from a stress tensor identical in form with that familiar in electrostatic theory, except that its components involve the squares of the average field components rather than the average of their squares. In the case of a uni-directional problem such as that of the forces on a plane phase boundary, the method leads at once to a first-order differential equation for the average potential.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Chain Mechanisms for the Reaction of Chlorine and Oxalic Acid

BY HENRY TAUBE

In an earlier paper,[1] it was shown that certain reducing agents and oxidizing agents which are capable of acting by one-electron changes induce the addition of chlorine to maleic acid by a chain mechanism. Numerous data on the kinetics of the reaction and observations on the effect of various substances as inhibitors made it appear likely that atomic chlorine[2] and an organic free radical were the chain carrying substances.

Similar effects can be expected in other reactions of chlorine with reducing agents. The present paper contains the results of a study of the mechanism of the reaction[3]

$$Cl_2 + H_2C_2O_4 \longrightarrow 2H^+ + 2Cl^- + 2CO_2$$

induced by Fe^{++}. At sufficiently high concentrations of hydrogen ion and chloride ion, the spontaneous reaction of chlorine and oxalic acid[3] becomes slow enough so that the induced reaction can be studied conveniently.

Many of the observations reported here are analogous to those made in the earlier study[1] and the general conclusions reached there are confirmed. All the data on the Fe^{++} induced reaction of chlorine and oxalic acid are consistent with the following steps.

Chain initiating step

$$Fe^{++} + Cl_2 \longrightarrow Fe^{+++} + Cl_2^- \text{ or } FeCl^{++} + Cl \quad (1)$$

Chain carrying steps

$$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^+ \text{ (rapid equilibrium)}$$

$$Cl + HC_2O_4^- \xrightarrow{k_2} H^+ + Cl^- + C_2O_4^- \quad (2)$$

$$C_2O_4^- + Cl_2 \xrightarrow{k_3} Cl + Cl^- + 2CO_2 \quad (3)$$

Chain breaking steps

$$Cl + C_2O_4^- \xrightarrow{k_4} Cl^- + 2CO_2 \quad (5)$$

$$Cl + Cl \xrightarrow{k_5} Cl_2 \quad (4)$$

Whether reaction (4) or (5) predominates as the chain-breaking step depends on the ratio of the chlorine and oxalic acid concentrations.

Substances which were observed to affect the rate of addition of chlorine to maleic acid by the chain mechanism are found to affect also the rate of the chain reaction of chlorine with oxalic acid. A striking difference in behavior is observed however. Co^{++}, Ce^{+++}, Mn^{++}, Vo^{++} and other ions all inhibit the induced addition of chlorine to maleic acid. While some of these inhibit the induced reaction of chlorine and oxalic acid, some enhance the rate of the reaction and some in fact enhance the rate under certain conditions, and reduce the rate under others. These observations can be explained in terms of simple, chemically reasonable reactions. The explanation advanced furthermore finds support in extensive work to be published later.

Experimental Methods

The experimental method differed from that employed in the previous work only in some details. Two stopcocks

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[1] Taube, THIS JOURNAL, **65**, 1876 (1943).

[2] Taube and Bray, *ibid.*, **66**, 3369 (1940), presented evidence that at 0° and chloride ion concentrations in excess of 0.01 *M*, atomic chlorine is largely associated with Cl^-. This evidence was not conclusive, and since the present work contributes no further data bearing on this point, the powerful one-electron oxidizing agent in the system under study is for simplicity called atomic chlorine and is represented by Cl.

[3] Griffith and McKeown have published results on the spontaneous reaction: *Trans. Faraday Soc.*, **28**, 518 (1932). Their data are consistent with a mechanism involving as slow step the reaction of $HC_2O_4^-$ with HOCl.