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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1964 Chilean earthquake. The authors use the relation for seismic energy release rather than total strain energy release. I believe the authors underestimate the total strain energy release by a factor of about 3, or 10 times. The seismic energy released is only a small fraction of the total strain energy released. The seismic energy released is only a small fraction of the total strain energy released. The seismic energy released is only a small fraction of the total strain energy released.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

Two Theorems Concerning Electrolytes

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(1) Fluctuations in the average total electrostatic energy E of the free ions of an electrolytic solution as calculated by the theory of Debye and Hückel are negligibly small in accessible concentration ranges. If $\delta E = \{E^2 - (\bar{E})^2\}^{1/2}$, then $\delta E/\bar{E} = (-kT/2\bar{E})^{1/2}$; i.e., the ratio of the fluctuation in energy to the total energy is of the order of the square

root of the ratio of the kinetic energy per degree of freedom of a *single molecule* to the *total* electrostatic energy of the system. (2) A general relationship connecting free energy F and average electrostatic energy \bar{E} is derived; for the case where the average potential around an ion is given by the Debye-Hückel formula, $F = 2\bar{E}/3$.

RECENT calculations² have been presented which showed that fluctuation terms in the electrostatic potential around a given ion become comparable to the mean value of this potential at low concentrations and hence the validity of the Debye-Hückel³ limiting law for electrolytes was apparently questioned. In view of the general importance of the Debye-Hückel result as a means of interpreting and correlating experimental data on strong electrolytes, it seems advisable to re-examine the fluctuation terms. Halpern's calculations do show that the fluctuations in potential around a *single* ion can become comparable with the Debye average value for the potential, but this result could perhaps have been foreseen without calculation. Of much greater interest is the fluctuation in the total average electrostatic energy of the system; after all, experiment is concerned with this quantity and not with the behavior of a particular ion. We should expect that a satisfactory method of calculating the average total energy would show negligible fluctuations as long as the total energy was large compared to kT . It can readily be shown that the energy calculated by the method of Debye and Hückel satisfies this requirement at accessible concentrations in solvents of high dielectric constant. In solvents of low dielectric constant, the same conclusion is reached, if the charges in short range ion pairs be excluded in calculating the ionic strength.

1. DISTRIBUTION OF IONS IN SOLUTION

Suppose we are given a solution containing N positive ions of charge $+\epsilon$ and N negative ions

of charge $-\epsilon$ in a total (large) volume V . In order to obtain information concerning the interionic distances (which are necessary in calculations of potential and energy), we consider the probability of existence of a general ion pair⁴ defined as follows: a positive ion i and a negative ion j within a range dr at r constitute an ion pair associated with the distance r , provided there is no unpaired negative ion k at a distance $r_{ik} \leq r_{ij}$ from i . The corresponding probability function $G(r)$ has in general two peaks as a function of r when the concentration is moderately low. The first lies at $r=a$, where a is the average diameter of the ions (which are assumed spherical). This peak is very sharp, because it is due to an exponential function $\exp(\beta/r)$, where

$$\beta = \epsilon^2/DkT, \quad (1)$$

in the region where $r < \beta$. At a distance given approximately by the Bjerrum⁵ radius $\beta/2$, $G(r)$ has a minimum. The second peak is a maximum at a distance $\rho \approx \sqrt[3]{V/2\pi N}$, a distance which corresponds in order of magnitude to the distance between uniformly distributed particles. Distances much greater than ρ are very improbable on account of a factor $\exp(-2r^3/3\rho^3)$ which appears in $G(r)$. The maximum at ρ always appears at low concentrations; the peak at $r=a$ appears only if

$$b > 2, \quad (2)$$

where

$$b = \epsilon^2/aDkT. \quad (3)$$

In water, $b=2$ corresponds to $a=3.5 \times 10^{-8}$ cm, so for ions (including solvation shells) as large or

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² Halpern, J. Chem. Phys. **2**, 85 (1934).

³ Debye and Hückel, Phys. Zeits. **24**, 185 (1933).

⁴ Fuoss, Trans. Far. Soc. **30**, 967 (1934).

⁵ Bjerrum, Kgl. Danske Vidensk. Selskab. **7**, No. 9 (1926).

larger than this value, ions in contact always represent the *least* probable configurations.⁶ The large fraction of the solute will have interionic distances of the order of ρ . But ions at this distance automatically satisfy, at small concentrations, the condition

$$\epsilon^2 e^{-\kappa r} / r D k T \ll 1 \quad (4)$$

necessary for the validity of the Debye-Hückel treatment. When $b > 2$, (4) is still valid for ions whose distances reckoned pairwise are near the peak at ρ , but it does not hold for ions whose distances are of the order of a . Ions in these configurations, however, are short range pairs, whose external field approximates that of a *dipole* at distances larger than a . We therefore exclude in first approximation this group of ions in calculating the long range interionic effects. (In second approximation, we take them into account by means of the triple ion⁷ interaction.) Short range pairs are defined as those for which $a \leq r \leq d$, where d is a distance equal to the thickness of a layer of several solvent molecules; its precise value is left to be determined by experiment. As long as $d \geq 2a$, the definition is sufficient to account for a large fraction of the ions for which $a \leq r \leq \beta/2$, and which do not satisfy the condition (4). We shall consider ions for which $r > d$ as free ions, and calculate their effect on the properties of the solution by means of the Debye-Hückel time average method, and rely on the fluctuation theorem to be proved below for the accuracy of the result.

2. FLUCTUATIONS IN ENERGY

We define the excess free energy F due to the potential energy of the free ions by the equation

⁶ The argument is of course subject to the approximations implied in the model used to represent the electrolytic solution. Described very briefly, it comprises uniformly charged spheres of diameter a in a homogeneous medium of dielectric constant D and viscosity η . The important physical approximations involved are the charge distribution in the ionic sphere (cf. Kirkwood, J. Chem. Phys. **2**, 351 (1934)) and the use of the macroscopic dielectric constant D for small distances. The error in the latter approximation is absorbed in a , which is chosen large enough to include rigidly oriented solvent dipoles, for which the effective dielectric constant is unity in order of magnitude. Fowler's phrase "omnium gatherum" seems to the writer to be the most descriptive term yet applied to the parameter a .

⁷ Fuoss and Kraus, J. Am. Chem. Soc. **55**, 2387 (1933).

$$e^{-F/kT} V^m = \int e^{-E/kT} d\omega, \quad (5)$$

where $d\omega$ includes integration over the elements of volume $dx dy dz$ for each of the m free ions ($m = 2N$ for complete absence of short range pairs, i.e., "complete dissociation") and E is the total potential energy of the free ions. Fowler,⁸ Kramers⁹ and Onsager¹⁰ have emphasized the importance of including the "van der Waals energy" in E , in order that the integral (5) converge. We therefore set

$$E = E_c + E_w, \quad (6)$$

where E_w is the non-Coulomb energy and

$$E_c = \frac{1}{2} \sum_j' \sum_k \epsilon_j \epsilon_k / D r_{jk}. \quad (7)$$

In (7), r_{jk} is the distance between two ions of charge ϵ_j and ϵ_k and the prime on the first summation sign indicates that all $j = k$ terms are omitted. (We may obviously omit the intrinsic energy $\epsilon^2/2aD$ of each ion because we are not concerned with F as a function of temperature.) The bilinear form (7) may be replaced in the conventional way by the linear form

$$E_c = \frac{1}{2} \sum_i \epsilon_i \psi_i, \quad (8)$$

$$\text{where} \quad \psi_i = \partial E_c / \partial \epsilon_i = \sum_j' \epsilon_j / D r_{ij} \quad (9)$$

is the instantaneous potential at a particular ion of charge ϵ_i , due to all of the other free ions present.

Differentiation of (5) with respect to ϵ_i gives $\bar{\psi}_i$, the mean value of ψ_i

$$\bar{\psi}_i = \partial F / \partial \epsilon_i = V^{-m} \int e^{(F-E)/kT} \psi_i d\omega. \quad (10)$$

Multiplying (10) by $\epsilon_i/2$ and summing over all ions gives

$$\bar{E}_c = \frac{1}{2} \sum_i \epsilon_i \bar{\psi}_i, \quad (11)$$

for the average value of the Coulomb energy.

⁸ Fowler, Trans. Far. Soc. **23**, 434 (1927).

⁹ Kramers, Amsterdam Proc. **30**, 145 (1927).

¹⁰ Onsager, Chem. Rev. **13**, 73 (1933). This reference contains an investigation of the fluctuation terms which explicitly includes the effects of van der Waals forces.

Differentiation of (11) with respect to ϵ_k and rearrangement of the result gives

$$\frac{1}{2} \sum_i \epsilon_i \partial \bar{\psi}_i / \partial \epsilon_k = \bar{\psi}_k / 2 + [\bar{\psi}_k \cdot \bar{E}_c - (\bar{E}_c \bar{\psi}_k)] / kT, \quad (12)$$

(where $i=k$ must be included in the summation the left). We now multiply (12) by ϵ_k and sum over all ions, obtaining after rearrangement

$$(\delta E)^2 = \overline{(E_c - \bar{E}_c)^2} = \frac{kT}{2} \left(\bar{E}_c - \frac{1}{2} \sum_k \epsilon_k \sum_i \epsilon_i \frac{\partial \bar{\psi}_i}{\partial \epsilon_k} \right). \quad (13)$$

This equation gives an explicit expression for the fluctuation in total electrostatic energy. It is derived (without qualifying assumptions or approximation) from the definition of F in (5), the classical expression for E_c in (7) and the definition of ψ_i in (9) simply by means of mathematical manipulation.

Now let us test the result of Debye and Hückel by means of Eq. (13). We shall assume that the concentration is so small that we may use the limiting form of their equation

$$\bar{\psi}_i = -\epsilon_i \kappa / D + O(\kappa^2) \quad (14)$$

for the *mean value* of the potential around an ion of species i , even if at these concentrations the instantaneous value of the potential around a particular ion of species i does exhibit fluctuations comparable with $\bar{\psi}_i$ itself.² That is, we assume that (14) gives the correct mean value of potential which is to be used in calculating the total average electrostatic energy by means of the summation (11). We shall find that the value of E_c calculated in this way shows only negligible fluctuations, unless the solution is so dilute that the total energy E_c is of the order of kT .

The parameter κ in (14) depends on the total number of ions present. We shall change the conventional formulation somewhat, in order to emphasize the fact that it depends on the charge of each ion present, by writing

$$\kappa^2 = 4\pi \sum_i \epsilon_i^2 / V kDT, \quad (15)$$

where the summation now extends over all free ions counted individually, instead of over all ions counted by species. For example, for a symmetrical electrolyte $\sum \epsilon_i^2 = m\epsilon^2$; if the number of short range pairs is negligible, $\sum \epsilon_i^2 = 2N\epsilon^2$.

By differentiation of (14), we find

$$\frac{\partial \bar{\psi}_i}{\partial \epsilon_k} = -\frac{\kappa}{D} \delta_{ik} - \frac{\epsilon_i}{D} \frac{\partial \kappa}{\partial \epsilon_k}, \quad (16)$$

where $\delta_{ik} = 1$ when $i=k$ and vanishes for $i \neq k$. Differentiation of (15) gives

$$\partial \kappa / \partial \epsilon_k = 4\pi \epsilon_k / \kappa D kTV. \quad (17)$$

Substituting (17) in (16) and the result in (13) gives

$$(\delta E)^2 = -kT \bar{E}_c / 2,$$

or

$$\delta E / \bar{E}_c = (-kT / 2 \bar{E}_c)^{1/2}, \quad (18)$$

where

$$\bar{E}_c = -\kappa \sum_i \epsilon_i^2 / 2D = -kTV\kappa^3 / 8\pi. \quad (19)$$

Combining (18) and (19) gives

$$\delta E / \bar{E}_c = (4\pi / V\kappa^3)^{1/2}. \quad (20)$$

Now as concentration approaches zero, $V\kappa^3$ approaches zero so that in the limit of zero concentration, (20) becomes infinite, i.e., the fluctuation terms become dominant even in the energy.

Two facts must, however, be borne in mind. First, the effects of Coulomb forces appear experimentally as deviations from ideal behavior, and second we can only measure properties of all of the ions present. Eq. (18) already shows that the fluctuations are not serious as long as

$$\bar{E}_c \gg kT/2 \quad (21)$$

as was pointed out in the introduction.

We now investigate numerical values, in order to see when this inequality is reversed. We have

$$\kappa = 2.92 \times 10^8 (c\gamma / D)^{1/2}, \quad (22)$$

where $c\gamma$ is the concentration of free ions in equivalents per liter. (Here γ is the fraction of salt existing as free ions, $0 < \gamma \leq 1$). In (20), \bar{E}_c is the average energy of m free ions and V is the volume containing them. If we take $m = 2L = 2 \times 6.06 \times 10^{23}$, then $V = 1000 / 2c\gamma$. Substituting these values, we find

$$-kT / 2 \bar{E}_c = 1.01 \times 10^{-27} D^{1/2} (c\gamma)^{-1/2}.$$

In practical cases, D will not exceed 100 in order of magnitude, giving

$$\delta E/\bar{E}_c \leq 10^{-12}/(c\gamma)^{\frac{1}{2}}. \quad (23)$$

The fluctuations will amount to 10 percent at a concentration of free ions $c\gamma = 10^{-44}$, and $\delta E/\bar{E}_c$ will be unity when $c\gamma = 10^{-48}$. These concentrations appear to be inaccessiblely small.

The conclusion we reach, therefore, is that the Debye-Hückel time average method will give accurate results when applied to the calculation of the properties of electrolytic solutions, insofar as they are due to the presence of free ions. The method will fail only at concentrations so low that the thermodynamic properties of the solution are so near those of the solvent that it is pointless to speak of deviations from ideal behavior. For example, the osmotic coefficient $(1 - \epsilon^2\kappa/6Dkt)$ for a 1-1 salt equals $(1 - 0.4\sqrt{c})$ in water. At $10^{-4} N$, this is 0.996, so that an error of only 0.1 percent in observed freezing point depression is already a 25 percent error in the interionic correction term. (The author hopes that this will not be interpreted as an "indeterminism principle"; the point of the argument is that fluctuations in unobservable quantities have no physical significance while, at accessible concentrations, the fluctuations in the observable quantities are negligible.)

3. RELATION BETWEEN AVERAGE ENERGY AND FREE ENERGY

In calculating free energies of electrolytic solutions, it is customary to use a charging process at some step in the procedure. Herewith is presented a proof of the theorem

$$F = 2\bar{E}/3, \quad (24)$$

which seems to be more straightforward than some of the earlier proofs.

We consider an electrolytic solution, in which all charges are linear functions of a parameter σ ,

where $0 \leq \sigma \leq 1$. Then by (7)

$$E(\sigma) = \sigma^2 E_0, \quad (25)$$

where $E(\sigma)$ is the total electrostatic potential energy of any instantaneous configuration of ions and E_0 is the value corresponding to $\sigma = 1$. If the potential energy arises by the charges being built up from 0 to σ , then

$$E(\sigma) = \int_0^\sigma \frac{dE(\sigma)}{d\sigma} d\sigma = \int_0^\sigma 2E(x) \frac{dx}{x}. \quad (26)$$

Furthermore

$$\bar{E}(\sigma) = V^{-m} \int \exp \{ [F(\sigma) - E(\sigma)]/kT \} E(\sigma) d\omega, \quad (27)$$

where $F(\sigma)$ is defined by the equation

$$\exp(-F(\sigma)/kT) V^m = \int \exp(-E(\sigma)/kT) d\omega. \quad (28)$$

Differentiation of (28), and use of (26) gives

$$dF(\sigma)/d\sigma = (2/\sigma)\bar{E}(\sigma). \quad (29)$$

Differentiation of (27), and use of (26) gives

$$\frac{d\bar{E}(\sigma)}{d\sigma} = -\frac{2}{\sigma} \bar{E}(\sigma) + \frac{\bar{E}(\sigma) \cdot \bar{E}(\sigma) - \overline{E(\sigma)^2}}{\sigma kT/2}. \quad (30)$$

If we now substitute (18) in (30), we obtain

$$d\bar{E}(\sigma)/d\sigma = (3/\sigma)\bar{E}(\sigma),$$

whence

$$F(\sigma) = 2\bar{E}(\sigma)/3. \quad (31)$$

When $\sigma = 1$, (31) gives the standard result (24). The result depends on explicit use of the Debye-Hückel potential.

The author takes this opportunity to thank Professor R. H. Fowler for valuable suggestions in regard to the treatment of these theorems.