VOLUME 1

MODERN ELECTROCHEMISTRY

An Introduction to an Interdisciplinary Area

John O'M. Bockris
Professor of Electrochemistry
University of Pennsylvania, Philadelphia, Pennsylvania
and
Amulya K. N. Reddy
Professor of Electrochemistry
Indian Institute of Science, Bangalore, India

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CHAPTER 2

ION–SOLVENT INTERACTIONS

2.1. INTRODUCTION

An electrochemical system (Fig. 2.1) includes two interfaces, at each one of which an electronic conductor is in contact with an ionic conductor (or electrolyte[†]). The electronic conductor is generally a metal but may well be a semiconductor. The ionic conductor, as the term suggests, is a material which consists of mobile ions.

How does one produce a medium of mobile ions? One method is based on the fact that certain substances, which, in the pure form, do not contain any significant concentration of ions, are able to interact to produce ions. This is how neutral, i.e., nonionic, molecules of water and of acetic acid interact to give an electrolytic solution of hydrogen ions and acetate ions (Fig. 2.2 and Table 2.1). This *chemical* method of producing an ionic conductor will be studied in Chapter 5.

Another approach is based on starting off with a *solid* ionic crystal and reducing the forces which hold the ions together. A stage is reached when the cohesive forces are so weakened that the ions, which could only

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[†] The term *electrolyte* is used in electrochemistry to refer not only to the *ionically conducting medium* through which electricity is passed but also to the substances which, when dissolved (or melted), give rise to a conducting medium.

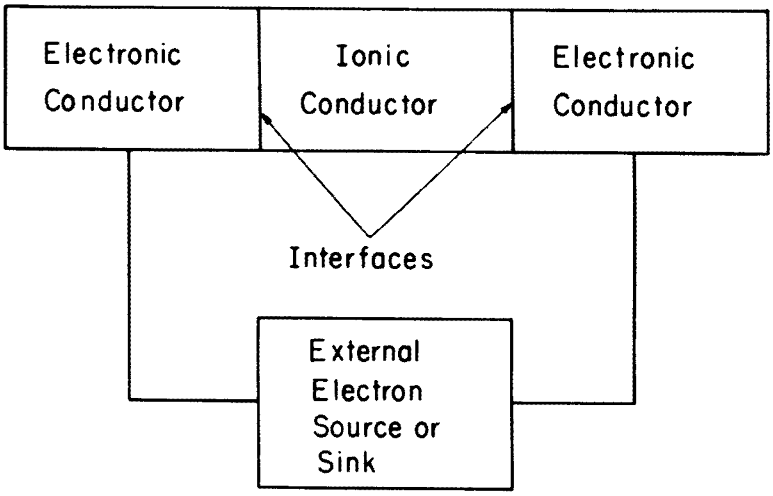


Fig. 2.1. The essential parts of an electrochemical system.

vibrate in the solid, acquire a new degree of freedom—the freedom of translational motion.

There are two distinct ways in which the interionic forces in a crystal can be overcome. One method is based simply on an agitational effect. Heat energy is used to increase the tempo of the ionic vibrations in the solid until thermal forces prevail and the long-range order of the ionic arrangement in the crystal lattice is wiped out—the ionic crystal "melts" (see Chapter 6).

One is left with a *pure liquid electrolyte*, a molten material teeming with positive and negative ions and with free space which is far more plentiful than in the solid. These ions are in ceaseless random motion and ready to respond to applied electric fields by conducting electricity. What has been described is a *thermal* method of obtaining a pure liquid electrolyte.

There is, however, another way of overcoming the interionic forces in an ionic crystal and producing mobile ions. This is with the aid of a *solvent*. A crystal of potassium chloride, e.g., is placed in water. Soon it becomes apparent that the crystal *as an entity* has disappeared. The solvent has

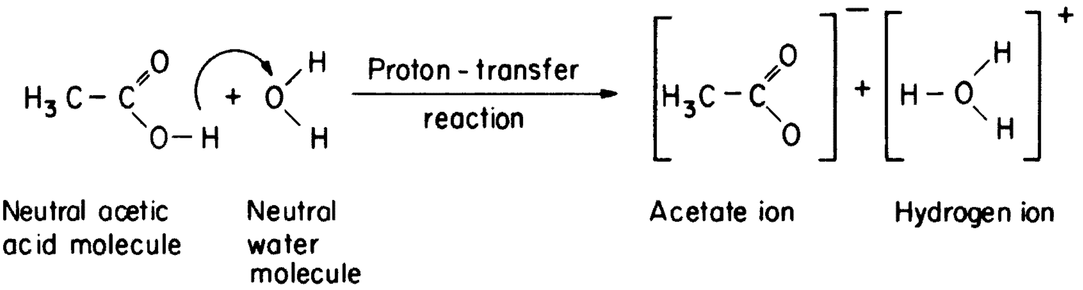


Fig. 2.2. The chemical method of producing ionic solutions.

TABLE 2.1

Ionic Concentrations in Pure Water, Pure Acetic Acid, and Acetic Acid Solution

	Ionic concentration g-ions liter^{-1} at 25 °C
Pure water	10^{-7}
Pure acetic acid	$10^{-6.5}$
$0.1N$ acetic acid solution	10^{-3}

enticed the ions out of the solid so that they can wander off into the solvent (Fig. 2.3). (The Greek word for *wanderer* is *ion.*) One has witnessed the process of *dissolution of an ionic crystal.*

What are the influences which the solvent brings to bear upon the ions of the crystal? What are the ion–solvent forces which overcome the ion–ion forces holding together the crystal?

It is obvious that questions such as these are of central significance to the understanding of ionic solutions and, hence, the electrochemical processes which occur in them. For the questions imply that ions in solution are constantly affected by ion–solvent forces, and that, to understand the behavior of ions inside an electrolytic solution, one has to reckon with the forces arising from the presence of the solvent. One must understand *ion–solvent interactions.*

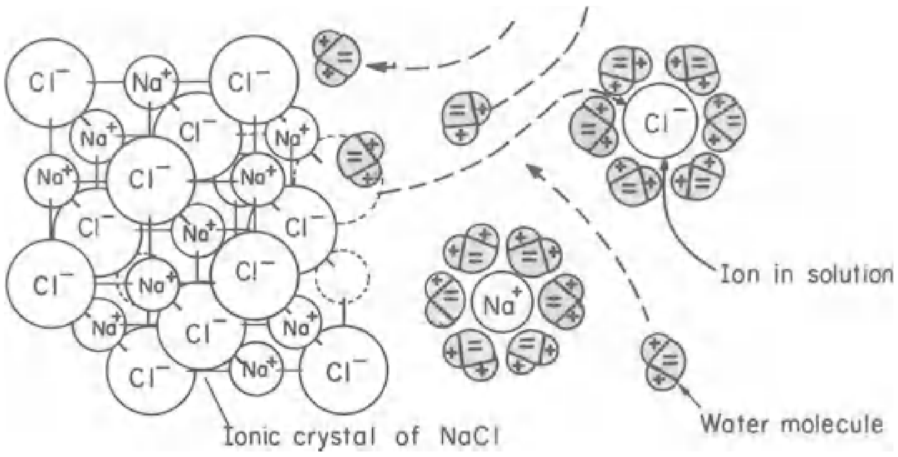


Fig. 2.3. Dissolution of an ionic crystal by the action of a solvent.

2.2. THE NONSTRUCTURAL TREATMENT OF ION–SOLVENT INTERACTIONS

2.2.1. A Quantitative Measure of Ion–Solvent Interactions

A field of study often undergoes a qualitative change when the concepts used can be associated with numbers and made quantitative. The problem, therefore, is to develop a quantitative measure of ion–solvent interactions. This type of problem is a common one in chemistry. It is often solved by considering two situations or states, one where the interactions operate (are "switched on") and the other where they do not exist (are "switched off"), and then computing the free-energy difference ΔG_{I-S} between the two states (Fig. 2.4).

In the case of ion–solvent interactions, the state in which the interactions exist is an obvious one; it is the situation in which ions are inside the solvent. Ions are charged particles, and charges interact with other charges. So there will also be ion–ion, as well as ion–solvent, interactions in the solution. But the former are excluded in the quantitative analysis of ion–solvent interactions; they will be given separate consideration later on (Chapter 3).

Now, what is a situation in which there are no ion–solvent interactions? Obviously, one in which there is no solvent. Hence, one must consider an initial state in which there are large spaces between individual ions, and nothing else present. The initial state, therefore, is that of *ions in vacuum* at an infinitely low pressure.

The problem, therefore, is to consider the free-energy change for the transfer of ions from vacuum to solution (Fig. 2.5).

Ions in vacuum → Ions in solution.

Recall, however, the thermodynamic relation (*cf.* Appendix 2.1) which states that, in a reversible process taking place at constant temperature and pressure, the free-energy change is equal to the *net* work done *on* the system, i.e., the total work done other than the work of producing a volume change.

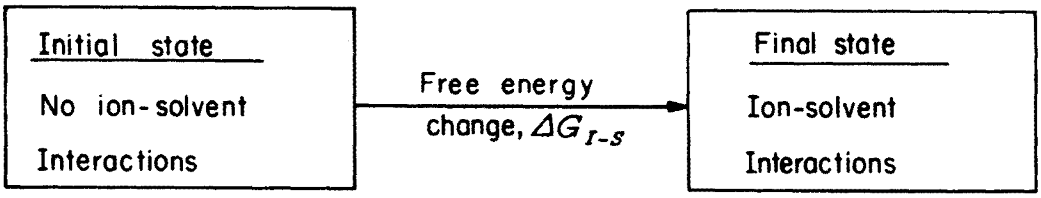


Fig. 2.4. The free-energy change arising from ion–solvent interactions.

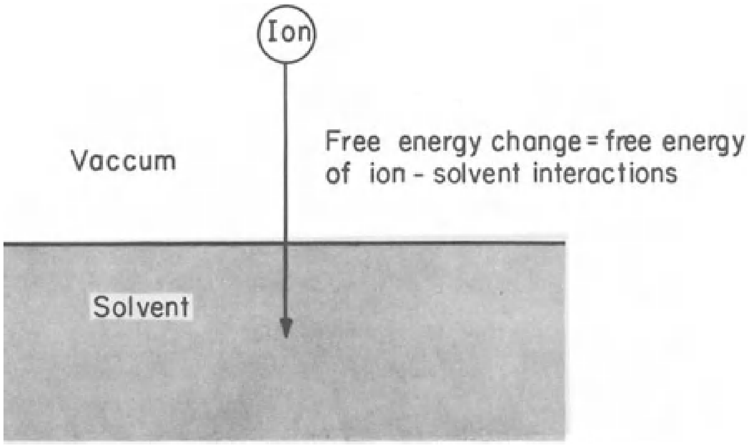


Fig. 2.5. The free energy of ion–solvent interactions is the free-energy change resulting from the transfer of ions from vacuum into solution.

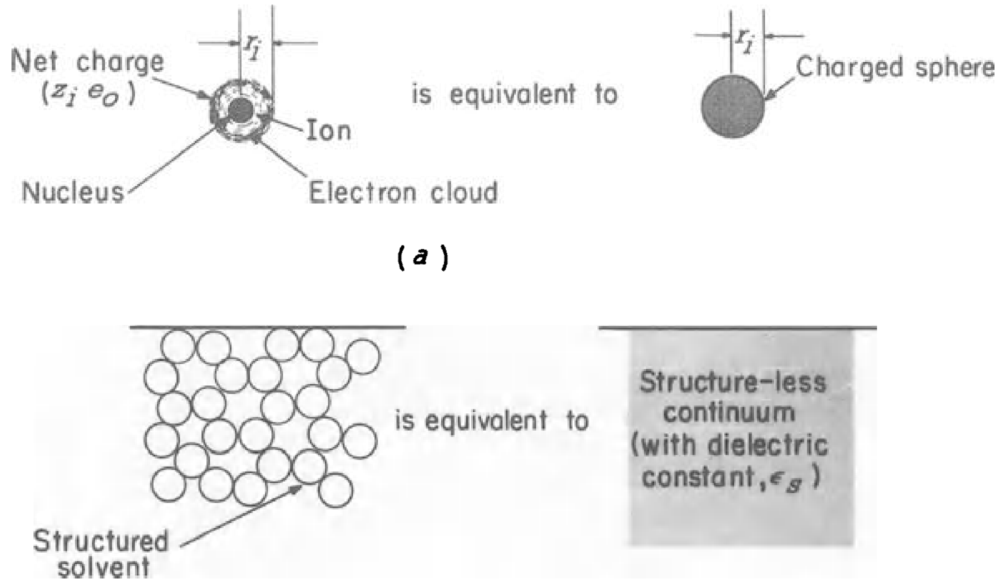
Hence, the basic problem of deriving an expression for the free energy of ion–solvent interaction can be defined as follows. What is the work done when one transfers an ion from vacuum into a position deep inside the solvent? This work will include the energy of all the interactions between the ion and the surrounding solvent, for example, water.

2.2.2. The Born Model: A Charged Sphere in a Continuum

A moment's thought will reveal that, to work out exactly all the ion–solvent interactions, one must know the structure of the solvent, i.e., the dispositions of all the particles constituting the solvent and the forces between the ion and these particles. But the solvent, e.g., water, may have a fairly complex structure. To understand this structure, one must be able to answer a vast number of questions. For example, are there discrete solvent molecules, or are they associated to such an extent that one should not speak of separate molecules? What do the ions do to the solvent structure? Do they disrupt it, or are there spaces inside the structure so that ions can be smuggled in but cause little damage to it?

The problem seems insuperable, but one can resort to modelistic thinking. Models are simplified representations of the real microstructure of nature, often as mental pictures derived from the macroscopic world. They are intended to reproduce approximately the essential features of the real situation. The better they are able to predict experimental quantities, the better do they serve as aids to thinking about how nature really works.

An example of a *very* crude and approximate model for ion–solvent interactions is that suggested by Born in 1920. In the Born model, an ion



(a)

(b)

Fig. 2.6. The Born model for ion–solvent interactions considers (a) an ion equivalent to a charged sphere and (b) the structured solvent equivalent to a structureless continuum.

is viewed as a rigid sphere (of radius r_i) bearing a charge $z_i e_0$ (e_0 is the electronic charge), and the solvent is taken to be a structureless continuum (Fig. 2.6). Thus, the problem of ion–solvent interaction assumes the following form: What is the work done in transferring a charged sphere from vacuum into a continuum (Fig. 2.7)?

By considering a charged sphere equivalent to an ion, the Born model is assuming that it is only the *charge* on the ion (or charged sphere) that is responsible for ion–solvent interactions. The interactions between the solvent and the ion are considered to be solely *electrostatic* in origin.

The Born model suggests a simple thought process for calculating the free energy ΔG_{I-S} of ion–solvent interactions, i.e., the work of transferring an ion from vacuum into the solvent (Fig. 2.8). One uses a thermodynamic cycle. The basic idea behind a thermodynamic cycle is the law of the conservation of energy. If one starts with a certain system (say, an ion in vacuum) and then goes through a hypothetical cycle of changes, ending up with the starting condition (i.e., the ion in vacuum), then the algebraic sum of all the energies involved in the various steps must be zero. The particular cycle that will be used is the following: (1) The ion (or charged sphere) is first considered in a vacuum, and the work W_1 of stripping it of its charge $z_i e_0$ is computed. (2) This uncharged sphere is slipped into the solvent; this process will involve no work, i.e., $W_2 = 0$ because the only

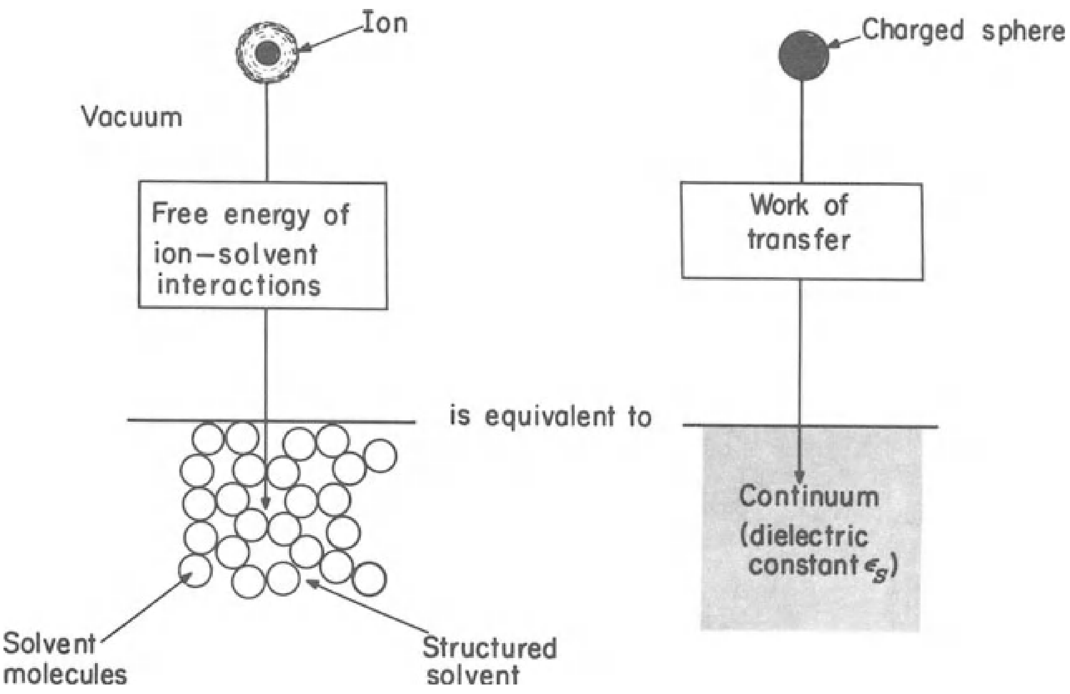


Fig. 2.7. The Born model views the free energy of ion–solvent interactions as equal to the work of transferring a charged sphere (of radius r_i and charge z_ie_0) from vacuum into a continuum (of dielectric constant ε_S).

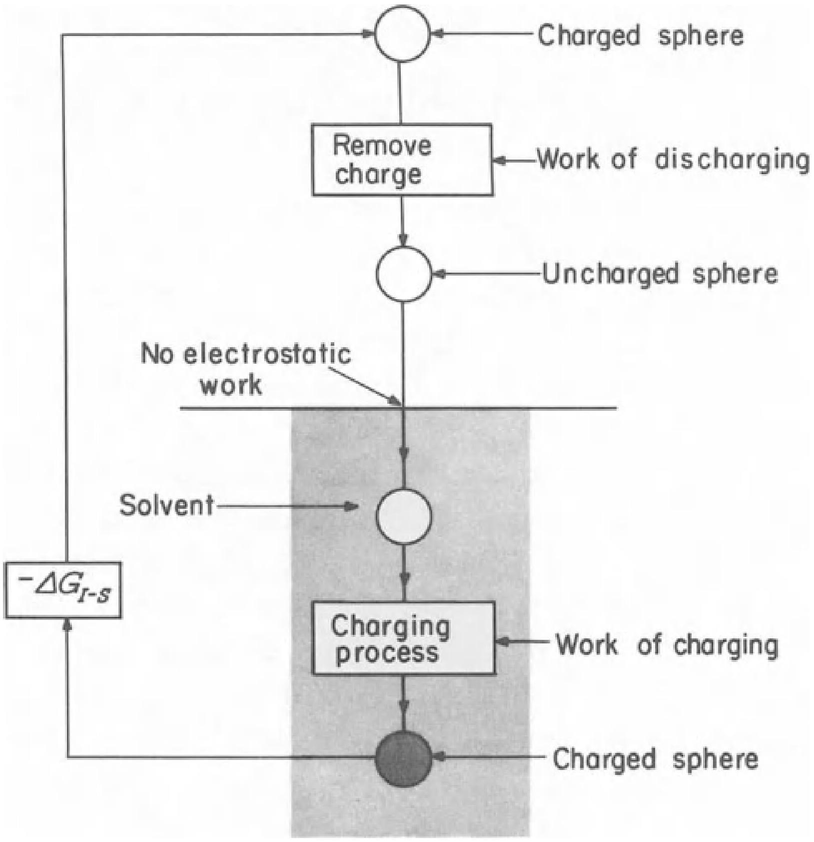


Fig. 2.8. Method of calculating the work of transferring a charged sphere from vacuum into the solvent by a thermodynamic cycle.

interactional work is assumed to arise from the charge on the ion.[†] (3) Then, the charge on the sphere inside the solvent is restored to the full value $z_i e_0$—one says, the sphere is charged up to the value $z_i e_0$—, and the charging work W_3 is computed. (4) Finally, the ion is transferred from the solvent to vacuum. Since this transfer process is opposite to that involved in the definition of the free energy ΔG_{I-S} of ion–solvent interactions, the work W_4 associated with this last step of the cycle, i.e., the transfer of an ion from the solvent to vacuum, yields $-\Delta G_{I-S}$.

Now, if the algebraic sum of the work terms associated with the steps of the cycle is set equal to zero, one gets

$$W_1 + W_2 + W_3 + W_4 = 0$$

or

$$\begin{matrix}\text{Work of discharging}\\ \text{ion in vacuum}\end{matrix} + 0 + \begin{matrix}\text{Work of charging}\\ \text{ion in solvent}\end{matrix} - \Delta G_{I-S} = 0$$

i.e.,

$$\Delta G_{I-S} = \begin{matrix}\text{Work of discharging}\\ \text{ion in vacuum}\end{matrix} + \begin{matrix}\text{Work of charging}\\ \text{ion in solvent}\end{matrix} \tag{2.1}$$

2.2.3. The Electrostatic Potential at the Surface of a Charged Sphere

In considering the work of charging up a sphere *in a vacuum*, one starts off from the definition of electrostatic potential. To facilitate the definition, it is assumed that there exists a reservoir of charge at an infinite distance away from the sphere under consideration.

The electrostatic potential ψ at a point in space is then defined as the work done to transport a unit *positive* charge from infinity up to that point. Thus, the potential ψ_r at a distance r from a charged sphere is the work done to transport a unit positive charge from infinity up to a distance r from the sphere. The reason there is a need to do work is that the charged sphere exerts an electric force on the charge being transported. The *magnitude* of the potential, $|\psi_r|$, i.e., the work done on the unit charge, is given by the electric field X_r (i.e., the electric *force* operating on the unit charge) times the distance r through which the charge is carried

$$|\psi_r| = X_r \cdot r \tag{2.2}$$

[†] What happens when charges cross interfaces is discussed in Section 7.2.

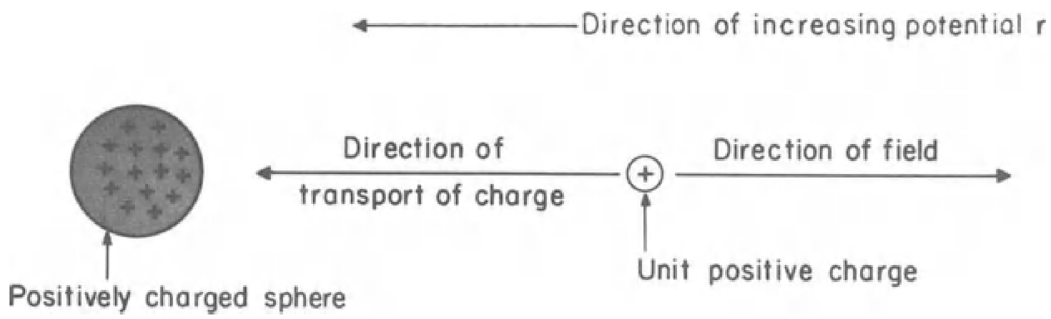


Fig. 2.9. The relative directions of the field due to a charged sphere, of the movement of the test charge, and of increasing electrostatic potential.

The *sign* of the potential ψ_r is thought out as follows. Suppose the sphere is charged positively. Then it exerts a repulsive force on the unit *positive* charge, and the potential ψ_r, the work which has to be done *by* an external agency in transporting the unit positive charge, i.e., overcoming the repulsive interaction, will be taken to be positive. But the electric force of the charged sphere on the unit positive charge, i.e., the field, acts in a direction *opposite* to that in which the charge is being moved (Fig. 2.9). Since both the field and the direction of transport are vectors (quantities with direction and magnitude) and since the vectors point in opposite ways, their product is negative.[†] Hence, to relate the *positive* potential ψ_r to the product of the field and distance, it is necessary to state that

$$\psi_r = -X_r \cdot r \tag{2.3}$$

Equation (2.2) for the electrostatic potential is valid only if the field X_r acting on the unit positive charge remains the same, independent of the distance of the unit charge from the source of the field. Suppose, however, as will be seen to be the case with the field due to a charged sphere, the field varies with distance from the source of the field. Then one must allow for the inconstancy of the field in the definition of the potential at a point. What one does is to take the field X_r as a constant over an infinitesimally short distance dr. In this case, the electrostatic potential ψ_r at a point r is obtained by summing up all the little bits of work, $X_r\,dr$, as the unit charge is carried from infinity up to the point r in steps of length dr, i.e.,

$$\psi_r = -\int_{\infty}^{r} X_r\,dr \tag{2.4}$$

[†] The product of two vectors A and B is $AB\cos\theta$, where θ is the angle between the two vectors. If the vectors are in opposite directions, $\theta = \pi$ and $\cos\theta = -1$ and the product is $-AB$.

By inserting an upper limit of r_i in the integration, one can indicate that the unit charge has been brought up to the surface of the sphere. Thus, the electrostatic potential at the surface of the charged sphere is

$$\psi_{r_i} = -\int_{\infty}^{r_i} X_r \, dr \tag{2.5}$$

The electric force X_r operating on a unit charge *in vacuum* is obtained from Coulomb's law for the electric force F between two charges q_1 and q_2, i.e.,

$$F = \frac{q_1 q_2}{r^2} \tag{2.6}$$

where r is the distance between the charges. Thus, by setting $q_1 = q$ and $q_2 = 1$, the electric force per unit charge (i.e., the electric field X_r) due to a charge q becomes

$$X_r = \frac{q}{r^2} \tag{2.7}$$

Substituting for X_r in equation (2.5), one gets for the potential at the surface of the sphere

$$\begin{aligned} \psi_{r_i} &= -\int_{\infty}^{r_i} \frac{q}{r^2} \, dr \\ &= +\frac{q}{r_i} \end{aligned} \tag{2.8}$$

2.2.4. On the Electrostatics of Charging (or Discharging) Spheres

The electrostatic potential at the surface of the sphere pertains to the work of transporting a *unit* charge to the sphere; hence, the work done in transporting a charge of any other magnitude is simply given by the product of the potential and the magnitude of that charge. It will be noticed, however, that the electrostatic potential at the surface of the sphere varies with the charge q on the sphere. So the work of adding on any charge to the sphere depends upon *how much charge q the sphere already has.* This is awkward. So the best thing to do is start with an uncharged sphere ($q = 0$) and add charge onto it in little driblets or infinitesimal amounts, dq, each of which requires an infinitesimal amount of work, dw, given by the product of the potential and the infinitesimal charge dq, i.e.,

$$dw = \psi_{r_i} \, dq \tag{2.9}$$

This procedure is known as a *charging process.*

If, therefore, one starts with an *uncharged* sphere of radius r_i *in a vacuum* and slowly builds up the charge from zero to a final value which can be taken as z_ie_0, corresponding to a charge on an ion containing z_i electronic charges, then the total work consists of all the little elements of work, dw, i.e.,

$$\begin{aligned} W &= \int dw = \int_0^{z_ie_0} \psi_{r_i} dq \\ &= \int_0^{z_ie_0} \frac{q}{r_i}\, dq = \left[\frac{q^2}{2r_i}\right]_0^{z_ie_0} \\ &= \frac{(z_ie_0)^2}{2r_i} \end{aligned} \tag{2.10}$$

Obviously, the work of discharging a charged sphere in a vacuum is the negative of the charging work because, in the discharging process, one is taking away charge from a charged sphere, i.e.,

$$W_{\text{disch}} = -\frac{(z_ie_0)^2}{2r_i} \tag{2.11}$$

Now that the process of discharging a sphere in a *vacuum* has been analyzed, one can consider the charging process when the sphere is placed inside the *solvent*. The question is: can one use the vacuum formula for the electrostatic potential at the surface of the sphere, i.e., Eq. (2.8)?

$$\psi_{r_i} = \frac{q}{r_i}$$

The answer is no, because this formula was obtained from the expression for the electric force between two charges in a vacuum and it is known that the electric force between two charges depends on the medium between them. The electric force in the presence of a material medium is less than that which operates when only a vacuum is present. A simple explanation of this phenomenon is given later on (*cf.* Section 2.5). The ratio of the force in vacuum to the force in the medium is a characteristic of the medium and is known as its *dielectric constant* ε (Fig. 2.10)

$$\varepsilon = \frac{\text{Electric force in vacuum}}{\text{Electric force in medium}} \tag{2.12}$$

Hence, the coulombic force between two charges in a medium of dielectric constant ε is

$$F = \frac{q_1q_2}{\varepsilon r^2} \tag{2.13}$$

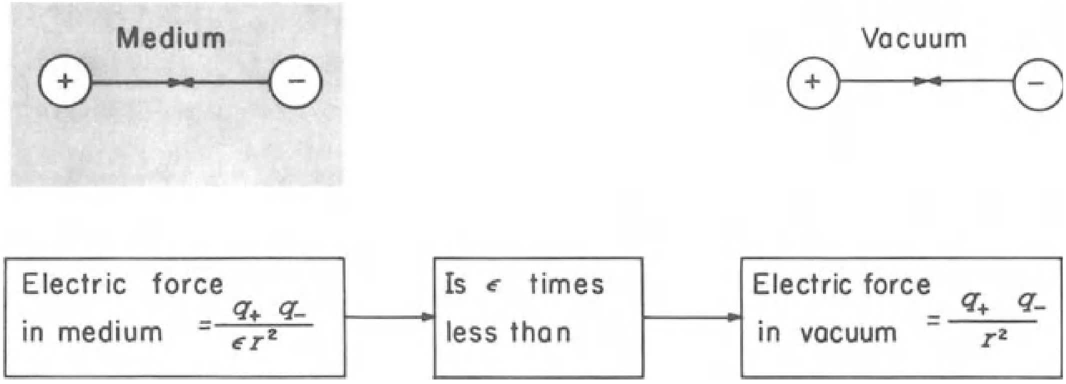


Fig. 2.10. The electric force between two charges q_+ and q_- in vacuum and in a medium.

and the electric field becomes

$$X = \frac{q}{\varepsilon r^2} \tag{2.14}$$

Hence, the potential at the surface of the sphere of radius r_i placed in a medium of dielectric constant ε is

$$\psi = \frac{q}{\varepsilon r_i} \tag{2.15}$$

In terms of this expression for the electrostatic potential at the surface of a charged sphere situated in a medium of dielectric constant ε, the electrostatic work of charging a sphere becomes

$$\begin{aligned} W_{\text{ch.}} &= \int_0^{z_i e_0} \psi_{r_i} \, dq \\ &= \int_0^{z_i e_0} \frac{q}{\varepsilon r_i} \, dq \\ &= \frac{(z_i e_0)^2}{2\varepsilon r_i} \end{aligned} \tag{2.16}$$

2.2.5. The Born Expression for the Free Energy of Ion–Solvent Interactions

Now that the basic electrostatics of charging and discharging spheres has been presented, it can be immediately applied to the model suggested by Born for the calculation of the free energy of ion–solvent interactions.

It has been argued in Section 2.2.2 (see also Fig. 2.8) that the free energy of ion–solvent interactions, ΔG_{I-S}, is given by the sum of the work done to discharge an ion in vacuum and the work done to charge it up in the solvent of dielectric constant ε_s. Since, according to the Born model, a sphere (of radius r_i and charge $z_i e_0$) is considered to be equivalent to an ion of radius r_i and charge $z_i e_0$, it follows that the work of discharging an ion in vacuum is equal to the work of discharging the equivalent sphere in vacuum and the work of charging an ion in the solvent is equal to the work of charging the equivalent sphere in the solvent. Hence [*cf.* Eq. (2.1)],

$$\begin{aligned}\Delta G_{I-S} &= \text{Work of discharging equivalent sphere in vacuum} \\ &\quad + \text{Work of charging equivalent sphere in solvent} \\ &= -\frac{(z_i e_0)^2}{2r_i} + \frac{(z_i e_0)^2}{2\varepsilon_s r_i} \qquad \text{per ion} \\ &= -\frac{(z_i e_0)^2}{2r_i}\left(1 - \frac{1}{\varepsilon_s}\right) \qquad \text{per ion} \\ &= -N_A \frac{(z_i e_0)^2}{2r_i}\left(1 - \frac{1}{\varepsilon_s}\right) \qquad \text{per mole of ions} \qquad (2.17)\end{aligned}$$

where N_A is the Avogadro number (Fig. 2.11).

Thus, by considering that the free energy of ion–solvent interactions is given by the net electrostatic work of discharging a sphere (of the same size and charge as the ion) in a vacuum, of transferring the discharged

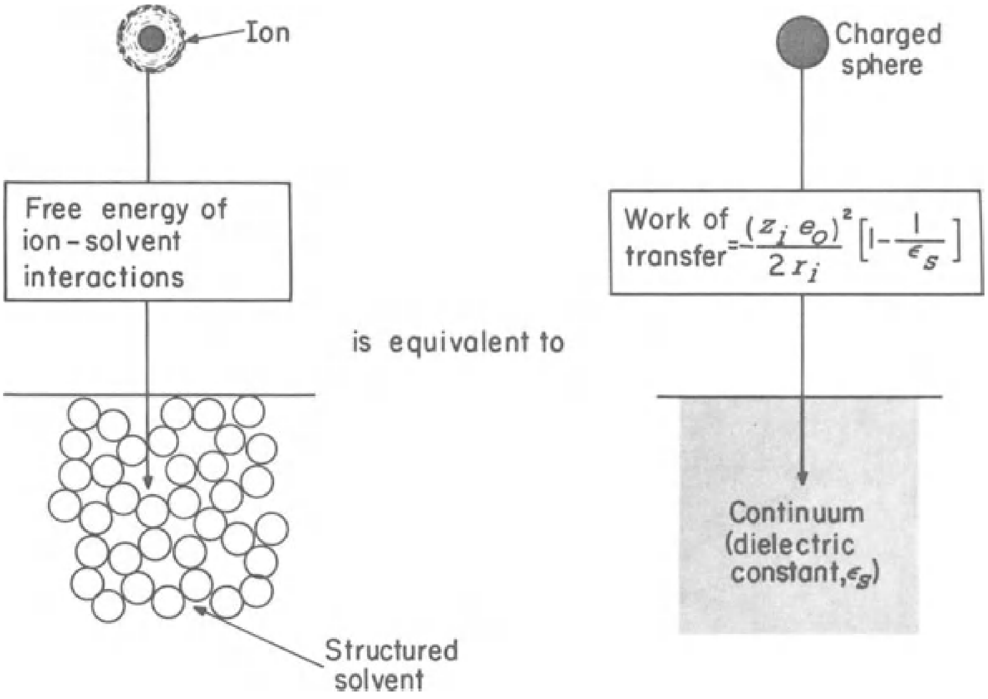


Fig. 2.11. The free-energy change resulting from the transfer of an ion from a vacuum into the solvent.

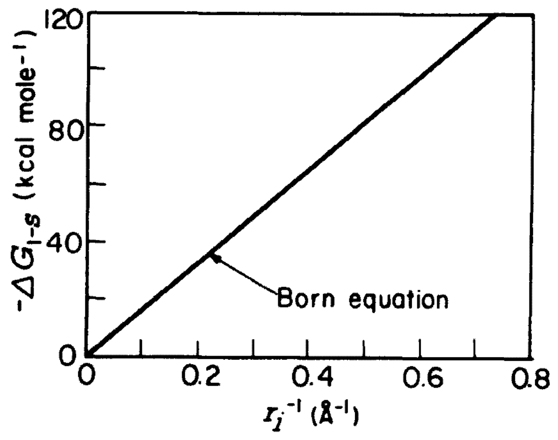


Fig. 2.12. The free energy of ion–solvent interactions as a function of the reciprocal of the ionic radius.

sphere into a medium with the same dielectric constant as the solvent, and of then charging the sphere till it has the same charge as the ion, the Born model has yielded the free-energy change resulting from the transfer of ions from a vacuum to solvent.

What is the importance of this free-energy change? The importance derives from the fact that systems in nature try to attain a state of minimum free energy. Thus, if the ΔG_{I-S} is negative, then ions exist more stably in the solvent than in vacuum. Since the dielectric constant of any medium is greater than unity, $1 > 1/\varepsilon_s$, and, therefore, ΔG_{I-S} is always negative; hence, the Born equation (2.17) shows that all ions would rather be involved in ion–solvent interactions than be left in vacuum. The Born equation predicts that the smaller the ion (smaller r_i) and the larger the dielectric constant ε_s, the greater will be the magnitude of the free-energy change in the negative direction (Fig. 2.12).

If one stands back and looks at the situation with regard to ions and their existence in solvents before and after the theory of Born (1920), several points emerge. One set out to discover the interactions of ions with a solvent, and one ended up doing a problem in electrostatics. This illustrates a feature of electrochemistry—it often involves the application of electrostatics to chemistry. The basis of this link is of course that electrochemistry is involved with ions and charged interfaces, and these can be most simply represented in models by charged spheres and charged plates, the stuff with which electrostatics deals.

One has also seen in the Born theory of ion–solvent interactions an example of very simple thinking based on models. A complicated situation has been reduced to a simple one by the choice of a simple model. In the case of ion–solvent interactions, once the analogies between an ion and a charged sphere and between a structured solved and a dielectric continuum are stressed, the rest is easy.

It will be shown later that, not unexpectedly, the Born model oversimplifies the problem, but one must see the model in its historical perspective. It was proposed at a time when the very existence of charged particles in solution was questioned. Indeed, the Born approach to ion–solvent interactions and the fact that it gave answers of the same order of magnitude as experiment (*cf.* Section 2.2.9) helped to confirm the hypothesis that ions exist in solution. Seen in historical perspective, the simple Born model may be recognized as an important step forward.

2.2.6. The Enthalpy and Entropy of Ion–Solvent Interactions

Before finding out about the experimental testing of the Born theory, it is preferable to recover from the theoretical expression for the free energy ΔG_{I-S}, the enthalpy (heat) and entropy changes associated with ion–solvent interactions. This is because it is the *heat* of ion–solvent interactions, rather than the free energy, which is obtained directly from the experimentally measured heat changes observed to occur when solids containing ions are dissolved in a solvent, i.e., when ion–solvent interactions are provoked.

By making use of the combined first and second laws ($dE = T\,dS - p\,dV$) in $G = H - TS = E + PV - TS$, one gets

$$dG = V\,dP - S\,dT \tag{2.18}$$

and, at constant pressure,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{2.19}$$

Thus, applying (2.19) to a transformation from state 1 to state 2 results in

$$\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -\,(S_2 - S_1) \tag{2.19a}$$

Hence

$$\frac{\partial \Delta G}{\partial T} = -\,\Delta S \tag{2.19b}$$

since $\Delta G = G_2 - G_1$ and $\Delta S = S_2 - S_1$.

Hence, all one has to do to get the entropy changes associated with ion–solvent interactions is to differentiate ΔG_{I-S} [given by Eq. (2.17)] with respect to temperature. During this differentiation, the question arises whether the dielectric constant should be treated as a constant or as a variable with temperature. At this stage of the presentation, one does not have a feel for dielectric constants to be able to answer the question (see, however, Section 2.5); so one has to appeal to experiment. It turns out that the dielectric constant does vary with temperature (Table 2.2) and must therefore be treated as a variable in differentiating Eq. (2.17) with respect to temperature.

Thus, the entropy change due to ion–solvent interactions is

$$\Delta S_{I-S} = -\left(\frac{\partial \Delta G_{I-S}}{\partial T}\right)_P = \frac{N_A(z_i e_0)^2}{2r_i} \frac{1}{\varepsilon_s^2} \frac{\partial \varepsilon_s}{\partial T} \tag{2.20}$$

and from

$$\Delta H_{I-S} = \Delta G_{I-S} + T\Delta S_{I-S} \tag{2.21}$$

one has for the heat change:

$$\Delta H_{I-S} = -\frac{N_A z_i^2 e_0^2}{2r_i}\left[1 - \frac{1}{\varepsilon_s} - \frac{T}{\varepsilon_s^2}\frac{\partial \varepsilon_s}{\partial T}\right] \tag{2.22}$$

Now that one has a theoretical expression for a *heat* change, it is time to think of comparing the predictions of the Born theory with experiment. There are, however, a few conceptual questions first to be considered.

TABLE 2.2

Variation of Dielectric Constant of Water with Temperature

Temperature, °C	Dielectric constant ε_W	Temperature, °C	Dielectric constant ε_W
0	87.74	50	69.91
10	83.83	60	66.81
20	80.10	70	63.85
25	78.30	80	61.02
30	76.54	90	58.31
40	73.15	100	55.72

the resumption of the normal bulk structure, cannot be sharply defined; the bulk properties and structure are asymptotically approached.

These structural changes in the primary and secondary regions are generally referred to as *solvation* (or as *hydration* when water is the solvent). Since they result from interactions between the ion and the surrounding solvent, one often uses the terms solvation and ion–solvent interactions synonymously; the former is the structural result of the latter.

2.3.3. The Ion–Dipole Model of Ion–Solvent Interactions

The above description of the solvent surrounding an ion can now be used as the basis of a *structural* treatment of ion–solvent interactions, initiated by Bernal and Fowler (1933).

Consider an isolated ion in the gas phase above the solvent. The total work done to transfer this ion from a very dilute gas of ions to the inside of the solvent defines the free energy of solvation (*cf.* Section 2.2.1), i.e., the free-energy change arising from ion–solvent interactions, ΔG_{I-S}. This free-energy change is composed of both enthalpy changes and entropy changes. The latter arise from changes in the degrees of freedom (translational, rotational, and vibrational) experienced by the water molecules as they come out of the water structure and associate with an ion. In this simplified treatment, only the enthalpy changes will be treated.

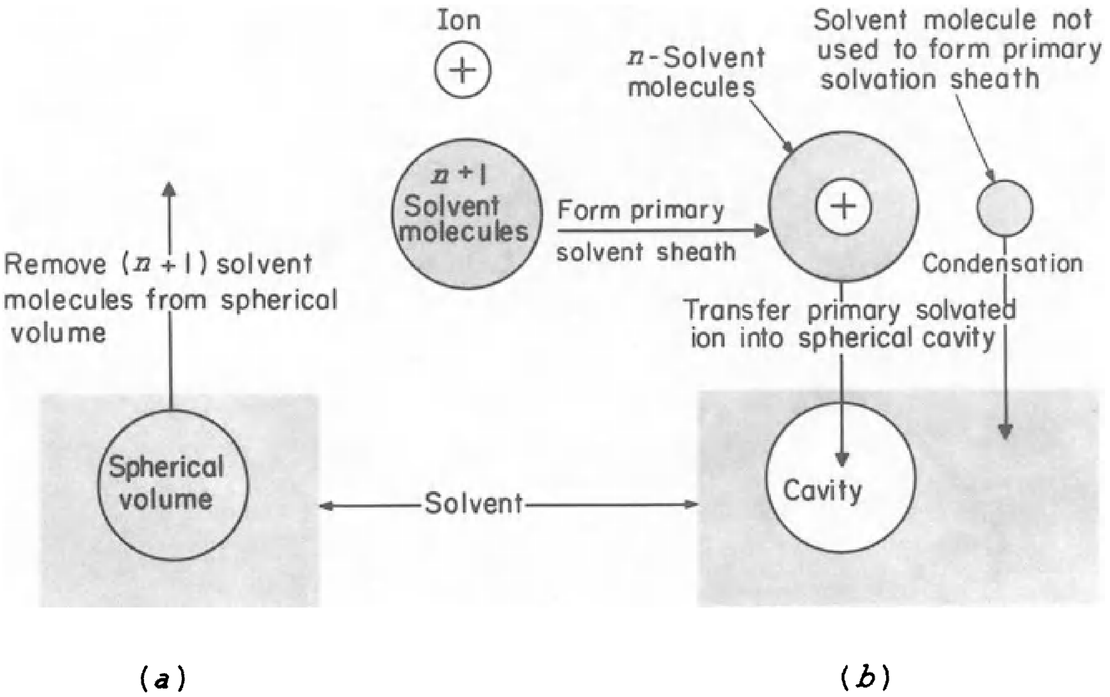


Fig. 2.29. A thought experiment to separate out various aspects of ion–solvent interactions.

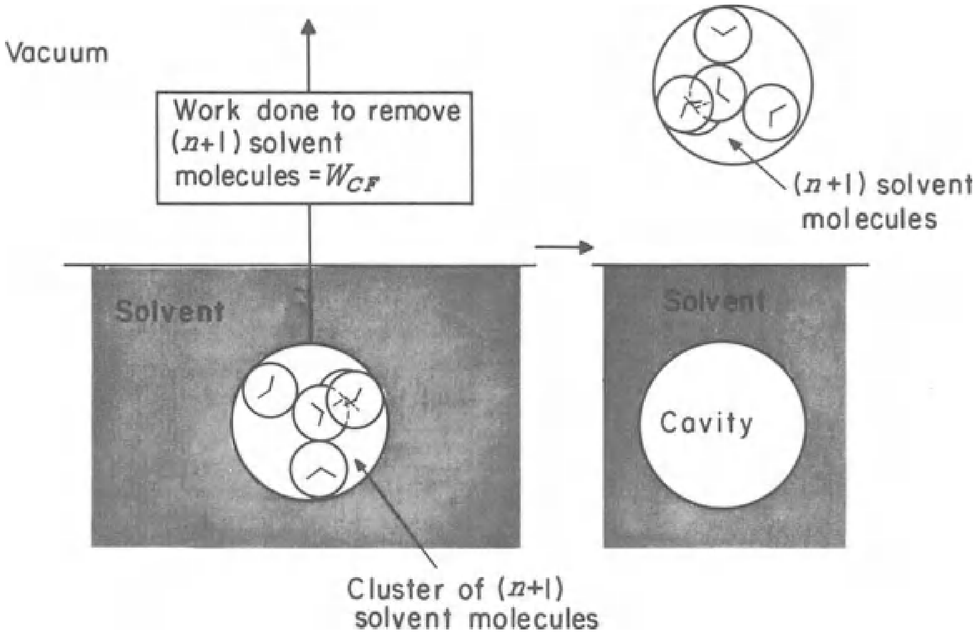


Fig. 2.30. The formation of a cavity in the solvent by the removal of $n + 1$ solvent molecules.

The ion–solvent interactions consist of several contributions. There is, for example, the interaction between the ion and the n nearest neighbors which surround the ion and make up the primary solvent sheath (see Fig. 2.28). Then, there is the energy used up for the structure breaking in the secondary region (Fig. 2.28), etc.

To separate out the various aspects of the total interaction, one can consider a thought experiment (Fig. 2.29) proposed by Eley and Evans in which the proper number of solvent dipoles are taken from the solvent to the gas phase and there oriented around the ion (by ion–dipole forces). Finally, the primary solvated ion is transferred into the solvent, upon which structure breaking, etc., occurs.

The steps of this thought experiment will now be described more elaborately.

1. One starts the thought experiment with the knowledge gained from various types of experiment that the primary solvated ion will occupy a volume corresponding to the volume of n primary solvent molecules *plus* one more to make room for the bare ion.[†] This volume corresponding to

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[†] Note that, as a first approximation, it is assumed that the volume of a water molecule is the same as that of a bare ion. For some ions, this is a reasonable approximation. Thus, the radius of a water molecule is 1.38 Å and that of K^+ is 1.33 Å.

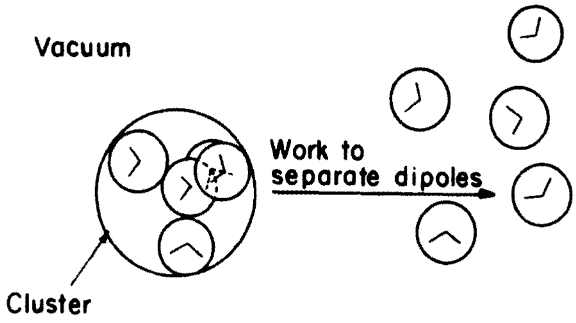

Fig. 2.31. Dissociation of a cluster of $n + 1$ molecules by breaking the bonds holding them together.

$n + 1$ solvent molecules must be made available in the solvent for immersing a primary solvated ion. Hence, $n + 1$ molecules will be removed from the solvent and taken into the vacuum phase (Fig. 2.30). Thus, the cavity which is left in the solvent will be large enough to accommodate an ion plus n molecules in its *primary solvation sheath*. Let this work of cavity formation be represented by W_{CF}.

2. Before the $n + 1$ solvent molecules just removed from the solvent can orient around the ion in the gas phase, they must be detached from the cluster of $n + 1$ molecules and made free to orient around the ion. To make this feasible, the bonds holding together these $n + 1$ solvent dipoles in the cluster are broken asunder (Fig. 2.31), i.e., the group is dissociated in the gas phase into $n + 1$ separate molecules. This dissociation will involve an amount of work represented by W_D.

3. Next, ion–dipole bonds are forged between the ion and n out of the $n + 1$ solvent dipoles, and, thus, the primary solvent sheath is formed. The work of interaction between an ion and a dipole (of moment μ_s and radius r_s) for the configuration shown in Fig. 2.32 is approximately

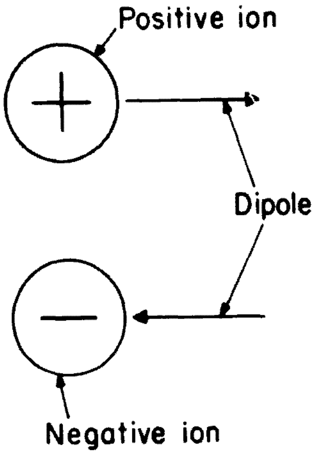

Fig. 2.32. The minimum interaction-energy orientation of a dipole to an ion.

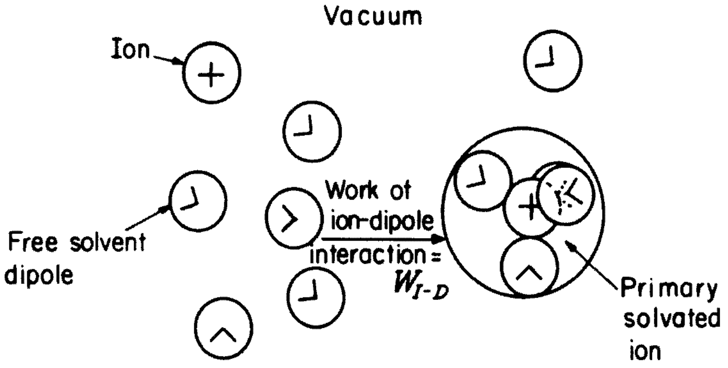

Fig. 2.33. Formation of a primary solvated ion.

given by (*cf.* Appendix 2.2)[†]

$$-\frac{z_i e_0 \mu_s}{(r_i + r_s)^2}$$

But, it is n solvent molecules that are involved in the primary solvent sheath. Hence, per mole of ions, the ion–dipole interaction work (Fig. 2.33) is[‡]

$$W_{I-D} = -\frac{N_A n z_i e_0 \mu_s}{(r_i + r_s)^2} \tag{2.25}$$

4. Now, the ion together with its primary solvent sheath is transferred from vacuum into the cavity in the solvent (Fig. 2.34). What work is involved in this transfer? A simple way to look at it is to imagine that the solvated ion in the gas phase is discharged and then, still preserving its solvent sheath, is sneaked into the cavity formed in step 1 of the thought experiment (*cf.* Fig. 2.30), whereafter the discharged but still solvated ion is charged up to its normal value $z_i e_0$. What has been described is simply a Born charging process (*cf.* Section 2.2.5). There is, however, an important difference between the Born charging done here and that previously described (Fig. 2.35). It is not a bare ion but a primary solvated ion which undergoes the charging process. Hence, the radius to be used in the Born expression (2.22) is no longer the crystallographic radius r_i but the radius of a solvated ion, i.e., $r_i + 2r_s$.

Since it has been decided to deal only with enthalpies (or heat-content

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[†] Note that the dielectric constant does not appear in this expression because there is only vacuum between the dipole (i.e., the water molecule) and the (adjacent) ion.

[‡] Note that the ion–dipole work always contributes a negative quantity to the heat of solvation, independently of the sign of z_i, because the dipole always orients so that that pole is in contact with the ion which makes the interaction attractive.

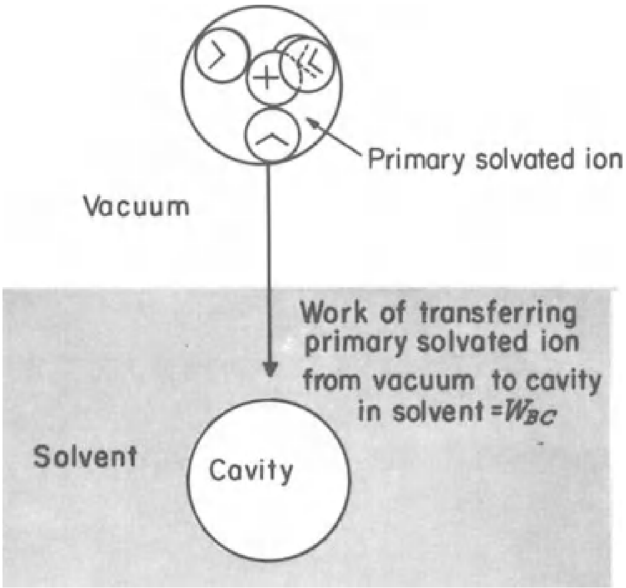

Fig. 2.34. Transfer of a primary solvated ion from vacuum into a cavity in the solvent.

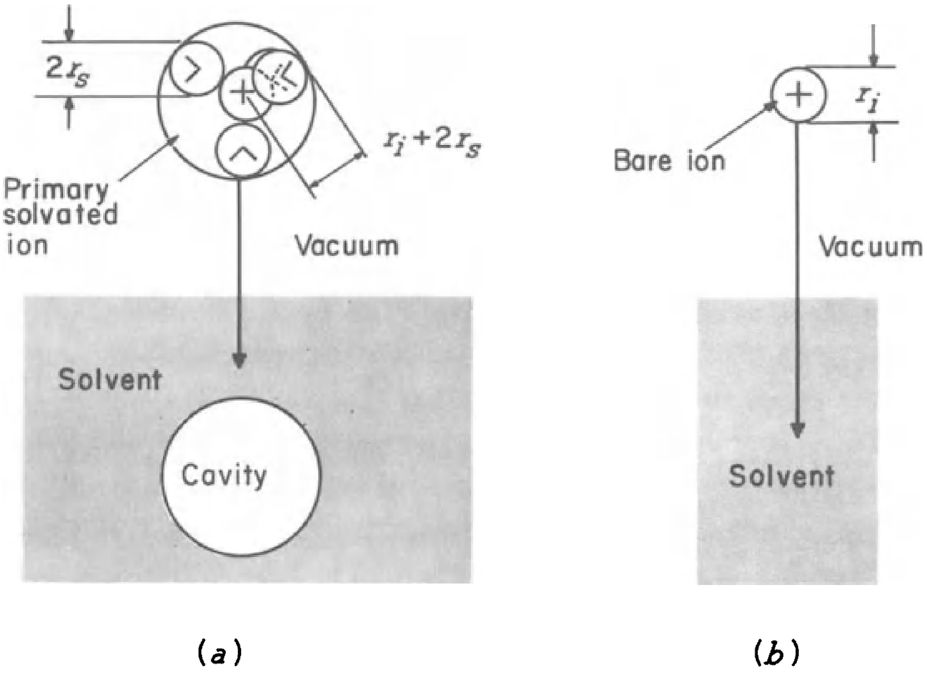

Fig. 2.35. The difference between the Born charging process in (a) the ion–dipole model of solvation in which a primary solvated ion of radius $r_i + 2r_s$ is transferred into the solvent (Section 2.3.3) and in (b) the nonstructural model of Born (*cf.* Section 2.2.5) in which a bare ion of radius r_i is involved.

changes), one can set the work of transferring a solvated ion from vacuum into a cavity in the solvent equal to the Born *heat* of solvation. This contribution to the total heat of ion–solvent interactions shall be called the *Born charging contribution*, W_{BC}. Thus, per mole of ions,

$$W_{\mathrm{BC}} = -\frac{N_A(z_i e_0)^2}{2(r_i + 2r_s)}\left(1 - \frac{1}{\varepsilon_s} - \frac{T}{\varepsilon_s^2}\frac{\partial \varepsilon_s}{\partial T}\right) \tag{2.26}$$

Is it reasonable to use here an equation based on the Born model even though one motivation for this structural treatment of solvation is to get away from the Born nonstructural approach? The justification is as follows. The radius $r_i + 2r_s$ has been precisely defined (its ambiguity was a problem in the Born model), the water outside the cavity is, at this stage of the thought experiment, normal and undisturbed, and, therefore, its dielectric constant (another ambiguity of the Born model) should be that of *bulk* water. Thus, by considering the process of ion–solvent interactions as occurring in steps with corresponding heat-content changes, one of the steps, namely, the introduction of a primary solvated ion into an *undisturbed* solvent, has been made to resemble a Born charging process.

5. Once the cavity is filled up with the solvated ion and the Born charging is carried out, one must ask whether the solvated ion leaves the surrounding water undisturbed. It does not (Figs. 2.28 and 2.36). The introduction of the primary solvated ion into the cavity does lead to some

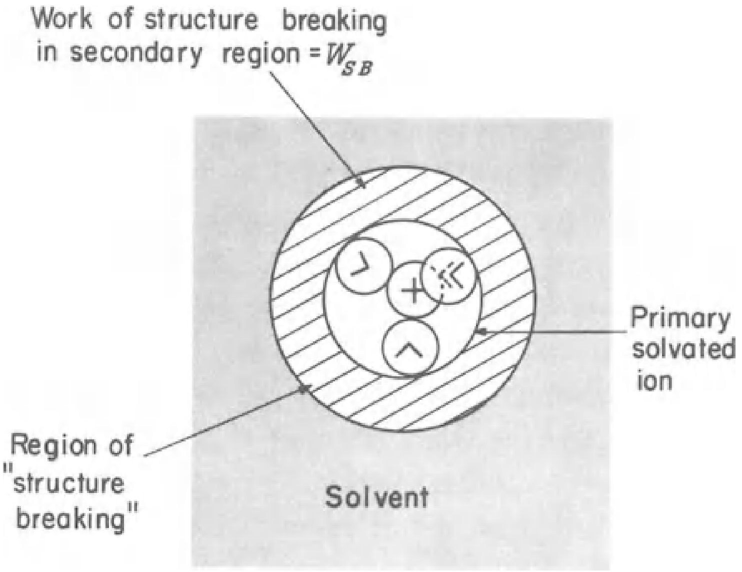

Fig. 2.36. The introduction of a primary solvated ion into the cavity causes disturbance to the structure of the solvent in the immediate vicinity of the solvated ion.

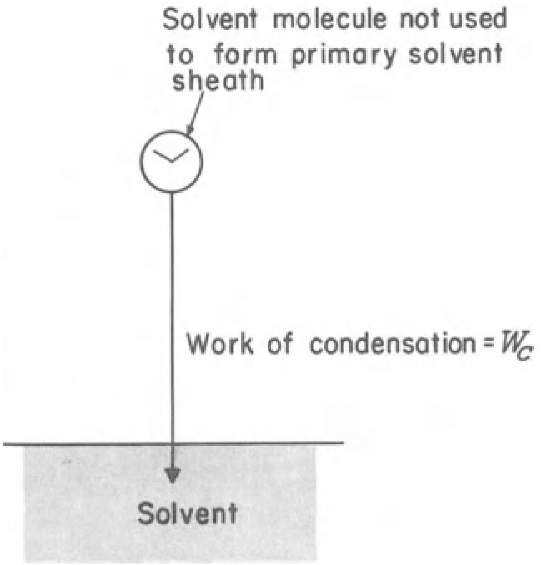

Fig. 2.37. The condensation of a water molecule left behind in vacuum because it was not used to form the primary solvent sheath.

disturbance of the structure of the surrounding solvent. In fact, this is the structure breaking that has been referred to in dealing with the secondary region, between the primary solvent sheath and the bulk water far away from the ion (Fig. 2.28). Let this work of structure breaking be represented by W_{SB}.

6. One must check up on the cycle now. Have all the solvent molecules (taken out of the solvent into vacuum to create the cavity) been returned to the solvent? Of the $n + 1$ solvent molecules removed, only n have returned in the company of the ion as members of its solvation sheath. The one water molecule which did not become part of the solvation sheath of the ion and which has been left behind in vacuum, has to be returned to the solvent to complete the cycle (Fig. 2.37). The work involved in this process is equal to the work of condensation, W_C.

Now, all the solvent molecules which were removed from the solvent in the thought experiment have returned to the solvent. In addition, the ion which was in vacuum at the beginning of the thought experiment has been transferred into the solvent. Hence, any work resulting from plunging the ion into the solvent must result purely from ion–solvent interactions. This work (or heat)[†] of solvation or ion–solvent interactions is therefore

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[†] Note that, as already stated, there is an approximation being made here: It is the free-energy change which is exactly equal to the work done (Appendix 2.1). One has

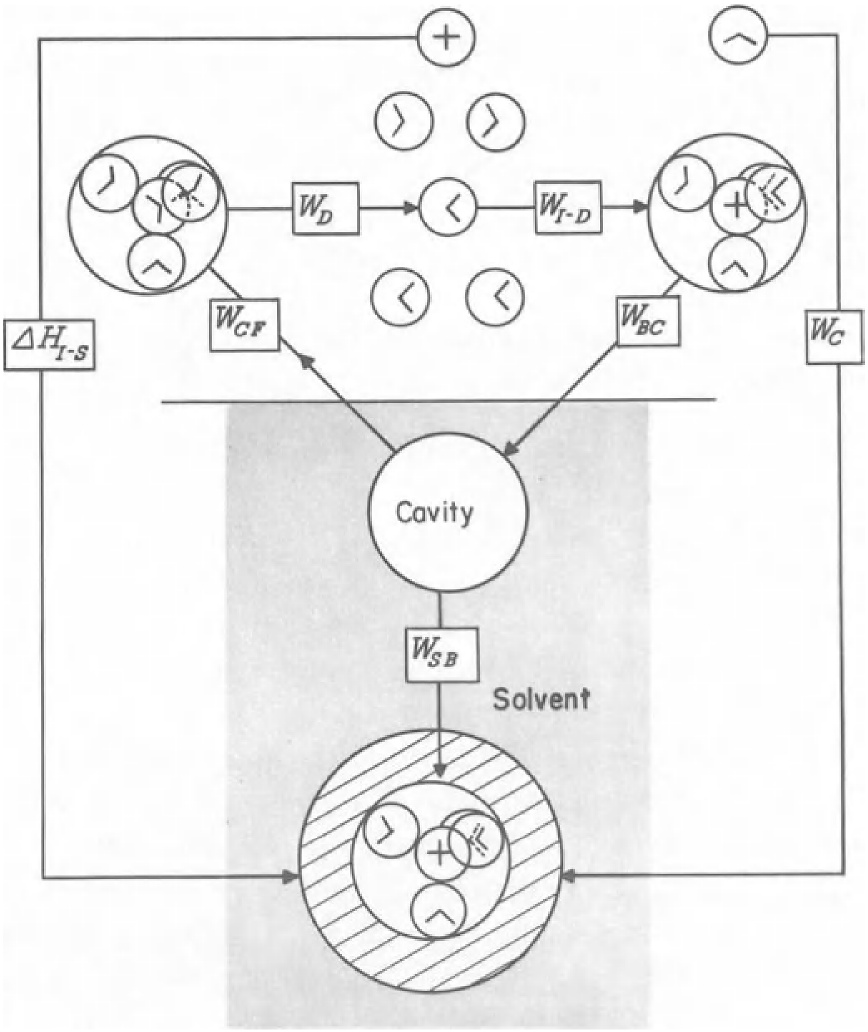


Fig. 2.38. How the total heat $\Delta H_{I\text{–}S}$ of ion–solvent interactions has been separated in a thought experiment into the various steps of cavity formation W_{CF}, cluster dissociation W_D, formation of primary solvated ion $W_{I\text{–}D}$, Born charging W_{BC}, structure breaking W_{SB}, and condensation, W_C.

given by (Fig. 2.38) the sum of all the pieces of work performed in each step, i.e.,

$$\Delta H_{I-S} = W_{\mathrm{CF}} + W_D + W_{I-D} + W_{\mathrm{BC}} + W_{\mathrm{SB}} + W_C \tag{2.27}$$

$$= W + W_{I-D} + W_{\mathrm{BC}} \tag{2.28}$$

where

$$W = W_{\mathrm{CF}} + W_D + W_{\mathrm{SB}} + W_C \tag{2.29}$$

---

neglected $T\Delta S$, where ΔS is the change of entropy during the solvation process. Structural theories of the entropy of hydration are known but will not be discussed here. The error introduced by the approximation is about 10%.

Hence,

$$\Delta H_{I-S} = W - \frac{N_A n z_i e_0 \mu_s}{(r_i + r_s)^2} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_s)} \left(1 - \frac{1}{\varepsilon_s} - \frac{T}{\varepsilon_s^2} \frac{\partial \varepsilon_s}{\partial T}\right) \tag{2.30}$$

where the Avogadro number has been introduced to get the heat of solvation per mole of ions.

2.3.4. Evaluation of the Terms in the Ion–Dipole Approach to the Heat of Solvation

The Born term, i.e., the last term in Eq. (2.30), can be easily calculated. One uses the crystallographic radius r_i of the ion, the radius r_s of the solvent molecules, and the bulk dielectric constant ε_s of the solvent. The ion–dipole term, i.e., the second term in the expression (2.30) for the heat of solvation, can also be calculated without difficulty *provided* one knows—or estimates—the number n of solvent molecules which coordinate (or are nearest neighbors to) the ion.

The first term in Eq. (2.30), however, is more awkward. It will be recalled [Eq. (2.29)] that it consists of W_{CF}, the work of forming a cavity in the solvent by the removal into the gas phase of a cluster of $n + 1$ solvent molecules; W_D, the work of splitting up the cluster and separating to infinity the $n + 1$ solvent molecules; W_{SB}, the work of altering the orientation of the solvent molecules in the solvent around the primary solvated ions; and W_C, the work of condensing the one solvent molecule (from the cluster) which is not used in the solvation of the ion.

The work W_D of breaking the cluster and separating the $n + 1$ solvent molecules can be considered either as the work of separating dipoles, i.e., the work arising from dipole–dipole forces or, in the case of hydrogen-bonded liquids such as water, the work of breaking hydrogen bonds (Fig. 2.39). Since about 5 kcal mole^{-1} is required to break hydrogen bonds, the value of W_D depends on the value of n in the cluster of $n + 1$ solvent mole-

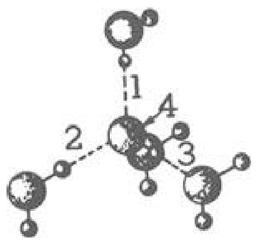


Fig. 2.39. Four hydrogen bonds (which are numbered) must be broken to separate the cluster of 4 + 1 = 5 water molecules.

cules which are removed from the solvent to make room for an ion and its n nearest neighbors. If, for example, an ion surrounds itself with four water molecules in a tetrahedral configuration, then the cluster consists of $4 + 1 = 5$ water molecules, and four hydrogen bonds must be broken per cluster to separate the water molecules. Since 1 mole of cluster must be removed from the solvent for the solvation of 1 mole of ions, it is necessary to break 4 moles of hydrogen bonds per mole of ions. This requires $4 \times 5 = 20$ kcal mole^{-1}.

The work W_C of condensing one solvent molecule per ion, or 1 mole of solvent molecules per mole of ions, can be taken from the experimental latent heat of condensation (Fig. 2.40); it is about -10 kcal mole^{-1}.

The cavity formation work W_{CF} and the structure-breaking work W_{SB} can be only roughly calculated. When the $n + 1$ water molecules are removed to form the cavity, a certain number of hydrogen bonds linking these molecules to those outside the cavity are broken (Fig. 2.41). When the primary solvated ion is introduced into the cavity, some of the solvent molecules surrounding the solvated ion have to reorient. This reorientation leads to the breakage of some hydrogen bonds and the formation of others. Thus, if one considers the combined steps of cavity formation *and* structure breaking, a certain *net* number of hydrogen bonds will be broken. Once this number is known, one can easily get $W_{\text{CF}} + W_{\text{SB}}$ by multiplying the net number of hydrogen bonds broken by 5 kcal mole^{-1}.

A simple way of getting this number is to look at the water structure before and after the solvated ion is introduced into the cavity. A careful study of Fig. 2.42 shows that, whereas 12 hydrogen bonds are broken in the cavity formation step involving the removal of $4 + 1 = 5$ water mole-

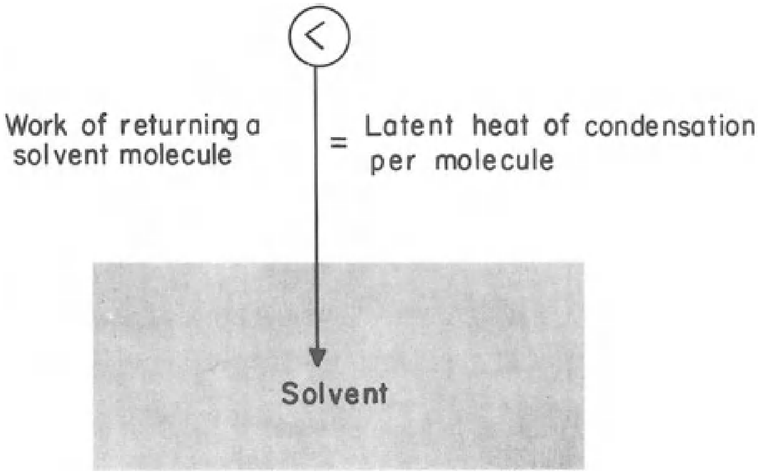


Fig. 2.40. The work of condensing a water molecule is equal to the latent heat of condensation per molecule.

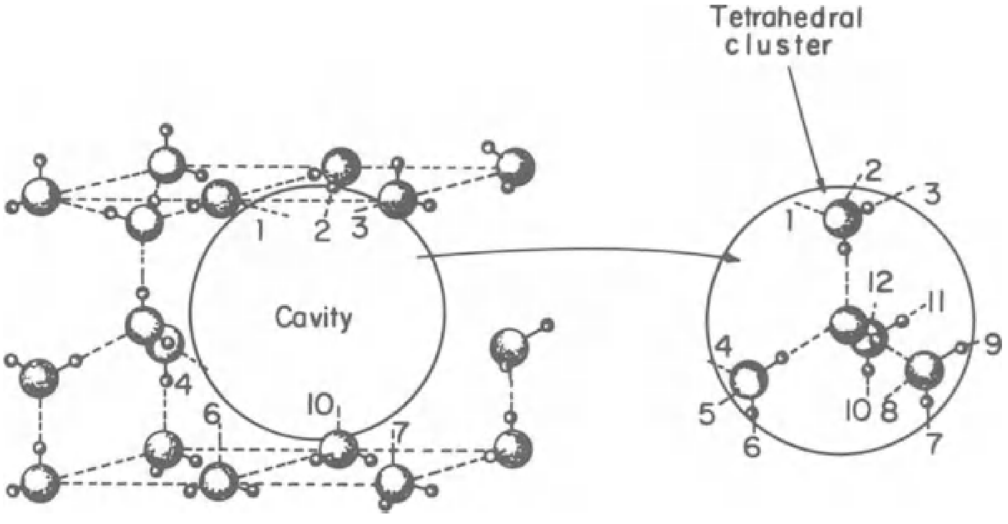
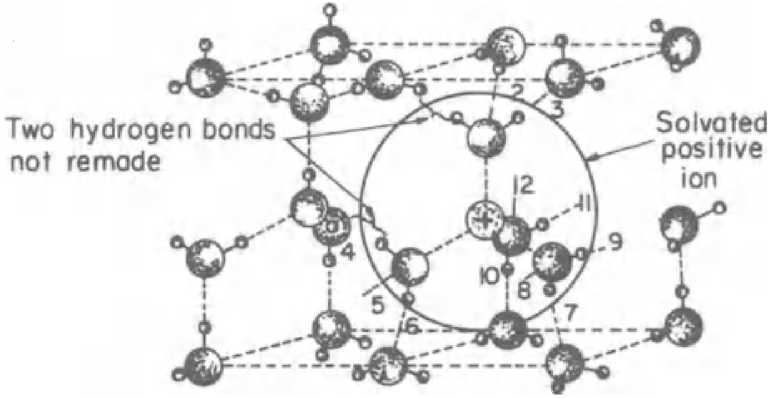


Fig. 2.41. A total of 12 hydrogen bonds are broken when a tetrahedral cluster of water molecules is removed from the solvent to form the cavity (numbers represent broken hydrogen bonds).

Cluster with its broken hydrogen bonds
(*a*)

Solvated positive ion
(*b*)



(*c*)

Fig. 2.42. Schematic diagram to show that, out of four coordinating water molecules [I, II, III, and IV in (a)] in a tetrahedral cluster removed from the cavity, two water molecules [I and II in (b)] reorient in the formation of a primary solvated positive ion, and, therefore, only 10 H bonds [see (a)] are remade when the solvated *positive* ion is introduced into the cavity.

cules, only 10 hydrogen bonds are remade when the primary solvated positive ion is introduced into the cavity. That is, a net number of 2 hydrogen bonds are broken per ion in the combined process of cavity formation and structure breaking. The corresponding heat change $W_{\text{CF}} + W_{\text{SB}}$ is $2 \times 5 = 10$ kcal mole^{-1} of ions.

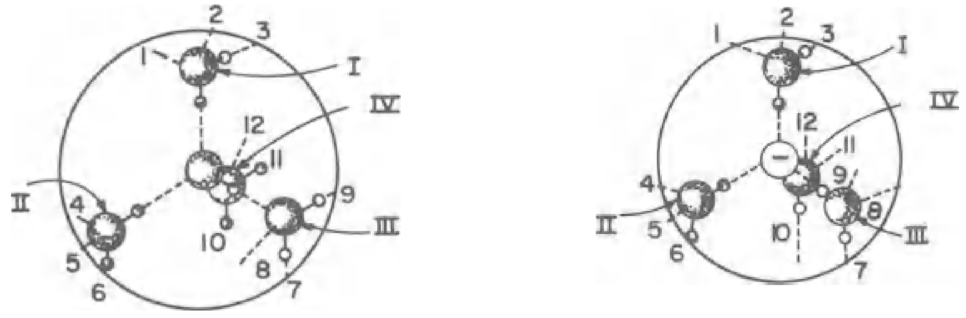
It is now possible to write down for a tetrahedrally coordinated positive ion an approximate value for the work term [*cf.* Eq. (2.29)] $W = W_D + W_C + W_{\text{CF}} + W_{\text{SB}}$. Using the arguments just presented, i.e., $W_D = 20$ kcal mole^{-1}, $W_C = -10$ kcal mole^{-1}, and $W_{\text{CF}} + W_{\text{SB}} = 10$ kcal mole^{-1}, one has for four-coordinated positive ions

$$\begin{aligned} W &= W_D + W_C + W_{\text{CF}} + W_{\text{SB}} \\ &= 20 - 10 + 10 \\ &= 20 \text{ kcal mole}^{-1} \end{aligned} \tag{2.31}$$

Now consider negative ions. If, once again, tetrahedral coordination is considered, then W_D continues to be the work required to break up a cluster of five water molecules, i.e., it is 20 kcal mole^{-1}. The latent heat of condensation of a water molecule obviously remains the same (-10 kcal mole^{-1}) for positive and negative ions. But a perusal of Fig. 2.43 shows that the negative ion differs from the positive ion in that more water molecules have to reorient when the primary solvated ion is introduced into the cavity. In other words, the orientation of water molecules *around* a primary solvated ion is less compatible with the water molecules *in* the primary solvation shell of negative ions than with those of positive ions. Thus, of the 12 hydrogen bonds broken in forming the cavity, only 8 are remade when the cavity is filled up with a solvated ion (see Fig. 2.43). That is, the net number of hydrogen bonds broken in the combined process of cavity formation and structure breaking is four in the case of tetrahedrally coordinated negative ions; and the corresponding work $W_{\text{CF}} + W_{\text{SB}}$ is $4 \times 5 = 20$ kcal mole^{-1}. Consequently, the work W [*cf.* Eq. (2.29)] for four coordinated negative ions is given by

$$\begin{aligned} W &= W_D + W_C + W_{\text{CF}} + W_{\text{SB}} \\ &= 20 - 10 + 20 \\ &= 30 \text{ kcal mole}^{-1} \end{aligned} \tag{2.32}$$

Now that the work W has been evaluated, it can be introduced into Eq. (2.30) for the heat of hydration. Thus, for four coordination, one has



Cluster with its broken H-bonds
(a)

Solvated negative ion
(b)

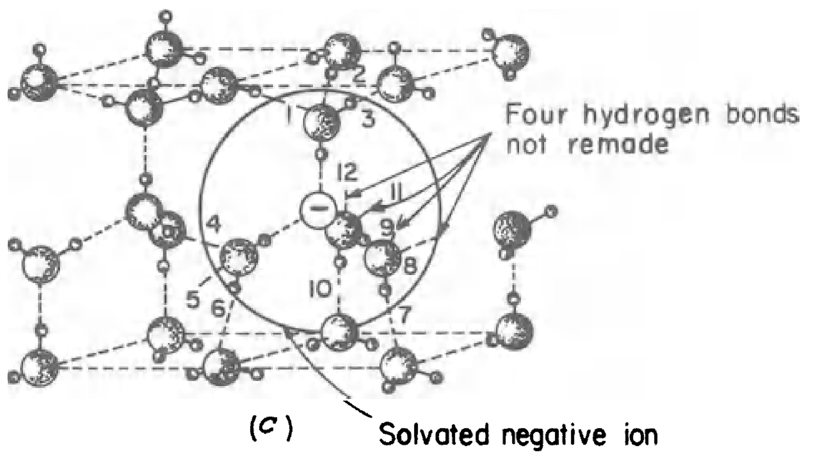


Fig. 2.43. Schematic diagram similar to Fig. 2.42 except that a *negative* ion is being considered here. Thus, two water molecules [III and IV in Fig. 2.42 (b)] reorient in the formation of a primary solvated negative ion; and, therefore, only 8 H bonds [1 to 7 and 10 in Fig. 2.42 (c)] out of 12 H bonds [see Fig. 2.42 (a)] are remade when the solvated ion is introduced into the cavity.

$$\Delta H_{I\text{-}S} = 20 - \frac{4N_A z_i e_0 \mu_W}{(r_i + r_W)^2} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)} \left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2} \frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.33}$$

for positive ions, and

$$\Delta H_{I\text{-}S} = 30 - \frac{4N_A z_i e_0 \mu_W}{(r_i + r_W)^2} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)} \left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2} \frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.34}$$

for negative ions.

By analyzing the structure breaking for octahedral ($n = 6$) coordination, one can develop expressions for the heat of solvation of ions with six solvent molecules in their primary solvent shells. In this case, the expression is

$$\Delta H_{I\text{-}S} = 15 - \frac{6N_A z_i e_0 \mu_W}{(r_i + r_W)^2} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)} \left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2} \frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.35}$$

2.3.5. How Good Is the Ion–Dipole Theory of Solvation?

The heats of ion–solvent interactions calculated on the basis of the ion–dipole approach [Eq. (2.33) and (2.34)] can now be compared with the experimental values used to test the Born theory. The comparison is therefore made with values obtained by equally dividing the experimental heat of solvation of the salt KF between K^+ and F^- ions and then using the individual values thus gained in data for the experimental hydration heats of other salts (*cf.* Section 2.2.7).

The comparison (Table 2.12) shows that the ion–dipole model is a considerable improvement over the rudimentary Born continuum model. The improvement indicates that the ion–dipole model is on the right track in considering that an ion sees the solvent in contact with it as consisting of discrete water dipoles which orient around it. It is only the solvent lying farther out which the ion views Born-wise as a dielectric continuum. Thus, by assuming that the solvent has the bulk dielectric constant right up to the surface of the ion, the Born model missed the work of orientation of water dipoles around the ion and the related change of dielectric constant of water near the ion.[†]

When one considers numerically the various contributions to the heats of ion–solvent interactions calculated from Eqs. (2.33) and (2.34), it can be seen (Table 2.13) that the main contributions come from the ion–dipole and Born charging terms, i.e.,

$$-\frac{N_A n z_i e_0 \mu_W}{(r_i + r_W)^2}$$

and

$$-\frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)}\left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2}\frac{\partial \varepsilon_W}{\partial T}\right)$$

respectively. This fact must be taken to mean that ion–solvent interactions are *essentially electrostatic in origin*. The ion behaves like a charged sphere to the water outside the primary solvent sheath and like an orienting attracting charge to the water molecules inside the primary solvent shell.

The approximately ± 10% agreement between the calculated and experimental values for the heats of solvation of ions should normally be cause for jubilation, but the situation here is abnormal. The so-called experimental values have been obtained by splitting the unambiguous experi-

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[†] The connection between the orientation of water dipoles around ions and the dielectric constant of the medium will be looked into much further in Section 2.5.

equal magnitude q—a charge of $+q$ near each hydrogen atom, and two charges each of value $-q$ near the oxygen atom. Thus, rather than consider that the water molecule can be represented by a dipole (an assembly of two charges), a better approximation, suggested by Buckingham (1957), is to view it as a *quadrupole*, i.e., an assembly of four charges. What may this increase in realism of model do to the remaining discrepancies in the theory of ion–solvent interactions?

2.3.9. The Ion–Quadrupole Model of Ion–Solvent Interactions

It will be recalled that the structural calculation of the heat of ion–solvent interactions (*cf.* Sections 2.3.3 and 2.3.4) involved the following cycle of hypothetical steps: (1) A cluster of $n + 1$ water molecules is removed from the solvent to form a cavity; (2) the cluster is dissociated into $n + 1$ independent water molecules; (3) n out of $n + 1$ water molecules are associated with an ion in the gas phase through the agency of ion–*dipole* forces; (4) the primary solvated ion thus formed in the gas phase is plunged into the cavity; (5) the introduction of the primary solvated ion into the cavity leads to some structure breaking in the solvent outside the cavity; and (6), finally, the water molecule left behind in the gas phase is condensed into the solvent. The heat changes involved in these six steps are W_{CF}, W_D, W_{I-D}, W_{BC}, W_{SB}, and W_C, respectively, where, for $n = 4$.

$$\begin{aligned} W = W_{\mathrm{CF}} + W_D + W_{\mathrm{SB}} + W_C &= +20 \text{ for positive ions} \\ &= +30 \text{ for negative ions} \end{aligned} \tag{2.29}$$

$$W_{I-D} = -\frac{4N_A z_i e_0 \mu_W}{(r_i + r_W)^2} \tag{2.25}$$

$$W_{\mathrm{BC}} = -\frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)}\left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2}\frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.26}$$

and the total heat of ion–water interactions is

$$\Delta H_{I-\mathrm{H_2O}} = W + W_{I-D} + W_{\mathrm{BC}} \tag{2.28}$$

If one scrutinizes the various steps of the cycle, it will be realized that only for one step, namely, step 3, does the heat content change [Eq. (2.25)] depend upon whether one views the water molecule as an electrical dipole or quadrupole. Hence, the expressions for the heat changes for all steps *except* step 3 can be carried over as such into the theoretical heat of ion–

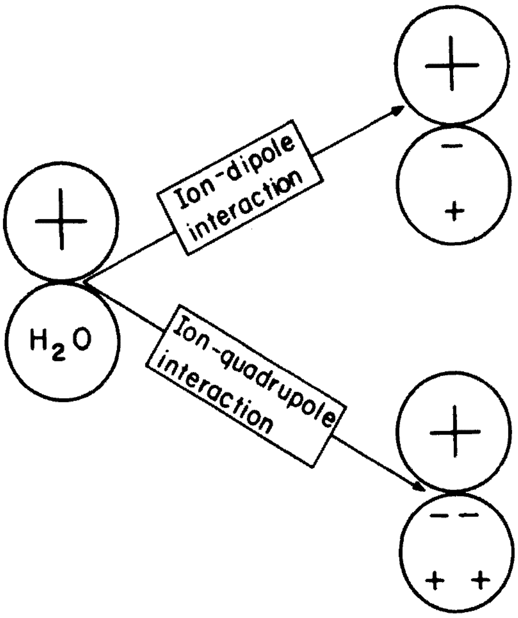

Fig. 2.46. Improvement in the calculation of the ion–water molecule interactions by altering the model of the water molecule from a dipole to a quadrupole.

water interactions, $\Delta H_{I-\mathrm{H_2O}}$, derived earlier. In step 3, one has to replace the heat of ion-dipole interactions, W_{I-D} [Eq. (2.25)] with the heat of ion–quadrupole interactions (Fig. 2.46).

But what is the expression for the energy of interaction between an ion of charge z_ie_0 and a quadrupole? The derivation of a general expression requires sophisticated mathematical techniques, but, when the water molecule assumes a symmetrical orientation (Fig. 2.47) to the ion, the ion–quadrupole interaction energy can easily be shown to be (Appendix 2.3)

$$E_{I-Q} = -\frac{z_ie_0\mu_W}{r^2} \pm \frac{z_ie_0p_W}{2r^3} \tag{2.49}$$

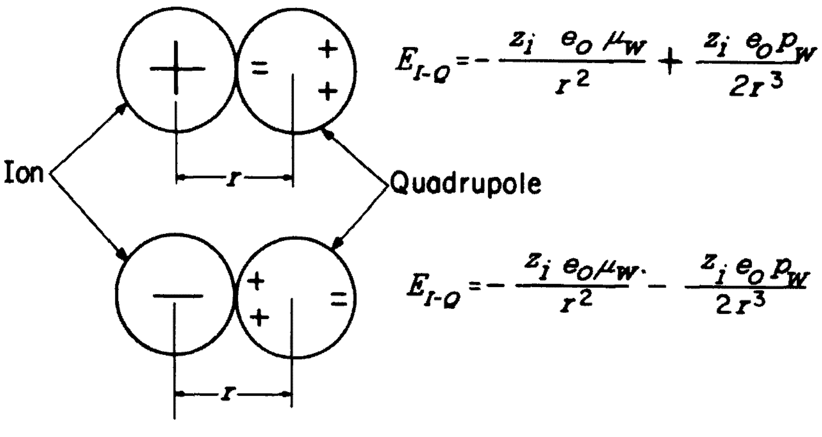

Fig. 2.47. The symmetrical orientation of a quadrupole to an ion.

where the + in the ± is for positive ions, and the − is for negative ions, and the p_W is the quadrupole moment (3.9×10^{-26} esu) of the water molecule. It is at once clear that a difference will arise for the energy of interaction of positive and negative ions with a water molecule, a result hardly forseeable from the rudimentary Born viewpoint and hence probably accountable for the result of Fig. 2.44.

The first term in this expression [Eq. (2.49)] is the dipole term, and the second term is the quadrupole term. It is obvious that, with increasing distance r between ion and water molecule, the quadrupole term becomes less significant. Or, in other words, the greater the value of r, the more reasonable it is to represent the water molecule as a dipole. But, as the ion comes closer to the water molecule, the quadrupole term becomes significant, i.e., the error involved in retaining the approximate dipole model becomes more significant.

When the ion is in contact with the water molecule, as is the case in the primary solvation sheath, the expression (2.49) for the ion–quadrupole interaction energy becomes

$$E_{I-Q} = -\frac{z_i e_0 \mu_W}{(r_i + r_W)^2} \pm \frac{z_i e_0 p_W}{(r_i + r_W)^3} \tag{2.50}$$

The quantity E_{I-Q} represents the energy of interaction between one water molecule and one ion. If, however, four water molecules surround one ion and one considers a mole of ions, the heat change W_{I-Q} involved in the formation of a primary solvated ion through the agency of ion–*quadrupole* forces is given by

$$W_{I-Q} = 4N_A E_{I-Q} = -\frac{4N_A z_i e_0 \mu_W}{(r_i + r_W)^2} \pm \frac{4N_A z_i e_0 p_W}{2(r_i + r_W)^3} \tag{2.51}$$

where, as before, the + in the ± refers to positive ions and the − to negative ions.

Substituting this expression for W_{I-Q} in place of W_{I-D} in expression (2.28) for the heat of ion–water interactions, one has

$$\Delta H_{I-\mathrm{H_2O}} = 20 - \frac{4N_A z_i e_0 \mu_W}{(r_i + r_W)^2} + \frac{4N_A z_i e_0 p_W}{2(r_i + r_W)^3} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)} \times \left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2}\frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.52}$$

for positive ions and

$$\Delta H_{I\text{-}H_2O} = 30 - \frac{N_A z_i e_0 \mu_W}{(r_i + r_W)^2} - \frac{4N_A z_i e_0 p_W}{2(r_i + r_W)^3} - \frac{N_A (z_i e_0)^2}{2(r_i + 2r_W)} \times \left(1 - \frac{1}{\varepsilon_W} - \frac{T}{\varepsilon_W{}^2}\frac{\partial \varepsilon_W}{\partial T}\right) \tag{2.53}$$

for negative ions.

2.3.10. Ion–Induced-Dipole Interactions in the Primary Solvation Sheath

If one compares Eqs. (2.52) and (2.53) with Eqs. (2.33) and (2.34), it is clear that the ion–quadrupole calculation of ΔH_{I-H_2O} differs from the ion–dipole calculation of the same quantity in only one respect: In representing the water molecule by a quadrupole, one is making a more refined assessment of the interactions between the ion and the water molecules of the primary solvation sheath. At this level of sophistication, one wonders whether there are other subtle interactions which one ought to consider.

For instance, when the water molecule is in contact with the ion, the field of the latter tends to distort the charge distribution in the water molecule. Thus, if the ion is positive, the negative charge in the water molecule tends to come closer to the ion and the positive charge to move away. This implies that the ion tends to induce an extra dipole moment in the water molecule over and above its permanent dipole moment. For small fields, one can assume that the induced dipole moment μ_{ind} is proportional to the inducing field X

$$\mu_{\text{ind}} = \alpha X \tag{2.54}$$

where α, the proportionality constant, is known as the *deformation polarizability* and is a measure of the "distortability" of the water molecule along its permanent dipole axis.

Thus, one must consider the contribution to the heat of formation of the primary solvated ion, i.e., step 3 of the cycle used in the theoretical calculation presented above, arising from interactions between the ion and the dipoles induced in the water molecules of the primary solvent sheath. The interaction energy between a dipole and an infinitesimal charge dq is $-\mu\, dq/r^2$, or, since dq/r^2 is the field dX due to this charge, the interaction energy can be expressed as $-\mu\, dX$. Thus, the interaction energy between the dipole and an ion of charge $z_i e_0$, exerting a field $z_i e_0/r^2$ can be found

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2.4. THE SOLVATION NUMBER

2.4.1. How Many Water Molecules Are Involved in the Solvation of an Ion?

Mathematically speaking, the electric force originating from an ion becomes zero only at infinity. In effect, however, the force fades out to a negligible value after quite a short distance (of the order of tens of angstroms). Beyond this cutoff distance, solvent molecules may be regarded as unaware of an ion's presence. There is therefore a certain effective volume around the ion within which its influence operates. How many solvent molecules are inside this volume and could therefore be said to be partici-

TABLE 2.17

Hydration Number Ascribed to the Sodium Ion in According to Different Experimental Methods

Ion	Hydration numbers reported
Na^+	1, 2, 2.5, 4.5, 6–7, 16.9, 44.5, 71

pants in the solvation of the ion? This number may be termed the *solvation number*[†] (or *hydration number* when water is the solvent).

The question of the value of the solvation number is an interesting one. It is no surprise, therefore, that a large number of different methods have in the past been used to determine the solvation number (more about these methods later). But, the alarming thing is that exceedingly discrepant results are obtained by the various methods. For instance, widely varying hydration numbers ranging from 1 to 71 (Table 2.17) have been ascribed to the sodium ion. Are some of the methods wholly incorrect, or is there a confusion as to what constitutes a hydration number?

The answer can be approached, if not attained precisely, by the following considerations. What value of hydration number a particular method gives depends on what types of ion–solvent interactions the method senses. If it can pick up the interactions of an ion with water molecules several molecular diameters away in the secondary region, it will report that a large number of water molecules are involved in solvation, i.e., a high hydration number. If, however, the method only detects how many water molecules an ion takes along in the course of its thermal motions through the solution (i.e., those tightly bound to it), then it will report a small hydration number.

To avoid ambiguity, it is best to define a *primary solvation number* as the number of solvent molecules which surrender their own translational freedom and remain with the ion when it moves relative to the surrounding solvent. Of course, a solvent molecule loses its independent translational motions only when it is overwhelmed by the ionic force field into adopting

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[†] This total effective number of solvent molecules involved in interactions should not be confused with the number n used in the structural treatment of the energetics of solvation. The latter number was meant to represent the number of solvent molecules in contact with the ion and assumed to be aligned in its field.

TABLE 2.18

Hydration Numbers

Ion	Hydration number	Number of independent methods on which result is based
Li^+	5 ± 1	5
Na^+	5 ± 1	5
K^+	4 ± 2	4
Rb^+	3 ± 1	4
F^-	4 ± 1	3
Cl^-	1 ± 1	3
Br^-	1 ± 1	3
I^-	1 ± 1	2

a minimum-energy orientation to the ion. Thus, the primary solvation number can also be defined as the number of solvent molecules which are aligned in the force field of the ion.

This definition provides a criterion for discussing the different methods of determining solvation numbers. The primary solvation number should be determined by only those methods which register the number of water molecules which are associated with the ion in its travels through the solution.

When, however, these methods are used (and they will be presented in Section 2.4.5), it turns out (Table 2.18) that the number of water molecules determined by some of them are *less* than what geometry says the number of water molecules in contact with the ion should be. This latter number is a coordination number,[†] i.e., the number of nearest-neighbor water molecules which are in contact with or coordinate or surround an ion. The question, therefore, arises: Why does not all the coordinated water join the ion in its zig-zag motions through the solution? In fact, why is the solvation number not always equal to the coordination number? Further,

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[†] In the structural treatment of the heats of solvation, it was tacitly assumed that the number *n* of primary solvent molecules aligned in the ionic field is equal to the coordination number. In other words, the structural treatment slurs over the distinction between the number that are oriented in the ionic field (i.e., move with the ion) and the number in contact with the ion.

what happens when coordinating solvent molecules desert their positions in the coordination shell of an ion as soon as it begins its voyage through the solvent, say, in response to an electric field? Do the missing solvent molecules leave voids in the coordination shell of a moving ion? The concept of solvation number will become clear only when such questions are answered.

2.4.2. Static and Dynamic Pictures of the Ion–Solvent Molecule Interaction

Suppose that, in a thought experiment, a bare ion is made to stop during its movements through the solution. At that instant, the hypothetical *stationary* ion will be surrounded or coordinated by water molecules still associated in a network structure (Fig. 2.57). What will happen? The ionic force field will operate on the neighboring water dipoles. The forces, which are essentially ion–dipole in nature, will cause some of the water molecules to break away from the water network and attach themselves to the ion.

What is the consideration on the basis of which a particular water molecule decides to embrace the ion by aligning into its field or to shun it and remain in the water network? The consideration is simple: Is the ion–dipole interaction energy greater in magnitude than the hydrogen-bond energy keeping the particular water molecule in the network? If the ion–dipole energy is greater in magnitude, the water molecule should link itself with the ion and form part of the primary solvation sheath. If not, the water molecule should remain in the water network.

The whole thought experiment described above is a *static* one. All that has been done is to consider the energies in the initial state (a water

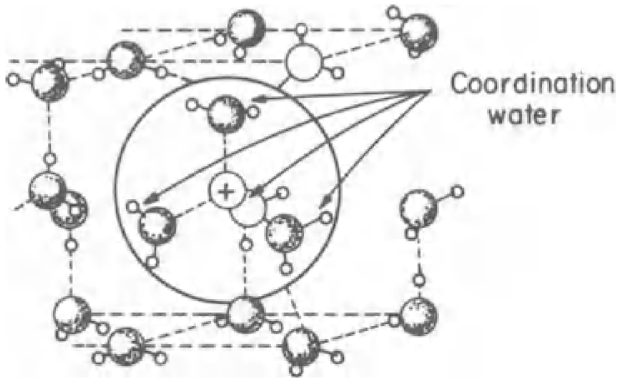

Fig. 2.57. A hypothetical stationary ion coordinated by water molecules still associated into a network structure.

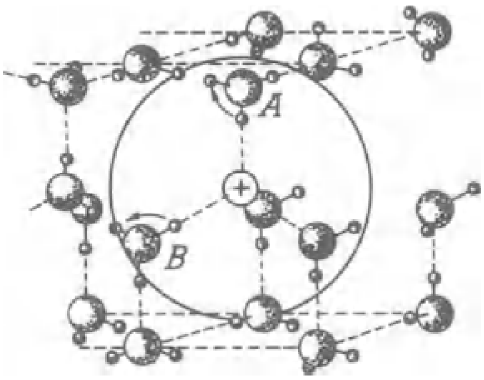

Fig. 2.58. Schematic diagram to show that, of four water molecules which coordinate an ion, two water molecules, *A* and *B* must reorient from positions in which one of their H atoms faces the ion to positions in which the same H atoms are away from the ion. (The required reorientation is shown by an arrow.)

molecule in the water network and an ion nearby) and in the final state (water bound to the ion by ion–dipole forces).

But ions can be kept stationary only in thought experiments. In reality, they exist in a state of ceaseless motion (see Chapter 4). So time and movement must come into the picture of ions interacting with water molecules. One must abandon a static view for a dynamic view.

One can develop a dynamic view along the following lines (Samoilov). Consider a water molecule bound by hydrogen bonds to the water network. Suppose that, at a time taken as zero ($t = 0$), an ion suddenly appears next to the water molecule. If the net force on the water molecule is in favor of its association with the ion rather than with the water network, it will try to get into an equilibrium position around the ion, i.e., the water molecule will try to align into a minimum-energy orientation. This usually means that the water molecule has to reorient (or jump through a small distance or both) from the position it had in the water structure to the new position of alignment in the ionic field (Fig. 2.58).

But these reorienting or *jumping movements* to be made by the water molecule will *require* a *finite time*, the value of which depends on the critical activation energy required for the reorientation or jumping process. Let this time required for the orientation of a water molecule into the coordination sheath around an ion be $\tau_{\text{water orient}}$ (Fig. 2.59). This orientation time will not have a unique value because it will depend on how far the ion is situated from and on how the ion is located with respect to the water

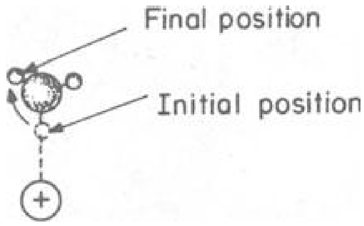

Fig. 2.59. The time required for a water molecule in contact with an ion to reorient from an initial to a final position (shown in figure) is τ_{orient}.

network holding the water molecule. So one is talking about an average water-orientation time.

Now, instead of considering the ion suddenly placed next to the water molecule at $t = 0$, one can visualize the ion resting or waiting near the water molecule in between its hops from location to location in the solvent (*cf.* Section 4.2). Of course, if a water molecule belonging to the water network is to orient toward the ion, it must do so when the ion is within a certain small distance of the water molecule. But how long does the ion stay within this jumping range? That depends on how long the ion pauses next to the water molecule in the course of its jumps through the solvent. The longer the ion waits near the water molecule, the longer is the time available for the water molecule to break out of the water lattice and swing into that intimate ion–dipole relationship with the ion which characterizes

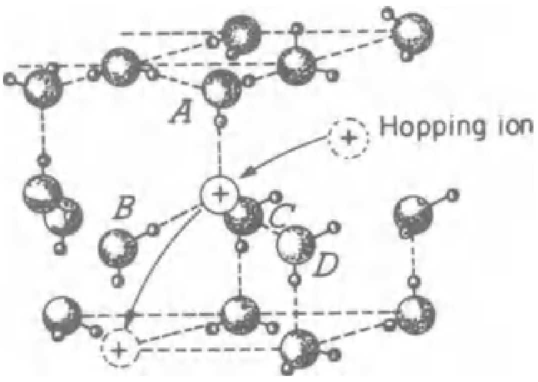

Fig. 2.60. In the course of its hops through the solution, the hopping ion can be considered to spend a time $\tau_{\text{ion wait}}$ in contact with the neighboring water molecules. Will one of these orient itself into a position of minimum interaction energy with the ion before the latter has jumped to a new position?

a seat in the primary hydration sheath. The hopping ion spends a certain time in "contact" with the particular water molecule under discussion. Call this contact time $\tau_{\text{ion wait}}$ (Fig. 2.60).

2.4.3. The Meaning of Hydration Numbers

Now, an interesting qualitative conclusion becomes clear. If the time an ion waits near a water molecule is *long* compared with the average time a water molecule takes to orient into association with an ion, then the probability of the water molecule's being captured by the ion is high. That is, the probability of an ion's capturing a water molecule depends on the ratio $\tau_{\text{ion wait}}/\tau_{\text{water orient}}$.

If $\tau_{\text{ion wait}}/\tau_{\text{water orient}}$ is large, then the ion will be surrounded by the full geometrically permitted complement of bonded water molecules *during all its zig-zag motions* through the solution. Under these circumstances, the hydration number (i.e., the number of water molecules which participate in the translational motions of the ion) will be equal to the coordination number.

If, however, $\tau_{\text{ion wait}}/\tau_{\text{water orient}}$ is of the order of unity, then the situation is interesting. The time an ion spends in the neighborhood of a water molecule is of the order of the water reorientation time, and, hence, though the ion is not sure to capture a water molecule, there is a certain probability, less than unity. At the same time, one must consider the opposite process: An ion with a bound water molecule collides with a water molecule belonging to the water network. There will be a certain probability that the ion will lose its water to the water network. But there are plenty of water molecules all around and the ion has a chance of making up its loss. Thus, over a period of time which is long compared with the period of contact between a moving ion and a specific water molecule, the ion has aligned and trapped in its field a certain number of water molecules which is less than the number of water molecules which geometrical close packing makes possible, i.e., the coordination number.

The collisions between ions and water molecules linked to the water network are analogous to any other collision process. Consider, for example, the collisions between neutrons and U^{238} nuclei, in which slow neutrons stand a better chance of being captured than fast neutrons. One says that there is a large capture cross section for slow neutrons. It is as if a slow moving neutron sees a bigger target than a fast moving one.

What happens if the ions wait for so short a time that, even before a water molecule has had time to break out of the water structure and turn around, the ion has hopped away? Then, the probability of a water molecule's being captured by the ion is zero, and, on a time average, the ion will not have any *aligned* water molecules in contact with it, i.e., its primary hydration sheath is empty. This does not mean that such ions are not surrounded by interacting solvent molecules or that they would have no coordination water. It only means that, because $\tau_{\text{ion wait}}/\tau_{\text{water orient}} \ll 1$, the ion does not wait long enough at any particular site for the contiguous water molecules to swing out of the water network into minimum-energy orientation with the ion. Even if the ion does capture a water molecule, it is bound to lose it soon. It also means that the moving ion exchanges water molecules so easily with the surrounding solvent that, in effect, the moving ion does not carry its sheath along with it. Its solvation number is zero, though its coordination number is that dictated by geometry.

The picture of solvation numbers presented here is a dynamic one. The solvation number refers to the number of water molecules which remain aligned with the ion *during* its jumps through the medium. But it is not necessary that the same individual water molecules serve in the solvation sheath for an indefinitely long time. A given water molecule may serve the ion for some time, but it is not imprisoned for life in its hydration shell. A chance collision, and the particular water molecule may link up again with the water network, get left behind by the hopping ion, and watch another water molecule yield to the attraction of the ionic field and be incorporated in the primary solvation sheath.

2.4.4. Why Is the Concept of Solvation Numbers Useful?

In all this dynamic exchange of solvent molecules between the coordination region and the main bulk of solvent, has the concept of solvation number any utility? Yes, the solvation number can be considered the *effective* number of solvent molecules to be "permanently" bound to the ion and to follow its motion from site to site. The kinetic entity is not the bare ion but the ion plus the solvation number of water molecules.

The concept of solvation number permits one to suppress the dynamic nature of the primary solvation sheath from many modelistic considerations of ions in solution. This is important particularly in situations where one would overcomplicate an analysis by considering the details of the constant exchange of water molecules between the ionic primary hydration shell and the solvent. The overall total action of the ion on the water may be replaced conceptually by a strong binding between the ion and some effective number (the solvation number) of solvent molecules; this effective number may well be almost zero in the case of large ions, e.g., iodide, cesium, and tetraalkylammonium. The solvation number clearly diminishes with increase of ionic radius because, with increasing ionic radius, the distance to the coordinating water molecules increases and, thus, the ionic force field which aligns the ion diminishes so that the water molecules have less inclination to reorient away from their solvent-structure positions.

Of course, there may be situations where, quite independent of the ratio $\tau_{\text{ion wait}}/\tau_{\text{water orient}}$, there are thermodynamic restrictions against the association of solvent molecules with the ion, e.g., the ion–solvent molecule interaction energy may be less in magnitude than the solvent molecule–solvent molecule energy. In such cases, the solvation number will be zero on static considerations alone.

2.4.5. On the Determination of Solvation Numbers

All this discussion would be pointless if there were no agreement between the different methods of measuring primary solvation numbers. Fortunately, it turns out that there *is* some degree of agreement between the values reported by different methods so long as they are methods which determine the *primary* solvation number (Section 2.4.1), as opposed to the vague and asymptotic concept of total solvation number (see Table 2.19).

TABLE 2.19

Comparison between the Hydration Numbers Determined by Different Methods

Ion	Compressibility	Mobility	Entropy	Theoretical calc.
Li^+	5–6	6	5	6
Na^+	6–7	2–4	4	5
Mg^+	16	14	13	
Ca^{++}	—	7.5–10.5	10	
Zn^{++}	—	10 –12.5	12	
Cd^{++}	—	10 –12.5	11	
Fe^{++}	—	10 –12.5	12	
Cu^{++}	—	10.5–12.5	12	
Pb^{++}	—	4 – 7.5	8	
K^+	6–7	—	3	3
F^-	2	—	5	5
Cl^-	0.1	0.9	3	3
Br^-	0	0.6	2	2
I^-	0	0.2	1	0

A detailed discussion of the various methods of determining solvation numbers is not intended in this treatment. Nevertheless, it is illustrative to present two examples.

Consider, for example, the compressibility method. The compressibility β is defined by the expression

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2.62}$$

If a pure solvent is considered, then its compressibility may be written thus

$$\beta_{\text{solv}} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2.63}$$

Now suppose that an ionic solution is considered. Will its compressibility be the same as that of the pure solvent, i.e., β_{solv}? A physical picture of why a solvent is compressible will provide a qualitative answer.

Let water be the solvent. It has been described (see Section 2.3) as having quite an open framework structure with many holes in it. When a pressure is applied, the water molecules can break out of the tetrahedral framework and enter the interstitial spaces; the water molecules become packed more closely (Fig. 2.61). Thus, the volume decreases.

This is not the only way of compressing water. When ions are introduced into the water, they are capable of wrenching water molecules out of the water framework so as to envelop themselves with solvent sheaths. Because the molecules are oriented in the ionic field, the water is more compactly packed in the primary solvation shell as compared to the packing if the

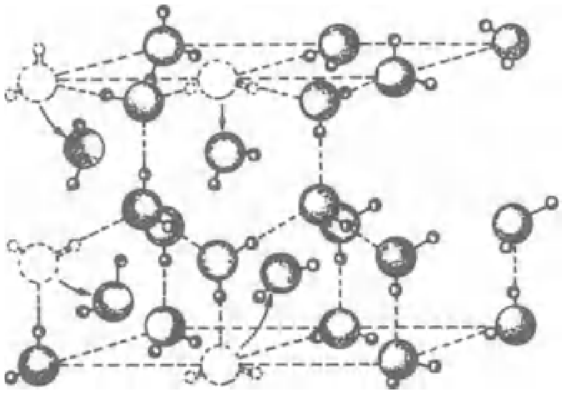

Fig. 2.61. Schematic diagram to show that, when an external pressure is applied to water, water molecules break out of the networks and occupy interstitial spaces.

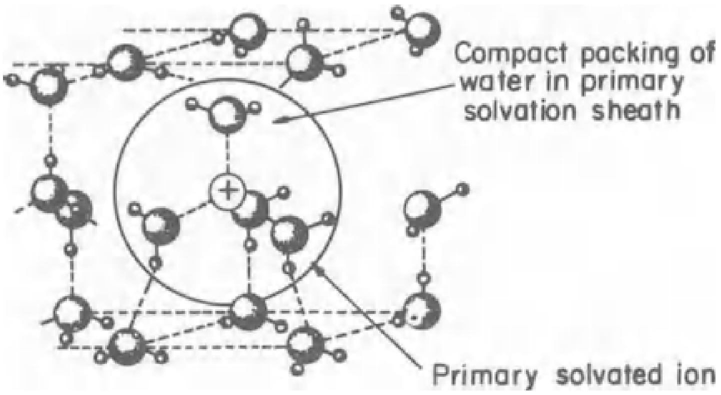

Fig. 2.62. Schematic diagram to illustrate the principle of electrostriction; owing to the ionic field, water molecules are more compactly packed in the primary solvation sheath than in the field.

ion were not there (Fig. 2.62). The water has become compressed by the introduction of the ion. But what is the origin of the influence of the ion? The origin is the electric field of the ion. Thus, electric fields cause compression of the material medium upon which they exert their influence; this phenomenon is known as *electrostriction.*

Since the introduction of ions into a solvent causes the solvent molecules *in the primary solvent shell* to be highly compressed, these water molecules may be supposed not to respond to any further pressure which may be applied. Thus, the compressibility of an ionic solution is less than that of the pure solvent because of the incompressibility of the primary solvation sheath.†

It is easy to calculate the ratio of the compressibility of a solvent β_{solv} to that of the solution β_{soln}. Suppose the primary hydration number is n_h. Then, n_i moles of ions are solvated with $n_i n_h$ moles of incompressible water. Now, if n_w moles of water correspond to a total volume V of solution, $n_i n_h$ moles of incompressible water would correspond to a volume $V n_h n_i / n_w$ of incompressible solution. Defining the symbol y thus

$$y = \frac{n_h n_i}{n_w} \tag{2.64}$$

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† Outside the primary solvent sheath, the water molecules are not oriented to the same degree as those inside the primary solvation sheath because the orienting ionic field is less. This means that the nonprimary water molecules are less electrostricted and free to respond to pressure. One can, to good approximation, say that the water outside the primary solvation shell has the same compressibility as the pure solvent.

the volume of the incompressible part of the solution is yV. This volume must be excluded from the expression for the compressibility of the ionic solution. Thus,

$$\beta_{\text{soln}} = -\frac{1}{V}\left[\frac{\partial}{\partial p}(V - yV)\right]_T \tag{2.65}$$

$$\beta_{\text{solv}} = -\frac{1}{V}\left[\frac{\partial}{\partial p}V\right]_T \tag{2.63}$$

$$\frac{\beta_{\text{soln}}}{\beta_{\text{solv}}} = 1 - y \tag{2.66}$$

Hence, from (2.64),

$$\frac{\beta_{\text{soln}}}{\beta_{\text{solv}}} = 1 - \frac{n_h n_i}{n_w} \tag{2.67}$$

$$n_h = \frac{n_w}{n_i}\left(1 - \frac{\beta_{\text{soln}}}{\beta_{\text{solv}}}\right) \tag{2.68}$$

This equation can be used to obtain the hydration number by determining the compressibility of the pure solvent and the ionic solution. There are several methods available for studying compressibilities. The ultrasonic method, for example, depends on the fact that sound travels by a compression–rarefaction process, and, thus, the velocity of an ultrasonic wave can be used to determine the compressibilities of solvent and solution, needed for Eq. (2.68) (Fig. 2.63).

The *mobility* method of measuring hydration numbers is based on the following argument (*cf.* also Section 4.4.8). Suppose an ion is made to

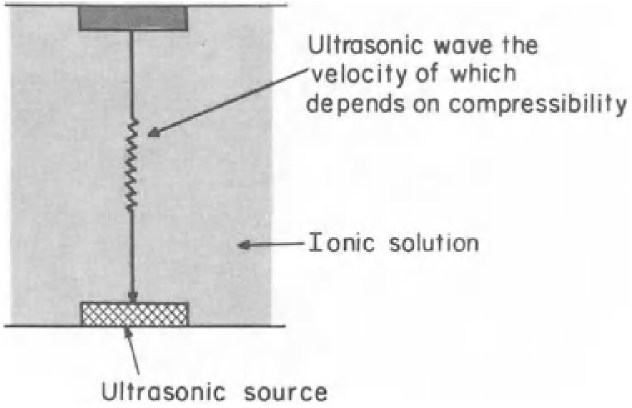

Fig. 2.63. The ultrasonic method of determining hydration numbers is based on the fact that the velocity of the ultrasonic wave depends, by the compressibility of the solution, on the extent of primary hydration in the ionic solution.

drift by the application of an external electric field. The motion of the ion is opposed by the viscous resistance of the solution. When a steady-state velocity is reached, the electric force is equal to the hydrodynamic viscous force (Fig. 2.64). The former is simply $z_i e_0 X$, where X is the electric field (or potential gradient) in the solution applied by two electrodes placed in solution (X is often measured in volts per centimeter). The latter is expressed by a famous classical formula of hydrodynamics called *Stokes' law*. This law, which describes the force experienced by a sphere moving in a viscous medium, states that

$$\text{Viscous force} = 6\pi r \eta v \tag{2.69}$$

where r is the radius of the moving ion and η is the viscosity of the medium. Thus,

$$z_i e_0 X = 6\pi r \eta v \tag{2.70}$$

or

$$\begin{aligned} r &= \frac{z_i e_0 X}{6\pi \eta v} \\ &= \frac{z_i e_0}{6\pi \eta u} \end{aligned} \tag{2.71}$$

where $u(= v/X)$, i.e., the velocity under unit electric field, is a measurable quantity and is often called the *electrical mobility* of the ion (*cf.* Section 4.4.3).

Once the radius r of the solvated ion is obtained from Eq. (2.71),

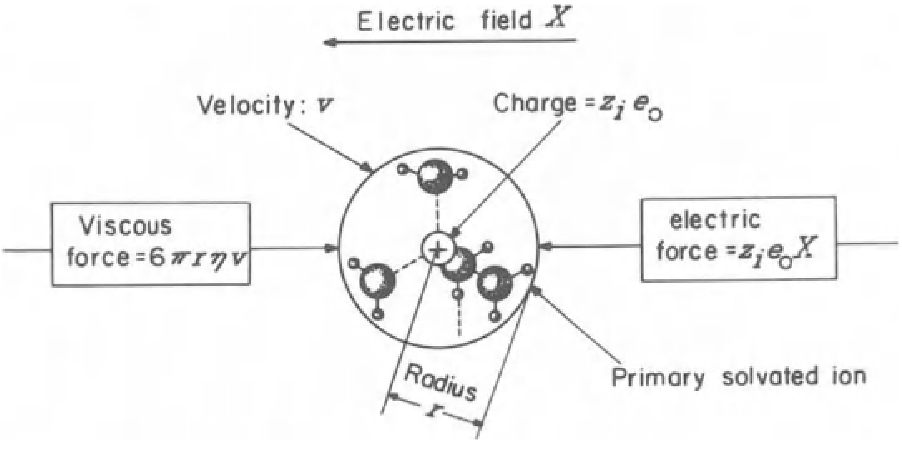

Fig. 2.64. The mobility method of determining hydration numbers is based on finding out the radius of a primary solvated ion from the fact that, when an ion in solution attains a steady-state velocity, the electric force $z_i e X_0$ is exactly balanced by opposing viscous force $6\pi \eta r v$.

one can calculate the hydration number n_h by a simple geometric argument (see Fig. 2.65)

$$n_h = \frac{\frac{4}{3}\pi r^3 - \frac{4}{3}\pi r_{\text{cryst}}^3}{\frac{4}{3}\pi r_{\text{H}_2\text{O}}^3}$$

$$= \frac{(r^3 - r_{\text{cryst}}^3)}{r_{\text{H}_2\text{O}}^3} \tag{2.72}$$

where r_{cryst} is the crystallographic radius of the ion and $r_{\text{H}_2\text{O}}$ is the radius of the water molecule, both of which are known from independent data.

Both the compressibility and the mobility methods of determining primary hydration numbers are based on quite loose approximations. The compressibility method assumes that the solvent *inside* the primary solvation sheath is completely incompressible and the water *outside* has the same compressibility as the pure solvent.

It will be recalled, however, that, in the secondary region (see Fig. 2.28 and Section 2.3.2) between the primary solvation sheath and the bulk water, there is structure breaking and partial alignment of the water molecules. Hence, instead of a sharp change of compressibilities at the boundary of the primary solvation shell, it is likely that there will be a smooth variation in compressibility from the ion out into the bulk solvent.

The mobility method, on the other hand, ignores the fact that, because the secondary region does not have the structure of the bulk solvent, the viscosity of the medium constituting the immediate neighborhood of the moving primary solvated ion is not the viscosity of the bulk solvent. It should be the *local* viscosity of the region surrounding the primary solvated ion. Such local viscosities are uncertain in value. Another approximation in the mobility method is that it neglects electrostrictional compression in computing the volume occupied by the water molecules in the primary hydration sheath (and, in the rudimentary version of the theory given here, also free space between water molecules).

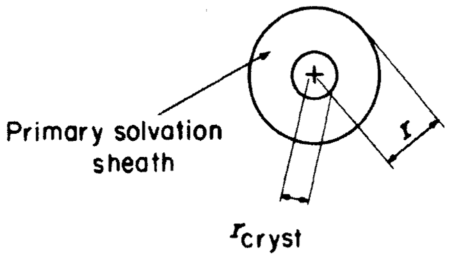

Fig. 2.65. The calculation of the hydration number from the radius of the primary solvated ion.

These approximations in the mobility method are offset by one big advantage. The method gives directly the hydration number of one ionic species, e.g., sodium ions, and not the *sum* of the hydration numbers of positive *and* negative ions. In the compressibility method, however, one only obtains the hydration number of the *salt*, and thus one has all the problems of resolving the value for the salt into the individual ionic values that were encountered in getting individual ionic heats of hydration from heats of hydration of salts (*cf.* Section 2.2.7). One has to depend on some independent (and sometimes somewhat circular) argument, for instance, that the relatively large iodide ion should have a hydration number of zero wholly to the positive ion. Of course, once one is certain of the hydration number of one ion, one can then get out those of other ions by taking the appropriate salts.

There are in all about five experimental methods which yield primary hydration numbers. The results show approximate agreement (±1). Each method involves some doubts and approximations, and, in some cases, it is difficult to estimate with even a tolerance of ±25% what effect the approximations would have on the hydration numbers. Nevertheless, when one recalls the wild spread (*cf.* Table 2.17) of the values of hydration numbers obtained by not distinguishing between methods which determine primary and total hydration numbers, it must be accepted that the results of Table 2.20 hang together at least very much better than those in which a distinction between primary and other types of solvation is neglected. The results permit one to conclude the basic correctness of the picture of an ion influencing quite a bit of the surrounding solvent but actually succeeding

TABLE 2.20

Primary Hydration Numbers

Ion	From compressibility	From entropies	From apparent molal vol	From mobility	Most probable integral value
Li^+	5–6	5	2.5	3.5–7	5 ± 1
Na^+	6–7	4	4.8	2.4	4 ± 1
K^+	6–7	3	1.0	—	3 ± 2
F^-	2	5	4.3	—	4 ± 1
Cl^-	0–1	3	0	—	2 ± 1
Br^-	0	2	—	—	2 ± 1
I^-	0	1	—	—	1 ± 1

in trapping in its field only a certain number of water molecules which become the baggage of the ion in its travels through the solution.

There is, however, one surprising thing in the extent of agreement between the various methods. The mobility method is based on the nonequilibrium process of conduction, and the compressibility method, for example, is based on the system's being in equilibrium. Yet, the two methods yield fairly concordant results. The point, however, is that, in considering hydration numbers, one is not concerned with whether the whole system (the assembly of ions and solvent particles) is in static equilibrium or dynamic change. One is concerned with the state of the individual ions. But these are in ceaseless motion irrespective of whether the whole assembly is in equilibrium or not. Thus, even methods, such as the compressibility method, which involve measurements of the solution at equilibrium, concern in fact *ions* in a very dynamic state and should therefore give nearly the same hydration and solvation numbers as one would expect when the ions are drifting under nonequilibrium conditions, e.g., under an electric field.

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2.5. THE DIELECTRIC CONSTANT OF WATER AND IONIC SOLUTIONS

2.5.1. An Externally Applied Electric Field Is Opposed by Counterfields Developed within the Medium

The solvation of ions arises from the interactions between solvent molecules and ions. These interactions result in the *orientation* of the, e.g., water molecules toward the *ions*. It follows that, as the ionic concentration increases, the fraction of the water in a solution which is trapped by ionic fields in the solvation sheaths also increases. Is this con-

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Appendix 2.1. Free Energy Change and Work

The free-energy change ΔG which a system undergoes in a process can be written quite generally as

$$\Delta G = \Delta E + p\,\Delta V + V\,\Delta p - T\,\Delta S - S\,\Delta T \tag{A2.1.1}$$

If the process occurs at constant pressure and temperature,

$$\Delta p = 0 = \Delta T \tag{A2.1.2}$$

and, therefore,

$$\Delta G = \Delta E + p\,\Delta V - T\,\Delta S \tag{A2.1.3}$$

If, further, the process is reversible, the heat Q put *into* the system is related to the entropy change through

$$Q = T\,\Delta S \tag{A2.1.4}$$

and, from the first law of thermodynamics,

$$\begin{aligned}\Delta E &= Q - W\\ &= T\,\Delta S - W\end{aligned} \tag{A2.1.5}$$

where W is the total work done *by* the system.

Substituting for $T\,\Delta S$ from Eq. (A2.1.5) in Eq. (A2.1.3), one has

$$\Delta G = -(W - p\,\Delta V) \tag{A2.1.6}$$

Since W is the total work (including mechanical work) and $p\,\Delta V$ is the mechanical work of volume expansion,

$$\Delta G = -(\text{work other than mechanical work done } \textit{by} \text{ the system}) \tag{A2.1 7}$$

or

$$\Delta G = \text{work other than mechanical work done } \textit{on} \text{ the system} \tag{A2.1.8}$$

Appendix 2.2. The Interaction between an Ion and a Dipole

The problem is to calculate the interaction energy between a dipole and an ion placed at a distance r from the dipole center, the dipole being oriented at an angle θ to the line joining the centers of the ion and dipole (Fig. A2.2.1). (By convention, the direction of the dipole is taken to be the direction from the negative end to the positive end of the dipole.)

The ion–dipole interaction energy U_{I-D} is equal to the charge $z_i e_0$ of the ion times the potential ψ_r due to the dipole at the site P of the ion

$$U_{I-D} = z_i e_0 \psi_r \tag{A2.2.1}$$

Thus, the problem reduces to the calculation of the potential ψ_r due to the dipole. According to the law of superposition of potentials, the potential due to an assembly of charges is the sum of the potentials due to each charge. Thus, the potential due to a dipole is the sum of the potentials $+q/r_1$ and $-q/r_2$ due to the charges $+q$ and $-q$ which constitute the dipole and are located at distances r_1 and r_2 from the point P. Thus,

$$\begin{aligned}\psi_r &= \frac{q}{r_1} - \frac{q}{r_2}\\ &= q\left(\frac{1}{r_1} - \frac{1}{r_2}\right)\end{aligned} \tag{A2.2.2}$$

From Fig. A2.2.2, it is obvious that

$$r_1^2 = Y^2 + (z + d)^2 \tag{A2.2.3}$$

and, therefore,

$$\begin{aligned}\frac{1}{r_1} &= [Y^2 + (z + d)^2]^{-\frac{1}{2}}\\ &= [(Y^2 + z^2) + d^2 + 2zd]^{-\frac{1}{2}}\\ &= (r^2 + d^2 + 2zd)^{-\frac{1}{2}}\\ &= \frac{1}{r}\left[1 + \left(\frac{d}{r}\right)^2 + \frac{2dz}{r^2}\right]^{-\frac{1}{2}}\end{aligned} \tag{A2.2.4}$$

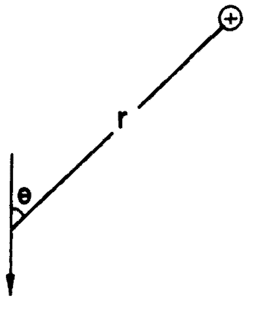


Fig. A2.2.1.

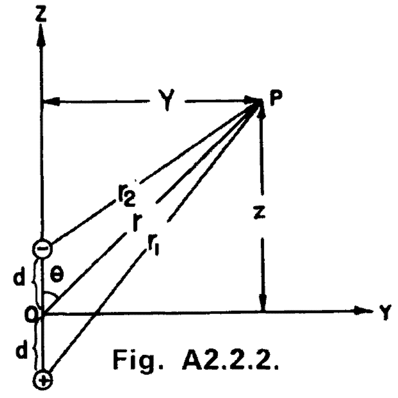


Fig. A2.2.2.

At this stage, an important approximation is made, namely, that the distance $2d$ between the charges in the dipole is negligible compared with r. In other words, the approximation is made that

$$1 + \left(\frac{d}{r}\right)^2 + \frac{2dz}{r^2} \sim 1 + \frac{2dz}{r^2} \tag{A2.2.5}$$

It is clear that the validity of the approximation decreases the closer the ion comes toward the dipole, i.e., as r decreases.

Making the above approximation, one has [see Eq. (A.2.2.4)]

$$\frac{1}{r_1} \sim \frac{1}{r}\left(1 + \frac{2dz}{r^2}\right)^{-\frac{1}{2}} \tag{A2.2.6}$$

which, by the binomial expansion taken to two terms, gives

$$\frac{1}{r_1} = \frac{1}{r}\left(1 - \frac{dz}{r^2}\right) \tag{A2.2.7}$$

By similar reasoning,

$$\frac{1}{r_2} = \frac{1}{r}\left(1 + \frac{dz}{r^2}\right) \tag{A2.2.8}$$

By using Eqs. (A2.2.7) and (A2.2.8), Eq. (A2.2.2) becomes

$$\psi_r = -\frac{2dq}{r^2}\frac{z}{r} \tag{A2.1.9}$$

Since $z/r = \cos\theta$ and $2dq$ is the dipole moment μ.

$$\psi_r = -\frac{\mu\cos\theta}{r^2} \tag{A2.2.10}$$

or the ion–dipole interaction energy is given by

$$U_{I-D} = \frac{-z_i e_0 \mu \cos\theta}{r^2} \tag{A2.2.11}$$

Appendix 2.3. The Interaction between an Ion and a Water Quadrupole

Instead of presenting a sophisticated general treatment for ion–quadrupole interactions, a particular case of these interactions will be worked out. The special case to be worked out is that corresponding to the water molecule being oriented with respect to a positive ion so that the interaction energy is a minimum.

In this orientation (see Fig. A2.3.1), the oxygen atom and a positive ion are on the Y axis which bisects the H—0—H angle. Further, the positive ion, the oxygen atom, and the two hydrogen atoms are all considered in the XY plane. The origin of the XY coordinate system is located at the point Q, which is the center of the water molecule. The ion is at a distance r from the origin.

The ion–quadrupole interaction energy U_{I-Q} is simply given by the charge on the ion times the potential ψ_r at the site of the ion due to the charges of the quadrupole,

$$U_{I-Q} = z_i e_0 \psi_r \tag{A2.3.1}$$

But the potential ψ_r is the sum of the potentials due to the four charges q_1, q_2, q_3, and q_4 in the quadrupole (1 and 2 are the positive charges at the hydrogen, and 3 and 4 are the negative charges at the oxygen). That is,

$$\psi_r = \psi_1 + \psi_2 + \psi_3 + \psi_4 \tag{A2.3.2}$$

Each one of these potentials is given by the usual coulombic expression for the potential

$$\psi_r = \frac{q_1}{r_1} + \frac{q_2}{r_2} - \frac{q_3}{r_3} - \frac{q_4}{r_4} \tag{A2.3.3}$$

where the minus sign appears before the third and fourth terms because q_3 and q_4

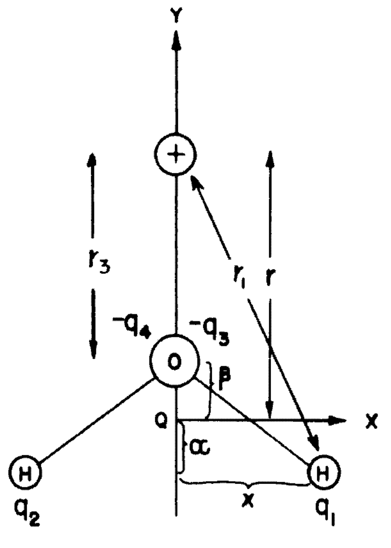


Fig. A2.3.1.

are negative charges. Further, the *magnitudes* of all the charges are equal

$$|q_1| = |q_2| = |q_3| = |q_4| = q \tag{A2.3.4}$$

and, because of symmetrical disposition of the water molecule,

$$r_2 = r_1 \qquad \text{and} \qquad r_4 = r_3 \tag{A2.3.5}$$

Hence, from Eqs. (A2.3.3), (A2.3.4), and (A2.3.5),

$$\psi_r = 2q\left(\frac{1}{r_1} - \frac{1}{r_3}\right) \tag{A2.3.6}$$

It is obvious (see Fig. A2.3.1) that

$$r_1^2 = (r + \alpha)^2 + x^2 \tag{A2.3.7}$$

$$= r^2\left(1 + \frac{\alpha^2 + x^2}{r^2} + \frac{2\alpha}{r}\right) \tag{A2.3.8}$$

and

$$r_3 = r - \beta \tag{A2.3.9}$$

$$= r\left(1 - \frac{\beta}{r}\right) \tag{A2.3.10}$$

Thus,

$$\frac{1}{r_1} = \frac{1}{r}\left(1 + \frac{\alpha^2 + x^2}{r^2} + \frac{2\alpha}{r}\right)^{-\frac{1}{2}} \tag{A2.3.11}$$

and

$$\frac{1}{r_3} = \frac{1}{r}\left(1 - \frac{\beta}{r}\right)^{-1} \tag{A2.3.12}$$

One can now use the binomial expansion, i.e.,

$$(1 \pm m)^{-n} = 1 \mp nm + \frac{n(n+1)}{2} m^2 \mp \cdots \tag{A2.3.13}$$

and drop off all terms higher than the *third*.[†] Thus,

$$\frac{1}{r_1} \sim \left\{\frac{1}{r} - \frac{1}{2}\,\frac{\alpha^2 + x^2}{r^3} - \frac{\alpha}{r^2} + \frac{3}{8}\left[\frac{(\alpha^2 + x^2)^2}{r^5} + \frac{4\alpha^2}{r^3} + \frac{4\alpha(\alpha^2 + x^2)}{r^4}\right]\right\} \tag{A2.3.14}$$

and, omitting all terms with powers r greater than 3, one has

$$\frac{1}{r_1} \approx \frac{1}{r} - \frac{\alpha}{r^2} + \frac{1}{2r^3}(2\alpha^2 - x^2) \tag{A2.3.15}$$

[†] It is at this stage that the treatment of ion–quadrupole interactions diverges from that of ion–dipole interactions (*cf.* Appendix 2.2). In the latter, the binomial expansion was terminated after the second term.

Further,

$$\frac{1}{r_3} \sim \frac{1}{r}\left(1 + \frac{\beta}{r} + \frac{\beta^2}{r^2}\right)$$
$$= \frac{1}{r} + \frac{\beta}{r^2} + \frac{\beta^2}{r^3} \tag{A2.3.16}$$

Subtracting Eq. (A2.3.16) from Eq. (A2.3.15), one has

$$\frac{1}{r_1} - \frac{1}{r_3} = -\frac{(\alpha+\beta)}{r^2} + \frac{1}{2r^3}(2\alpha^2 - x^2 - 2\beta^2) \tag{A2.3.17}$$

and, therefore, by substitution of (A2.3.17) in (A2.3.6),

$$\psi_r = -\frac{2q(\alpha+\beta)}{r^2} + \frac{1}{2r^3}[2(2q\alpha^2 - 2q\beta^2) - 2qx^2] \tag{A2.3.18}$$

The first term on the right-hand side of (A2.3.18) can be rearranged as follows:

$$2q(\alpha+\beta) = 2q\alpha + 2q\beta$$
$$= \Sigma\,(2q)d \quad \text{where} \quad d = \alpha \text{ or } \beta \tag{A2.3.19}$$

Thus, as a first approximation, the water molecule can be represented as a dipolar charge distribution in which there is a positive charge of $+2q$ (due to the H atoms) at a distance α from the origin on the bisector of the H—0—H angle and a charge of $-2q$ (due to the lone electron pair) at a distance $-\beta$ from the origin, it follows that

$$\Sigma\,(2q)d = \Sigma \text{ magnitude of each charge of dipole}$$
$$\times \text{ distance of the charge from origin} \tag{A2.3.20}$$

The right-hand side of this expression is the *general* expression for the dipole moment μ, as is seen by considering the situation when $\alpha = \beta$, i.e., $\Sigma\,(2q)d = (2q)2d$, where $2d$ is the distance between the charges of the dipole, in which case one obtains the familiar expression for the dipole moment μ,

$$\mu = 2q2d \tag{A2.3.21}$$

Thus, the first term on the right-hand side of Eq. (A2.3.18) is

$$-\frac{2q(\alpha+\beta)}{r^2} = -\frac{\mu}{r^2} \tag{A2.3.22}$$

The second term can be interpreted as follows: Consider $(2q\alpha^2 - 2q\beta^2)$. It can be written thus

$$2q\alpha^2 - 2q\beta^2 = q\alpha^2 + q\alpha^2 + (-q)\beta^2 + (-q)\beta^2$$
$$= \Sigma\, qd_v^2 \quad \text{where} \quad d_v = \alpha \text{ or } \beta \tag{A2.3.23}$$

But the general definition of a quadrupole moment is the magnitude of each charge of quadrupole times the *square* of the distance of the charge from the origin. Thus, $\Sigma\, q d_y^2$ is the y component p_{yy} of the quadrupole moment for the particular coordinate system which has been chosen. Similarly, $\Sigma\, 2qx^2$ is the x component p_{xx} of the quadrupole moment. Thus,

$$2(2q\alpha^2 - 2q\beta^2) - 2qx^2 = 2p_{yy} - p_{xx} \tag{A2.3.24}$$

One can combine $2p_{yy} - p_{xx}$ into a single symbol and talk of the quadrupole moment p_W of the water molecule in the particular orientation of Fig. A2.3.1. Hence,

$$2(2q\alpha^2 - 2q\beta^2) - 2qx^2 = p_W \tag{A2.3.25}$$

and, therefore, by substituting (A2.3.22) and (A2.3.25) in (A2.3.18),

$$\psi_r = -\frac{\mu}{r^2} + \frac{p_W}{2r^3} \tag{A2.3.26}$$

The ion–quadrupole interaction energy [*cf.* Eq. (A2.3.1)] thus becomes

$$U_{I-Q} = -\frac{z_i e_0 \mu}{r^2} + \frac{z_i e_0 p_W}{2r^3} \tag{A2.3.27}$$

When a negative ion is considered, the water molecule turns around through π, and one obtains by an argument similar to that for positive ions

$$U_{I-Q} = -\frac{z_i e_0 \mu}{r^2} - \frac{z_i e_0 p_W}{2r^3} \tag{A2.3.28}$$

CHAPTER 3

ION–ION INTERACTIONS

3.1. INTRODUCTION

A model has been given for the breaking-up of an ionic crystal into free ions which stabilize themselves in solution with solvent sheaths. One central theme guided the account, the interaction of an ion with its neighboring water molecule.

But ion–solvent interactions are only part of the story relating an ion to its environment. When an ion looks out upon its surroundings, it sees not only solvent dipoles but also other ions. The mutual interaction between these ions constitutes an essential part of the picture of an electrolytic solution.

Why are ion–ion interactions of importance? Because, as will be shown, they affect the equilibrium properties of ionic solutions, and also because they interfere with the drift of ions, for instance, under an externally applied electric field (Chapter 4).

Now, the degree to which these interactions affect the properties of solutions will depend on the mean distance apart of the ions, i.e., on how densely the solution is populated with ions, because the interionic fields are distance dependent. This ionic population density will in turn depend on the nature of the electrolyte, i.e., on the extent to which the electrolyte gives rise to ions in solution.

3.2. TRUE AND POTENTIAL ELECTROLYTES

3.2.1. Ionic Crystal Are True Electrolytes

An important point to recall regarding the dissolution of an ionic crystal (Chapter 2) is that *ionic* lattices consist of ions *even before they come into contact with a solvent.* In fact, all that a polar solvent does is to use ion–dipole (or ion–quadrupole) forces to disengage the ions from the lattice sites, solvate them, and disperse them in solution.

Such ionic crystals are known as *true* electrolytes or *ionophores* (the Greek suffix *phore* means "bearer of"; thus, an ionophore is a "substance which bears ions"). When a true electrolyte is melted, its ionic lattice is dismantled and the *pure* liquid true electrolyte shows considerable ionic conduction (Chapter 2). Thus, the characteristic of a *true* electrolyte is that, in the pure liquid form, it is an ionic conductor. All salts belong to this class. Sodium chloride, therefore, is a typical true electrolyte.

3.2.2. Potential Electrolytes: Nonionic Substances Which React with the Solvent to Yield Ions

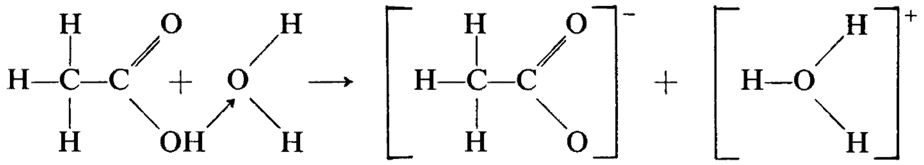
A large number of substances, e.g., organic acids, show little conductivity in the pure liquid state. Evidently, there must be some fundamental difference in structure between organic acids and inorganic salts, and this difference is responsible for the fact that one pure liquid (the true electrolyte) is an ionic conductor and the other is not.

What is this difference between, say, sodium chloride and acetic acid? Electron diffraction studies furnish an answer. They show that gaseous acetic acid consists of *separate*, *neutral* molecules and the bonding of the atoms inside these molecules is essentially nonionic. These neutral molecules retain their identity and separate existence when the gas condenses to give liquid acetic acid. Hence, there are hardly any ions in liquid acetic acid and, therefore, little conductivity.

Now, the first requirement of an electrolyte is that it should give rise to a conducting solution. From this point of view, it appears that acetic acid will never answer the requirements of an electrolyte; it is nonionic. When, however, acetic acid is dissolved in water, an interesting phenomenon occurs: ions are *produced*, and, therefore, the solutions conduct electricity. Thus, acetic acid, too, is a type of electrolyte; it is not a true electrolyte, but a *potential* one ("one which can, but has not yet, become"). Potential electrolytes are also called *ionogens*, i.e., "ion producers."

How does acetic acid, which does not consist of ions in the pure liquid state, generate ions when dissolved in water? In short, how do potential electrolytes work? Obviously, there must be some reaction between neutral acetic acid molecules and water, and this reaction must lead to the splitting of the acetic acid molecules into charged fragments, or ions.

A simple picture is as follows. Suppose that an acetic acid molecule collides with a water molecule and, in the process, the H of the acetic acid OH group is transferred from the oxygen atom of the OH to the oxygen atom of the H_2O. A proton has been transferred from CH_3COOH to H_2O



The result of the proton transfer is that two ions have been produced: (1) an acetate ion and (2) a hydrated proton. Thus, potential electrolytes (organic acids and most bases) dissociate into ions by ionogenic, or ion-forming, *chemical reactions* with solvent molecules, in contrast to true electrolytes, which give rise to ionic solutions by *physical interactions* between ions present in the ionic crystal and solvent molecules (Fig. 3.1).

The mechanism of the functioning of potential electrolytes will be described in detail later (Chapter 5).

3.2.3. An Obsolete Classification: Strong and Weak Electrolytes

The classification into true and potential electrolytes is a modern one. It is based on a knowledge of the structure of the electrolyte: whether, in the pure form, it consists of an ionic lattice or neutral molecules (Fig. 3.2). It is not based on the behavior of the solute in any particular solvent.

Historically, however, the classification of electrolytes was made on the basis of their behavior in one particular solvent, i.e., water. *Weak* electrolytes were those which yielded relatively poorly conducting solutions when dissolved in *water*, and *strong* electrolytes were those which gave highly conducting solutions when dissolved in water.

The disadvantage of this classification into strong and weak electrolytes lies in the following fact: As soon as a different solvent, i.e., a nonaqueous solvent, is chosen, what was a strong electrolyte in water may behave as a weak electrolyte in the nonaqueous solvent. For example, sodium chloride behaves like a strong electrolyte (i.e., yields highly conducting solutions) in water; and acetic acid, like a weak electrolyte. In liquid ammonia, however, the conductance behavior of acetic acid is similar to that of sodium

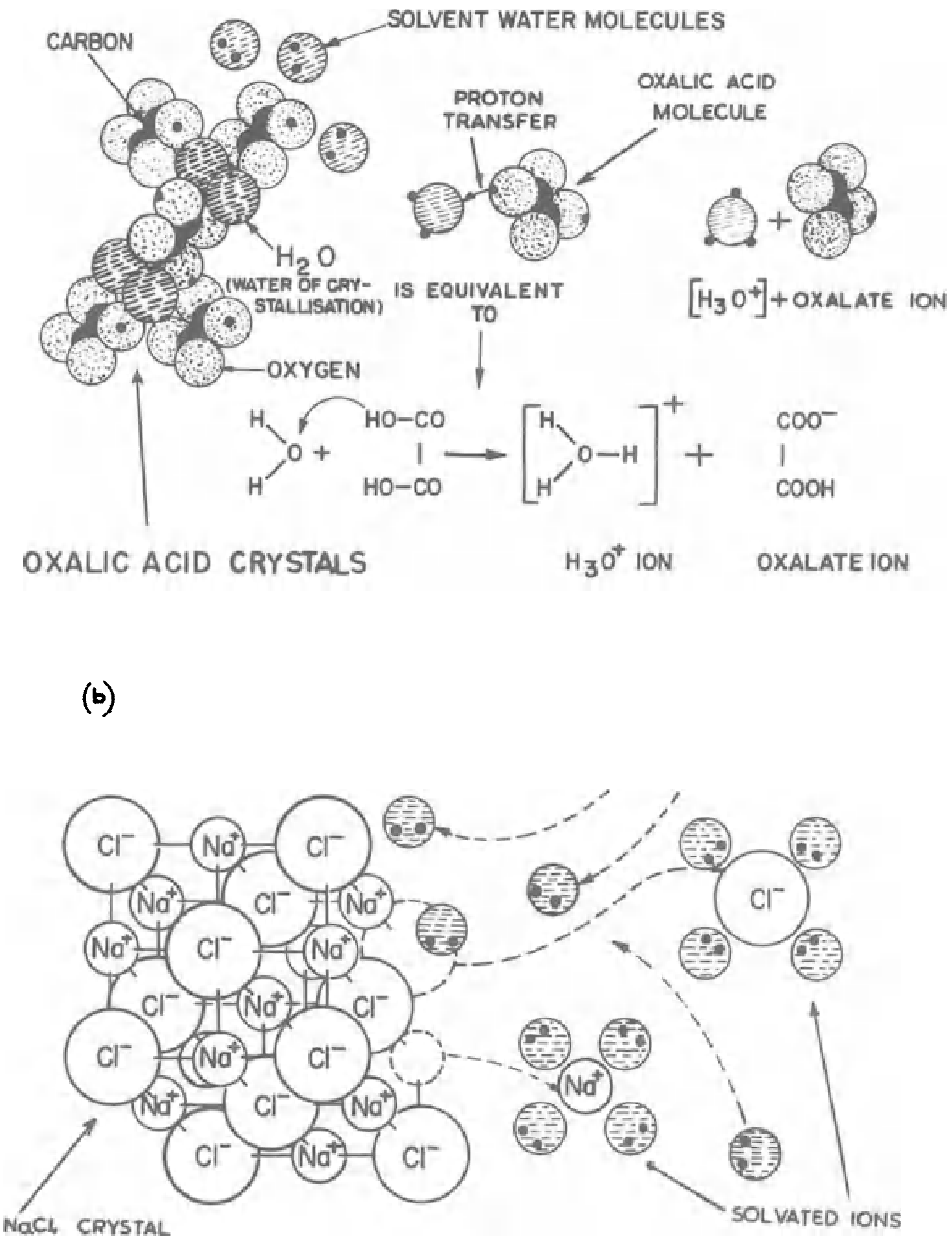


Fig. 3.1. Schematic diagram to illustrate the difference in the way potential electrolytes and true electrolytes dissolve to give ionic solutions: (a) Oxalic acid (a potential electrolyte) undergoes a proton-transfer chemical reaction with water to give rise to hydrogen ions and oxalate ions. (b) Sodium chloride (a true electrolyte) dissolves by the solvation of the Na^+ and Cl^+ ions in the crystal.

chloride in water, i.e., the solutions are highly conducting (Table 3.1). This is an embarrassing situation. Can one say: Acetic acid is weak in water and strong in liquid ammonia? What is wanted is a classification

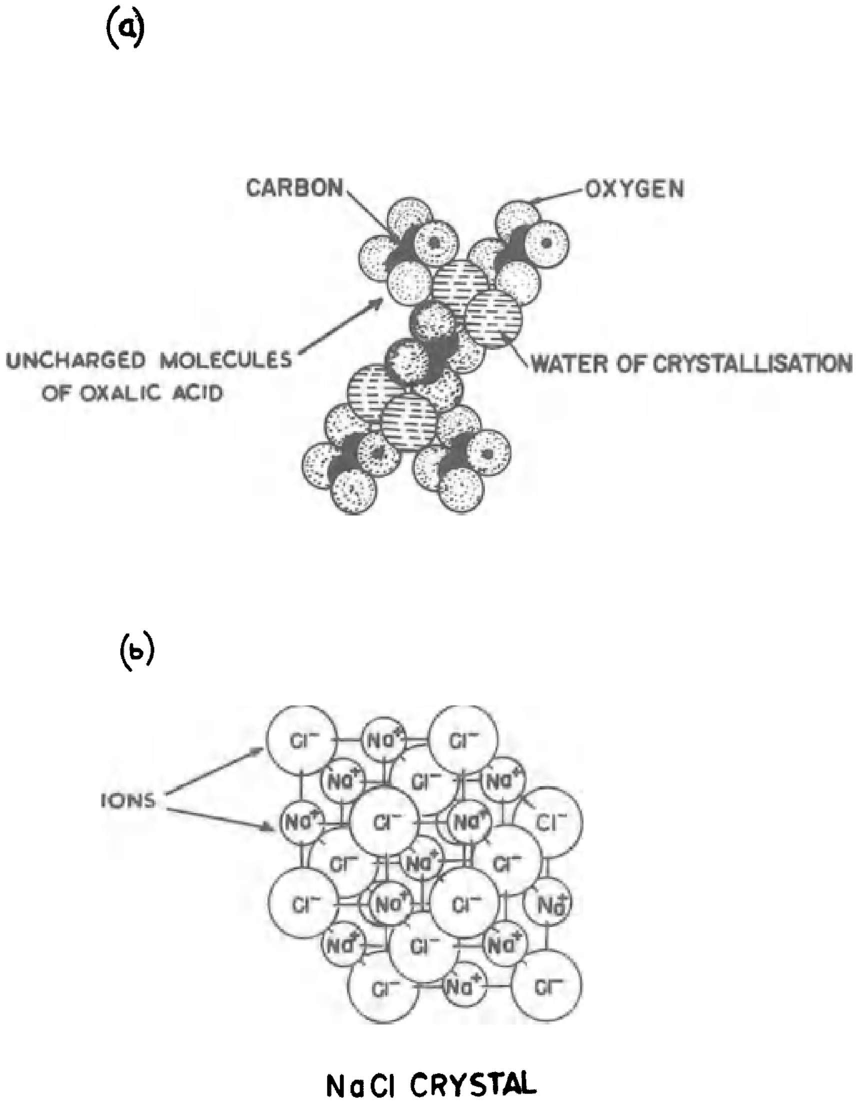


Fig. 3.2. Electrolytes can be classified as (a) potential electrolytes (e.g., oxalic acid) which, in the pure state, consist of uncharged molecules and (b) true electrolytes (e.g., sodium chloride) which, in the pure state, consist of ions.

TABLE 3.1

Conductance Behavior of Substances in Different Media

	Equivalent conductance	
	Water	Liquid ammonia
NaCl	106.7	284.0
Acetic acid	4.7	216.6

of electrolytes which is independent of the solvent concerned. The classification into true and potential electrolytes is such a classification. It does not depend on the solvent.

3.2.4. The Nature of the Electrolyte and the Relevance of Ion–Ion Interactions

Solutions of most potential electrolytes in *water* generally contain only small concentrations of ions, and, therefore, ion–ion interactions in these solutions are negligible; the ions are on the average too far apart. The behavior of such solutions is governed predominantly by the position of the equilibrium in the proton-transfer reaction between the potential electrolyte and water (see Chapter 5).

In contrast, true electrolytes are completely dissociated into ions when the parent salts are dissolved in water. The resulting solutions generally consist only of solvated ions and solvent molecules. The dependence of many of their properties on concentration (and, therefore, mean distance apart of the ions in the solution) is determined, therefore, by the interactions between ions. To understand these properties, one must understand ion–ion interactions.

Further Reading

1. G. Kortum and J. O'M. Bockris, *Textbook of Electrochemistry*, Vol. I, Elsevier, Amsterdam, 1951.
2. R. M. Fuoss and F. Accascina, *Electrolytic Conductance*, Interscience Publishers, Inc., New York, 1959.

3.3. THE DEBYE–HÜCKEL (OR ION-CLOUD) THEORY OF ION–ION INTERACTIONS

3.3.1. A Strategy for a Quantitative Understanding of Ion–Ion Interactions

The first task in thinking in detail about ion–ion interactions is to evolve a quantitative measure of these interactions.[†]

One approach is to follow a procedure similar to that used in the discussion of ion–solvent interactions (*cf.* Section 2.2.1). Thus, one can consider an initial state in which ion–ion interactions do not exist (are

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[†] The question of how one obtains an experimental measure of ion–ion interactions is discussed in Section 3.4.

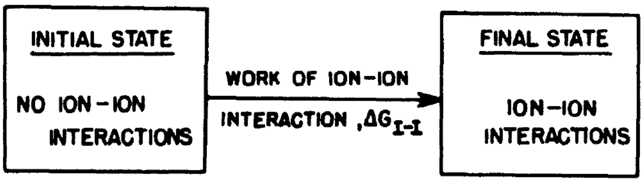

Fig. 3.3 The free energy ΔG_{I-I} of ion–ion interactions is the free-energy change in going from a hypothetical electrolytic solution, in which ion–ion interactions do not operate, to a real solution, in which these interactions do operate.

“switched off”) and a final state in which the interactions are in play (are “switched on”). Then, the free-energy change in going from the initial state to the final state can be considered the free energy ΔG_{I-I}, of ion–ion interactions (Fig. 3.3).

The final state is obvious; it is ions in solution. The initial state is not so straightforward; one cannot take ions in vacuum, because then there will be ion–solvent interactions when these ions enter the solvent. The following approach is therefore adopted. One conceives of a *hypothetical* situation in which the ions are there in solution but are nevertheless not interacting. Now, if ion–ion interactions are assumed to be electrostatic in origin (a similar assumption was made with regard to ion–solvent interactions, *cf.* Section 2.2.2), then the imaginary initial state of noninteracting ions implies an assembly of *discharged* ions.

Thus, the process of going from an initial state of noninteracting ions to a final state of ion–ion interactions is equivalent to taking an assembly of discharged ions, charging them up, and setting the electrostatic charging work equal to the free energy ΔG_{I-I} of ion–ion interactions (Fig. 3.4).

One point about the above procedure should be borne in mind. Since,

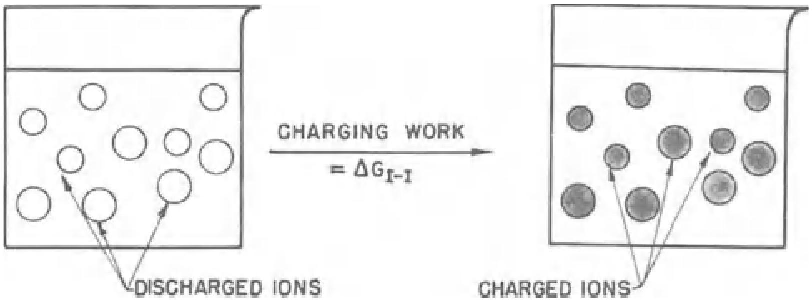

Fig. 3.4. The free energy ΔG_{I-I} of ion–ion interactions is the electrostatic work of taking an imaginary assembly of discharged ions and charging them up to obtain a solution of charged ions.

in the charging process, both the positively charged and negatively charged ionic species are charged up, one obtains a free-energy change which involves *all* the ionic species constituting the electrolyte. Generally, however, the desire is to isolate the contribution to the free energy of ion–ion interactions arising from one ionic species i only. This partial free-energy change is, by definition, the *chemical-potential change* $\Delta\mu_{i-I}$ arising from the interactions of one ionic species with the ionic assembly.

To compute this chemical-potential change $\Delta\mu_{i-I}$, rather than the free-energy change ΔG_{I-I}, one must adopt an approach similar to that used in the Born theory of solvation. One thinks of an ion of species i and imagines that this reference ion alone of all the ions in solution is in a state of zero charge (Fig. 3.5). If one computes the work of charging up the reference ion (of radius r_i) from a state of zero charge to its final charge of z_ie_0, then the charging work W times the Avogadro number N_A is equal to the partial molar free energy of ion–ion interactions, i.e., to the chemical potential of ion–ion interactions

$$\Delta\mu_{i-I} = N_A W \tag{3.1}$$

Further, one can consider a charged sphere (of radius r_i and charge z_ie_0) as a model for an ion (*cf.* Section 2.2.2) and use the expression for the work of charging the sphere from a state of zero charge to a charge of z_ie_0 to represent the work W of charging an ion, i.e.,

$$W = \frac{(z_ie_0)^2}{2\varepsilon r_i} \tag{2.16}$$

$$= \frac{z_ie_0}{2}\,\frac{z_ie_0}{\varepsilon r_i} \tag{3.2}$$

But $z_ie_0/\varepsilon r_i$ is the electrostatic potential ψ at the surface of the ion, and, therefore,

$$\Delta\mu_{i-I} = N_A W = \frac{N_A z_i e_0}{2}\,\psi \tag{3.3}$$

The essence of the task, therefore, in computing the chemical-potential change due to the interactions of the ionic species i with the ionic solution, is the calculation of the electrostatic potential produced at a reference ion by the rest of the ions in solution. Theory must aim at this quantity.

If one knew the *time-average spatial distribution* of the ions, then one could find out how all the other charges are distributed as a function of distance from the reference ion. At that stage, one of the fundamental laws of electrostatics could be used, namely, the law of the superposition of

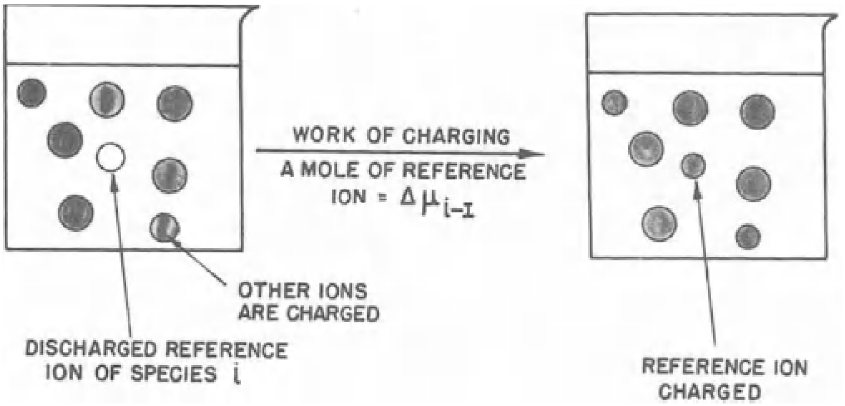

Fig. 3.5. The chemical potential $\Delta\mu_{i-I}$ arising from the interactions of an ionic species i with the electrolytic solution is equal to the Avogadro number times the electrostatic work of taking an imaginary solution in which one reference ion alone is discharged and charging this reference ion up to its normal charge.

potentials, according to which the potential at a point due to an assembly of charges is the sum of the potentials due to each of the charges in the assembly.

Thus, the problem of calculating the chemical-potential change $\Delta\mu_{i-I}$ due to the interactions between one ionic species and the assembly of all the other ions has been reduced to the following problem: On a time average, how are the ions distributed around any specified ion? If that distribution becomes known, it would be easy to calculate the electrostatic potential of the specified ion, due to the other ions and then, by Eq. (3.3), the energy of that interaction. Thus, the task is to develop a model that describes the equilibrium spatial distribution of ions inside an electrolytic solution and then to describe the model mathematically.

3.3.2. A Prelude to the Ionic-Cloud Theory

A spectacular advance in the understanding of the distribution of charges around an ion in solution was achieved in 1923 by Debye and Hückel. It was as significant in the understanding of ionic solutions as the Maxwell theory of the distribution of velocities in the understanding of gases.

Before going into the details of their theory, a moment's reflection on the magnitude of the problem would promote appreciation of their achievement.

Consider, for example, a 10^{-3} mole liter^{-1} aqueous solution of sodium chloride. There will be $10^{-6} \times 6.023 \times 10^{23}$ sodium ions per cubic centimeter of solution and the same number of chloride ions, together, of course, with the corresponding number of water molecules. Nature takes these $2 \times 6.023 \times 10^{17}$ ions cm^{-3} and arranges them so that there is a particular time-average[†] spatial distribution of the ions. The number of particles involved are enormous, and the situation appears far too complex for mathematical treatment.

But there exist conceptual techniques for tackling complex situations. One of them is model building. What is done is to conceive a model which contains only the *essential* features of the real situation. All the thinking and mathematical analysis is done on the (relatively simple) model, and, then, the theoretical predictions are compared with the experimental behavior of the real system. A good model simulates nature. If the model yields wrong answers, then one tries again by changing the imagined model until one arrives at a model, the theoretical predictions of which agree well with experimental observations.

The genius of Debye and Hückel lay in their formulation of a very simple but powerful model for the time-average distribution of ions in very dilute solutions of electrolytes. From this distribution, they were able to get the electrostatic potential contributed by the surrounding ions to the total electrostatic potential at the reference ion and, hence, the chemical-potential change arising from ion–ion interactions [*cf.* Eq.(3.3)]. Attention will now be focused on their approach.

The electrolytic solution consists of solvated ions and water molecules. The first step in the Debye–Hückel approach is to select arbitrarily any one ion out of the assembly and call it a *reference ion* or *central ion.* Only the reference ion is given the individuality of a discrete charge. What is done with the water molecules and the remaining ions? The water molecules are looked upon as a continuous dielectric medium. The remaining ions of the solution (i.e., all ions except the central ion) are lapsed into anonymity, their charges being "smeared out" into a continuous spatial distribution of charge (Fig. 3.6). Whenever the concentration of ions of one sign exceeds that of the opposite sign, there will arise a *net* or excess charge in the particular region under consideration. Obviously, the total charge in the atmosphere must be of opposite sign and exactly equal to the charge on the reference ion.

[†] Using an imaginary camera (with exposure time of $\sim 10^{-12}$ sec), suppose that it were possible to take snapshots of the ions in an electrolytic solution. Different snapshots would show the ions distributed differently in the space containing the solution; but the scrutiny of a large enough number of snapshots (say, $\sim 10^{12}$) would permit one to recognize a certain average distribution characterized by average positions of the ions; this is the time-average spatial distribution of the ions.

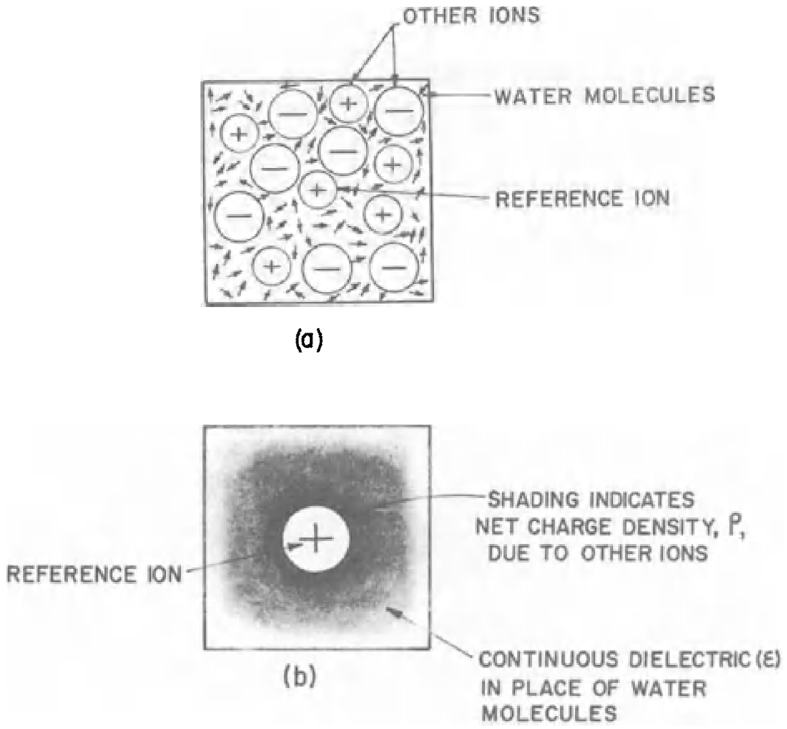

Fig. 3.6. A schematic comparison of (a) the assembly of ions and solvent molecules which constitute a real electrolytic solution and (b) the Debye–Hückel picture in which a reference ion is surrounded by net charge density ϱ due to the surrounding ions and a dielectric continuum of the same dielectric constant ε as the bulk solvent.

Thus, the electrolytic solution is considered to consist of a central ion standing alone in a continuum. Thanks to the water molecules, this continuum acquires a dielectric constant (taken to be the value for bulk water). The charges of the discrete ions which populate the environment of the central ion are thought of as smoothed out and contribute to the continuum dielectric a *net* charge density (*excess* charge per unit volume). Thus, water enters the analysis in the guise of a dielectric constant ε; and the ions, except the specific one chosen as the central ion, in the form of an excess charge density ϱ (Fig. 3.7).

Thus, the complicated problem of the time-average distribution of ions inside an electrolytic solution reduces, in the Debye–Hückel model, to the mathematically simpler problem of finding out how the excess charge density ϱ varies with distance r from the central ion.

An objection may be raised at this point. The electrolytic solution as a whole is electroneutral, i.e., the net charge density ϱ is zero. Then, why is not $\varrho = 0$ everywhere?

So as not to anticipate the detailed discussion, an intuitive answer

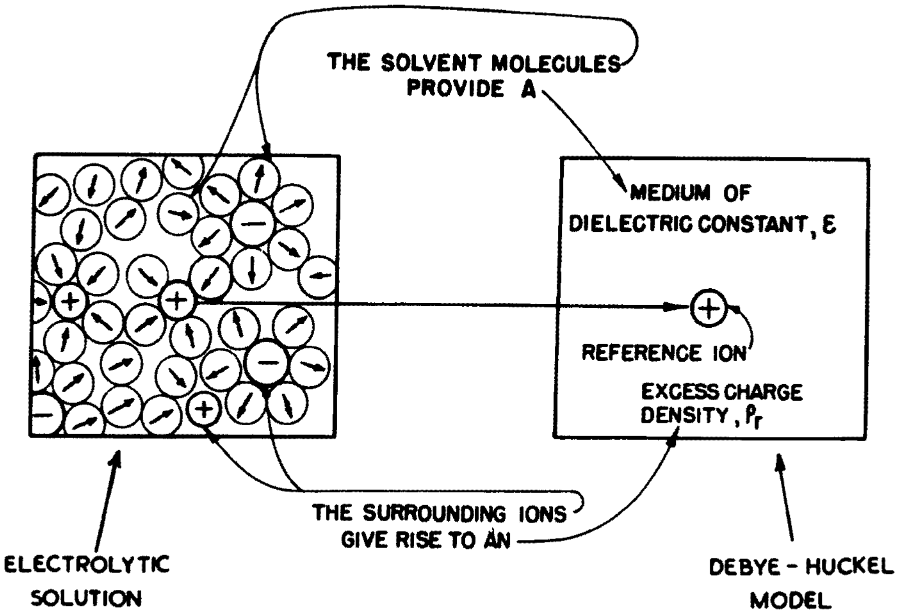

Fig. 3.7. The Debye-Hückel model is based upon selecting one ion as a reference ion, replacing the solvent molecules by a continuous medium of dielectric constant ε and the remaining ions by an excess charge density ϱ_r (the shading used in this book to represent the charge density is not indicated in this figure).

will first be given. If the central ion is, for example, positive, it will exert an attraction for negative ions; hence, there should be a greater aggregation of negative ions than of positive ions in the neighborhood of the central positive ion, i.e., $\varrho \neq 0$. An analogous situation, but with a change in sign, obtains near a central negative ion. At the same time, the thermal forces are knocking the ions about in all directions and trying to establish electroneutrality, i.e., the thermal motions try to smooth everything to $\varrho = 0$. Thus, the time average of the electrostatic forces of ordering and the thermal forces of disordering is a *local* excess of negative charge near a positive ion and an excess of positive charge near a negative ion. Of course, the excess positive charge near a negative ion compensates the excess negative charge near a positive ion, and the overall effect is electroneutrality, i.e., a ϱ of zero for the whole solution.

3.3.3. How the Charge Density near the Central Ion Is Determined by Electrostatics: Poisson's Equation

Consider an infinitesimally small volume element dv situated at a distance r from the arbitrarily selected central ion, upon which attention is to be fixed during the discussion (Fig. 3.8), and let the net charge density

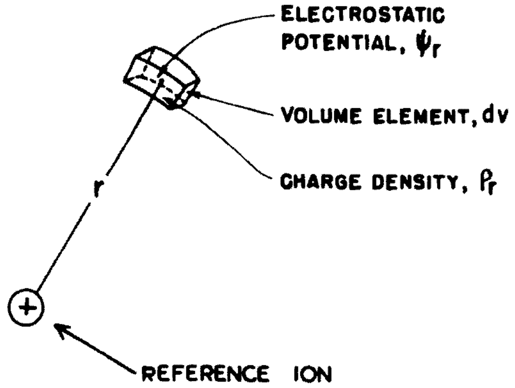

Fig. 3.8. At a distance r from the reference ion, the excess charge density and electrostatic potential, in an infinitesimal volume element dv, are ϱ_r and ψ_r, respectively.

inside the volume element be ϱ_r. Further, let the average[†] electrostatic potential in the volume element be ψ_r. The question is: What is the relation between the excess density ϱ_r in the volume element and the time-average electrostatic potential ψ_r?

One relation between ϱ_r and ψ_r is given by Poisson's equation (Appendix 3.1). There is no reason to doubt that there is spherically symmetrical distribution of positive and negative charge and, therefore, excess charge density around a given central ion. Hence, Poisson's equation can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi}{\varepsilon}\varrho_r \tag{3.4}$$

where ε is the dielectric constant of the medium and is taken to be that of bulk water.

3.3.4. How the Excess Charge Density near the Central Ion Is Given by a Classical Law for the Distribution of Point Charges in a Coulombic Field

The excess charge density in the volume element dv is equal to the total ion density (total number of ions per unit volume) times the charge on these ions. Let there be, *per unit volume*, n_1 ions of type 1, each bearing charge z_1e_0, n_2 of type 2 with charge z_2e_0, and n_i of type i with charge z_ie_0,

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[†] Actually, there are discrete charges in the neighborhood of the central ion and, therefore, discontinuous variations in the potential. But, because in the Debye-Hückel model the charges are smoothed out, the potential is averaged out.

where z_i is the valency of the ion and e_0 is the electronic charge. Then, the excess charge density ϱ_r in the volume element dv is given by

$$\varrho_r = n_1 z_1 e_0 + n_2 z_2 e_0 + \cdots + n_i z_i e_0 \tag{3.5}$$

$$= \sum n_i z_i e_0 \tag{3.6}$$

To proceed further, one must link up the unknown quantities n_1, $n_2, \ldots, n_i, \ldots$ to known quantities. The link is made on the basis of the Boltzmann distribution law of classical statistical mechanics. Thus, one writes

$$n_i = n_i^0 e^{-U/(kT)} \tag{3.7}$$

where U can be described either as the change in potential energy of the i particles when their concentration in the volume element dv is changed from the bulk value n_i^0 to n_i or as the work that must be done by a hypothetical external agency against the time average of the electrical and other forces between ions in producing the above concentration change. Since the potential energy U relates to the time average of the forces between ions rather than to the actual forces for a given distribution, it is also known as the *potential of average force.*

If there are no ion–ion interactional forces, $U = 0$; then, $n_i = n_i^0$, which means that the local concentration would be equal to the bulk concentration. If the forces are attractive, then the potential change U is negative (i.e., negative work is done by the hypothetical external agency) and $n_i > n_i^0$; there is a local *accumulation* of ions in excess of their bulk concentrations. If the forces are repulsive, the potential-energy change is positive (i.e., the work done by the external agency is positive) and $n_i < n_i^0$; there is local *depletion* of ions.

In the first instance, and as a first approximation, one may ignore all types of ion–ion interactions except those deriving from simple coulombic[†] forces. Thus, short-range interactions (e.g., dispersion interactions) are excluded. This is a fundamental assumption of the Debye–Hückel theory. Thus, the potential of average force U simply becomes the *coulombic* potential energy of an ion of charge $z_i e_0$ in the volume element dv, i.e., to

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[†] In this book, the term *coulombic* is restricted to forces (with r^{-2} dependence on distance) which are based directly on Coulomb's law. More complex forces, e.g., those which vary as r^{-4} or r^{-7}, may result as a net force from the resultant of several different coulombic interactions. Nevertheless, such more complex results of the interplay of several coulombic forces will be called *noncoulombic.*

the charge $z_i e_0$ on the ion times the electrostatic potential ψ_r in the volume element dv. That is,

$$U = z_i e_0 \psi_r \tag{3.8}$$

The Boltzmann distribution law (3.7) thus assumes the form

$$n_i = n_i^0 e^{-z_i e_0 \psi_r/(kT)} \tag{3.9}$$

Now that n_i, the concentration of the ionic species i in the volume element dv, has been related to its bulk concentration n_i^0, the expression (3.6) for the excess charge density in the volume element dv becomes

$$\varrho_r = \sum_i n_i z_i e_0 = \sum_i n_i^0 z_i e_0 e^{-z_i e_0 \psi_r/(kT)} \tag{3.10}$$

3.3.5. A Vital Step in the Debye–Hückel Theory of the Charge Distribution around Ions: Linearization of the Boltzmann Equation

At this point of the theory, Debye and Hückel made a move which was not only mathematically expedient but also turned out to be wise. They decided to carry out the analysis only for systems in which the average electrostatic potential ψ_r would be small so that

$$z_i e_0 \psi_r \ll kT \qquad \text{or} \qquad \frac{z_i e_0 \psi_r}{kT} \ll 1 \tag{3.11}$$

Based on this assumption, one can expand the exponential of Eq. (3.10) in a Taylor series, i.e.,

$$e^{-z_i e_0 \psi_r/(kT)} = 1 - \frac{z_i e_0 \psi_r}{kT} + \frac{1}{2}\left(\frac{z_i e_0 \psi_r}{kT}\right)^2 \cdots \tag{3.12}$$

and neglect all except the first two terms. Thus, in (3.10),

$$\varrho_r = \sum_i n_i^0 z_i e_0 \left(1 - \frac{z_i e_0 \psi_r}{kT}\right) \tag{3.13}$$

$$= \sum_i n_i^0 z_i e_0 - \sum_i \frac{n_i^0 z_i^2 e_0^2 \psi_r}{kT} \tag{3.14}$$

The first term $\sum n_i^0 z_i e_0$ gives the charge on the electrolytic solution as a whole. But this is zero because the solution as a whole must be electrically neutral. The local excess charge densities near ions cancel out because the excess positive charge density near a negative ion is compensated for by an excess negative charge density near a positive ion. Hence,

$$\sum_i n_i^0 z_i e_0 = 0 \tag{3.15}$$

and one is left with

$$\varrho_r = -\sum_i \frac{n_i^0 z_i^2 e_0^2 \psi_r}{kT} \tag{3.16}$$

3.3.6. The Linearized Poisson–Boltzmann Equation

The stage is now set for the calculation of the potential ψ_r and the charge density ϱ_r in terms of known parameters of the solution.

Notice that one has obtained two expressions for the charge density ϱ_r in the volume element *dv* at a distance *r* from the central ion. One has the Poisson equation [*cf.* Eq. (3.4)]

$$\varrho_r = -\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] \tag{3.17}$$

and one has the "linearized" Boltzmann distribution

$$\varrho_r = -\sum_i \frac{n_i^0 z_i^2 e_0^2 \psi_r}{kT} \tag{3.18}$$

where $\sum_i$ refers to the summation over all species of ions typified by *i*.

If one equates these two expressions one can obtain the linearized Poisson–Boltzmann (P–B) expression

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 z_i^2 e_0^2\right)\psi_r \tag{3.19}$$

The constants in the right-hand parentheses can all be lumped together and called a new constant $\varkappa^2$, i.e.,

$$\varkappa^2 = \frac{4\pi}{\varepsilon kT}\sum_i n_i^0 z_i^2 e_0^2 \tag{3.20}$$

At this point, the symbol $\varkappa$ has come in only to reduce the tedium of writing. It turns out later, however, that $\varkappa$ is not only a shorthand symbol; it contains information concerning several fundamental aspects of the distribution of ions around an ion in solution. In Chapter 7, it will be shown that it also contains information concerning the distribution of charges near a metal surface in contact with an ionic solution. In terms of $\varkappa$, the linearized P–B expression (3.19) is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=\varkappa^2\psi_r \tag{3.21}$$

3.3.7. The Solution of the Linearized P–B Equation

The rather messy-looking linearized P–B equation (3.21) can be tidied up by a mathematical trick. Introducing a new variable μ defined by

$$\psi_r=\frac{\mu}{r} \tag{3.22}$$

one has

$$\frac{d\psi_r}{dr}=\frac{d}{dr}\frac{\mu}{r}=-\frac{\mu}{r^2}+\frac{1}{r}\frac{d\mu}{dr}$$

and, therefore,

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)&=\frac{1}{r^2}\frac{d}{dr}\left(-\mu+r\frac{d\mu}{dr}\right)\\&=\frac{1}{r^2}\left(-\frac{d\mu}{dr}+r\frac{d^2\mu}{dr^2}+\frac{d\mu}{dr}\right)\\&=\frac{1}{r}\frac{d^2\mu}{dr^2}\end{aligned} \tag{3.23}$$

Hence, the differential equation (3.21) becomes

$$\frac{1}{r}\frac{d^2\mu}{dr^2}=\varkappa^2\frac{\mu}{r} \tag{3.24}$$

or

$$\frac{d^2\mu}{dr^2}=\varkappa^2\mu \tag{3.25}$$

To solve this simple differential equation, it is recalled that the differentiation of an exponential function results in the multiplication of that function by the constant in the component. For example,

$$\frac{d}{dr}e^{\pm\varkappa r}=\pm\varkappa e^{\pm\varkappa r}$$

and

$$\frac{d^2}{dr^2}e^{\pm\varkappa r}=\varkappa^2 e^{\pm\varkappa r} \tag{3.26}$$

Hence, if μ is an exponential function of r, one will obtain a differential equation of the form of Eq. (3.25). In other words, the "primitive" or "origin" of the differential equation must have had an exponential in $\varkappa r$.

Two possible exponential functions, however, would lead to the same final differential equation; one of them would have a positive exponent and the other a negative one [*cf.* Eq. (3.26)]. The general solution of the linearized P–B equation can, therefore, be written as

$$\mu = Ae^{-\varkappa r} + Be^{+\varkappa r} \tag{3.27}$$

where A and B are constants to be evaluated. Or, from Eq. (3.22),

$$\psi_r = A\frac{e^{-\varkappa r}}{r} + B\frac{e^{+\varkappa r}}{r} \tag{3.28}$$

The constant B is evaluated by using the boundary condition that, far enough from a central ion situated at $r = 0$, the thermal forces completely dominate the coulombic forces which decrease as r^2, and there is electroneutrality, i.e., the electrostatic potential ψ_r vanishes at distances sufficiently far from such an ion, $\psi_r \to 0$ as $r \to \infty$. This condition would be satisfied only if $B = 0$. Thus, if B had a finite value, Eq. (3.29) shows that the electrostatic potential would shoot up to infinity, i.e., $\psi_r \to \infty$ as $r \to \infty$, a physically unreasonable proposition. Hence,

$$\psi_r = A\frac{e^{-\varkappa r}}{r} \tag{3.29}$$

To evaluate the integration constant A, a hypothetical condition will be considered in which the solution is so dilute and, on the average, the ions are so far apart that there is a negligible interionic field. Further, the central ion is assumed to be a *point* charge, i.e., to have a radius negligible compared with the distances otherwise to be considered. Hence, the potential near the central ion is, in this special case, simply that due to an isolated point charge of value $z_i e_0$,

$$\psi_r = \frac{z_i e_0}{\varepsilon r} \tag{3.30}$$

At the same time, for this hypothetical solution in which the concentration tends to zero, i.e., $n_i^0 \to 0$, it is seen from Eq. (3.20) that $\varkappa \to 0$. Thus, in Eq. (3.29), $e^{-\varkappa r} \to 1$, and one has

$$\psi_r = \frac{A}{r} \tag{3.31}$$

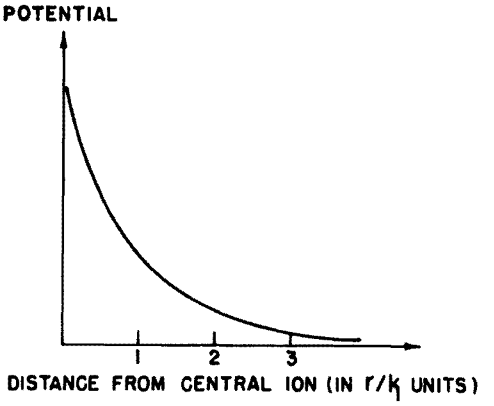

Fig. 3.9. The variation of the electrostatic potential ψ as a function of distance from the central ion expressed in units of $r/\varkappa$.

Hence, by combining Eqs. (3.30) and (3.31),

$$A = \frac{z_i e_0}{\varepsilon} \tag{3.32}$$

By introducing this expression for A into Eq. (3.29), the result is

$$\psi_r = \frac{z_i e_0}{\varepsilon} \frac{e^{-\varkappa r}}{r} \tag{3.33}$$

Here, then, is the appropriate solution of the *linearized* P–B equation (3.21). It shows how the electrostatic potential varies with distance r from an arbitrarily chosen reference ion (Fig. 3.9).

3.3.8. The Ionic Cloud around a Central Ion

In the Debye–Hückel model of a dilute electrolytic solution, a reference ion sitting at the origin of the spherical coordinate system is surrounded by the smoothed-out charge of the other ions. Further, because of the local inequalities in the concentrations of the positive and negative ions, the smoothed-out charge of one sign does not (locally) cancel out the smoothed-out charge of the opposite sign; there is a local excess charge density of one sign.

Now, as explained in Section 3.3.2, the principal objective of the Debye–Hückel theory is to calculate the time-average spatial distribution of the excess charge density around a reference ion. How is this objective attained?

The Poisson equation (3.4) relates the potential at r from the sample ion to the charge density at r, i.e.,

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d\psi_r}{dr}\right) = -\frac{4\pi}{\varepsilon} \varrho_r \tag{3.4}$$

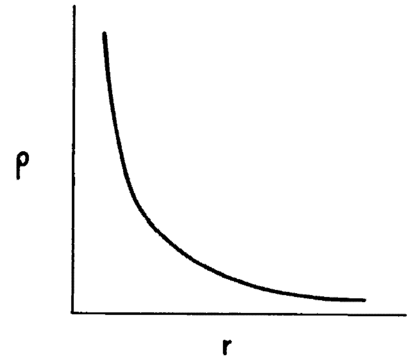

Fig. 3.10. The variation of the excess charge density ϱ as a function of distance from the central ion.

Further, one has the linearized P–B equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=\varkappa^2\psi_r \tag{3.21}$$

From these two Eqs. (3.4) and (3.21), one has the linear relation between excess charge density and potential, i.e.,

$$\varrho_r=-\frac{\varepsilon}{4\pi}\varkappa^2\psi_r \tag{3.34}$$

and by inserting the solution (3.33) for the linearized P–B equation, the result is

$$\varrho_r=-\frac{z_ie_0}{4\pi}\varkappa^2\frac{e^{-\varkappa r}}{r} \tag{3.35}$$

Here then is the desired expression for the spatial distribution of the charge density with distance *r* from the central ion (Fig. 3.10). Since the excess charge density results from an unequal distribution of positive and negative ions, Eq. (3.35) also describes the distribution of ions around a reference or sample ion.

To understand this distribution of ions, however, one must be sufficiently attuned to mathematical language to read the physical significance of Eq. (3.35). The physical ideas implicit in the distribution will therefore be stated in pictorial terms. One can say that the central reference ion is surrounded by a "cloud," or "atmosphere," of excess charge (Fig. 3.11). This ionic cloud extends into the solution (i.e., *r* increases), and the excess charge density ϱ decays with distance *r* in an exponential way. The excess charge residing on the ion cloud is opposite in sign to that of the

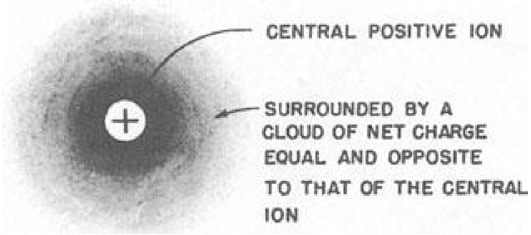

Fig. 3.11. The distribution of excess charge density around a central ion can be pictured as a cloud, or atmosphere, of net charge around the central ion.

central ion. Thus, a positively charged reference ion has a negatively charged ion atmosphere, and *vice versa* (Fig. 3.12).

Up to now, the charge *density* at a given distance has been discussed. The *total* excess charge contained in the ionic atmosphere which surrounds the central ion can, however, easily be computed. Consider a spherical shell of thickness dr at a distance r from the origin, i.e., from the center of the reference ion (Fig. 3.13). The charge dq in this thin shell is equal to the charge density ϱ_r times the volume $4\pi r^2\,dr$ of the shell, i.e.,

$$dq = \varrho_r 4\pi r^2\,dr \tag{3.36}$$

The total charge q_{cloud} contained in the ion atmosphere is obtained by summing the charges dq contained in all the infinitesimally thick spherical shells. In other words, the total excess charge surrounding the reference ion is computed by integrating dq (which is a function of the distance r from the central ion) from a lower limit corresponding to the distance from the central ion at which the cloud is taken to commence to the point where the cloud ends. Now, the ion atmosphere begins at the surface of the ion; so the lower limit depends upon the model of the ion. The first model chosen by Debye and Hückel was that of point-charge ions, in which case the lower limit is $r = 0$. The upper limit for the integration is $r \rightarrow \infty$ be-

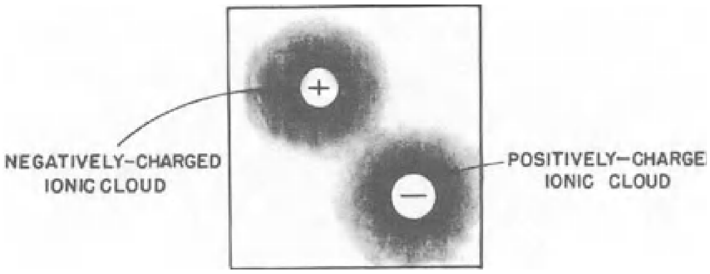

Fig. 3.12. A positively charged ion has a negatively charged ionic cloud, and *vice versa.*

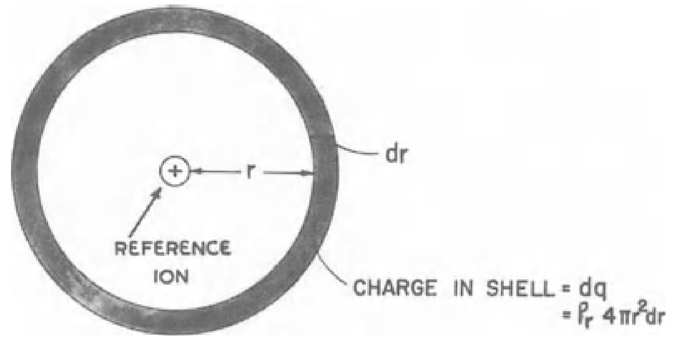

Fig. 3.13. A spherical shell, of thickness *dr*, at a distance *r* from the center of the reference ion.

cause the charge of the ionic cloud decays exponentially into the solution and becomes zero only in the limit $r \to \infty$.

Thus,

$$q_{\text{cloud}} = \int_{r=0}^{r\to\infty} dq = \int_{r=0}^{r\to\infty} \varrho_r 4\pi r^2 \, dr \tag{3.37}$$

and, by substituting for ϱ_r from Eq. (3.35), the result is

$$\begin{aligned} q_{\text{cloud}} &= -\int_{r=0}^{r\to\infty} \frac{z_i e_0}{4\pi} \varkappa^2 \frac{e^{-\varkappa r}}{r} 4\pi r^2 \, dr \\ &= -z_i e_0 \int_{r=0}^{r\to\infty} e^{-\varkappa r} (\varkappa r) \, d(\varkappa r) \end{aligned} \tag{3.38}$$

The integration can be done by parts (Appendix 3.2), leading to the result

$$q_{\text{cloud}} = -z_i e_0 \tag{3.39}$$

which means that a central ion of charge $+z_i e_0$ is enveloped by a cloud containing a total charge of $-z_i e_0$ (Fig. 3.14). Thus, the total charge on the surrounding volume is just equal and opposite to that on the reference ion. This is of course precisely how things should be so that there can be electroneutrality for the ionic solution taken as a whole; a given ion, together with its cloud, has a zero net charge.

How is this equal and opposite charge of the ion atmosphere distributed in the space around the central ion? It is seen from Eqs. (3.35) and (3.36) that the net charge in a spherical shell of thickness *dr* and at a distance *r* from the origin is

$$dq = -z_i e_0 e^{-\varkappa r} \varkappa^2 r \, dr \tag{3.40}$$

Thus, the excess charge on a spherical shell varies with *r* and has a maximum

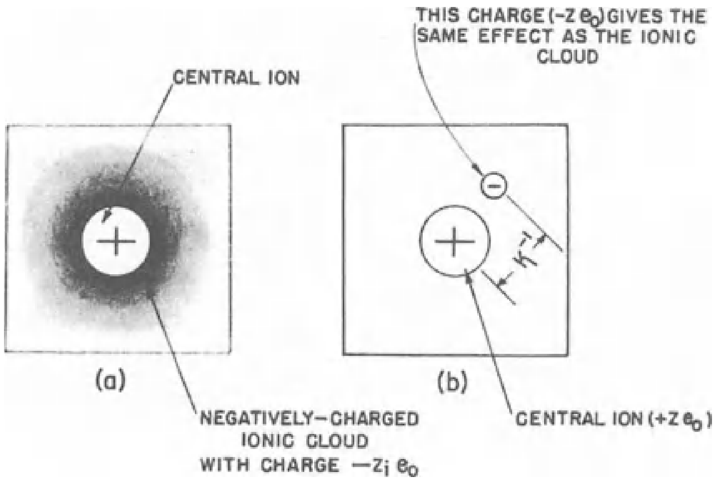

Fig. 3.14. The total charge $-z_i e_0$ on the ionic cloud is just equal and opposite to that $+z_i e_0$ on the central ion.

value for a value of r given by

$$\begin{aligned} 0 &= \frac{dq}{dr} \\ &= \frac{d}{dr}\left[-z_i e_0 \varkappa^2 (e^{-\varkappa r} r)\right] \\ &= -z_i e_0 \varkappa^2 \frac{d}{dr}(e^{-\varkappa r} r) \\ &= -z_i e_0 \varkappa^2 (e^{-\varkappa r} - r\varkappa e^{-\varkappa r}) \end{aligned} \tag{3.41}$$

Since $(z_i e_0 \varkappa^2)$ is finite, Eq. (3.41) can be true only when

$$0 = e^{-\varkappa r} - r\varkappa e^{-\varkappa r}$$

or

$$r = \varkappa^{-1} \tag{3.42}$$

Hence, the maximum value of the charge contained in a spherical shell (of infinitesimal thickness dr) is attained when the spherical shell is at a distance $r = \varkappa^{-1}$ from the reference ion (Fig. 3.15). For this reason (but see also Section 3.3.9), $\varkappa^{-1}$ is known as the *thickness*, or *radius*, of the ionic cloud which surrounds a reference ion. An elementary dimensional analysis [e.g., of Eq. (3.43)] will indeed reveal that $\varkappa^{-1}$ has the dimensions of length. Also, $\varkappa^{-1}$ is sometimes referred to as *the Debye-Hückel reciprocal length.*

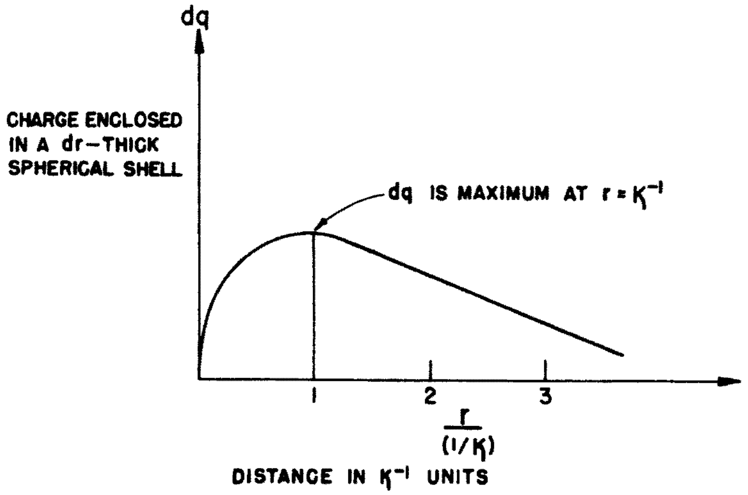

Fig. 3.15. The distance variation (in $\varkappa^{-1}$ units) of the charge *dq* enclosed in a *dr*-thick spherical shell, showing that *dq* is a maximum at $r = \varkappa^{-1}$.

It may be recalled that $\varkappa^{-1}$ is given [from Eq. (3.20)] by

$$\varkappa^{-1} = \left(\frac{\varepsilon kT}{4\pi}\,\frac{1}{\sum\limits_i n_i^0 z_i^2 e_0^2}\right)^{\frac{1}{2}} \tag{3.43}$$

As the concentration tends toward zero, the cloud tends to spread out increasingly (Fig. 3.16). Values of the thickness of the ion atmosphere for various concentrations of the electrolyte are presented in Table 3.2.

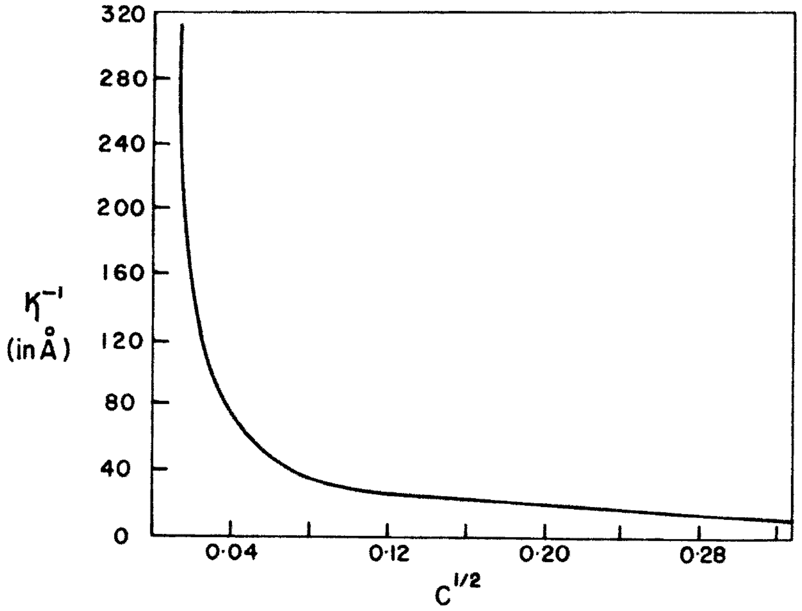

Fig. 3.16. The variation in the thickness $\varkappa^{-1}$ of the ionic cloud as a function of electrolyte concentration.

TABLE 3.2

Thickness of Ionic Atmosphere (in Angstroms) at Various Concentrations and for Various Types of Salts

C, moles liter^{-1}	Type of salt			
	1,1	1,2	2,2	1.3
10^{-4}	304	176	152	124
10^{-3}	96	55.5	48.1	39.3
10^{-2}	30.4	17.6	15.2	12.4
10^{-1}	9.6	5.5	4.8	3.9

3.3.9. How Much Does the Ionic Cloud Contribute to the Electrostatic Potential ψ_r at a Distance r from the Central Ion?

An improved feel for the effects of ionic clouds emerges from considering the following interesting problem.

Imagine, in a thought experiment, that the *charge* on the ionic cloud does not exist. There is only one charge now, that on the central ion. What is the potential at distance r from the central ion? It is simply given by the familiar formula for the potential at a distance r from a single charge, namely,

$$\psi_r = \frac{z_i e_0}{\varepsilon r} \tag{3.44}$$

Then, let the charge on the cloud be switched on. The potential ψ_r at the distance r from the central ion is no longer given by the central ion only. It is given by the law of superposition of potentials (Fig. 3.17), i.e.,

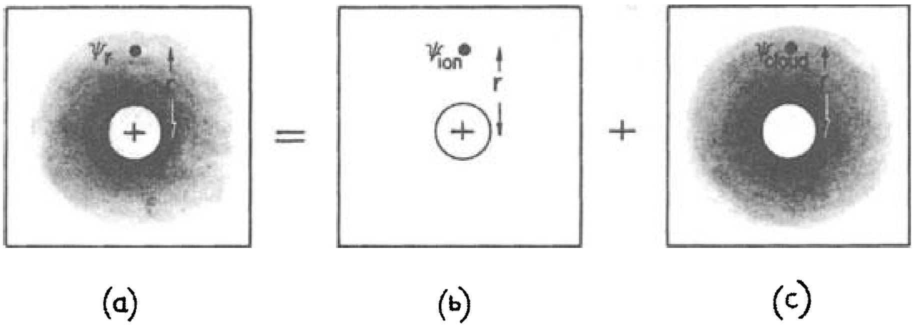

Fig. 3.17. The superposition of the potential ψ_{ion} due to the ion and that ψ_{cloud} due to the cloud yields the total potential at a distance r from the central ion.

ψ_r is the sum of the potential due to the central ion and that due to the ionic cloud

$$\psi_r = \psi_{\text{ion}} + \psi_{\text{cloud}} \tag{3.45}$$

The contribution ψ_{cloud} can thus be easily found. One rearranges Eq. (3.45) to read

$$\psi_{\text{cloud}} = \psi_r - \psi_{\text{ion}} \tag{3.46}$$

and substitutes for ψ_{ion} with Eq. (3.44) and for ψ_r with the Debye–Hückel expression [Eq. (3.33)]. Then,

$$\begin{aligned}\psi_{\text{cloud}} &= \frac{z_i e_0}{\varepsilon} \frac{e^{-\varkappa r}}{r} - \frac{z_i e_0}{\varepsilon r} \\ &= \frac{z_i e_0}{\varepsilon r}(e^{-\varkappa r} - 1) \end{aligned} \tag{3.47}$$

The value of $\varkappa$ [*cf.* Eq. (3.20)] is proportional to $\sum n_i^0 z_i^2 e_0^2$. In sufficiently dilute solutions, $\sum n_i^0 z_i^2 e_0^2$ can be taken as sufficiently small to make $\varkappa r \ll 1$,

$$e^{-\varkappa r} - 1 \sim 1 - \varkappa r - 1 \sim -\varkappa r \tag{3.48}$$

and, based on this approximation,

$$\psi_{\text{cloud}} = -\frac{z_i e_0}{\varepsilon \varkappa^{-1}} \tag{3.49}$$

By introducing the expressions (3.44) and (3.49) into the expression (3.45) for the total potential ψ_r at a distance r from the central ion, it follows that

$$\psi_r = \frac{z_i e_0}{\varepsilon r} - \frac{z_i e_0}{\varepsilon \varkappa^{-1}} \tag{3.50}$$

The second term, which arises from the cloud, reduces the value of the potential to a value *less* than that if there were no cloud. This is consistent with the model; the cloud has a charge opposite to that on the central ion and must, therefore, alter the potential in a sense opposite to that due to the central ion.

The expression

$$\psi_{\text{cloud}} = -\frac{z_i e_0}{\varepsilon \varkappa^{-1}} \tag{3.49}$$

leads to another, and helpful, way of looking at the quantity $\varkappa^{-1}$. It is seen that ψ_{cloud} is independent of r, and, therefore, the contribution of the

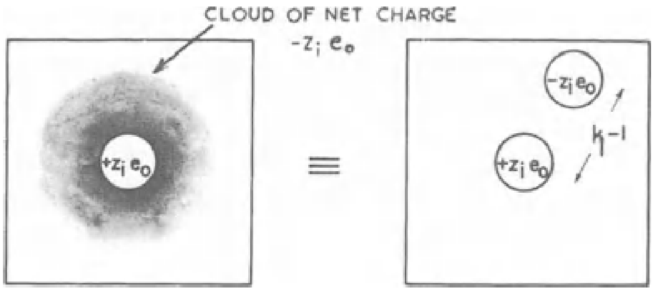

Fig. 3.18. The contribution ψ_{cloud} of the ionic cloud to the potential at the central ion is equivalent to the potential due to a single charge, equal and opposite to that of the central ion, placed at a distance κ^{-1} from the central ion.

cloud to the potential *at the site of the point-charge central ion* can be considered given by Eq. (3.49) above. But, if the entire charge of the ionic atmosphere [which is $-z_i e_0$ as required by electroneutrality—*cf.* Eq. (3.39)] were placed at a distance κ^{-1} from the central ion, then the potential produced at the reference ion would be $-z_i e_0/(\varepsilon\kappa^{-1})$. It is seen therefore from Eq. (3.49) that the effect of the ion cloud, namely, ψ_{cloud}, is equivalent to that of a single charge, equal in magnitude but opposite in sign to that of the central ion, placed at a distance κ^{-1} from the reference ion (Fig. 3.18). This is an added—and more important—reason that the quantity κ^{-1} is termed the effective thickness or radius of the ion atmosphere surrounding a central ion (*cf.* Section 3.3.8).

3.3.10. The Ionic Cloud and the Chemical-Potential Change Arising from Ion–Ion Interactions

It will be recalled (see Section 3.3.1) that it was the potential at the surface of the reference ion which needed to be known in order to calculate the chemical-potential change $\Delta\mu_{i-I}$ arising from the interactions between a particular ionic species i and the rest of the ions of the solution, i.e., one needed to know ψ in Eq. (3.3),

$$\Delta\mu_{i-I} = \frac{N_A z_i e_0}{2}\,\psi \tag{3.3}$$

It was to obtain this potential ψ that Debye and Hückel conceived their model of an ionic solution. The analysis threw up the picture of an ion being enveloped in an ionic cloud. But what is the origin of the ionic cloud? It is born of the interactions between the central ion and the ions of the environment. If there were no interactions (e.g., coulombic forces between ions), thermal forces would prevail, distribute the ions randomly ($\varrho = 0$), and wash out the ionic atmosphere. It appears therefore that the simple ionic cloud picture has not only led to success in describing the distribution of ions but also given the electrostatic potential ψ_{cloud} at the surface of a reference ion due to the interactions between this reference ion and the rest of the ions in the solution (the quantity required for reasons declared in Section 3.3.1).

Thus, the expression (3.49) for ψ_{cloud} can be substituted for ψ in Eq. (3.3) with the result that

$$\Delta\mu_{i-I} = -\frac{N_A}{2}\,\frac{(z_i e_0)^2}{\varepsilon\varkappa^{-1}} \tag{3.51}$$

The Debye–Hückel ionic-cloud model for the distribution of ions in an electrolytic solution has permitted the theoretical calculation of the chemical-potential change arising from ion–ion interactions. But, how is this theoretical expression to be checked, i.e., connected with a measured quantity? It is to this testing of the Debye–Hückel theory that attention will now be turned.

Further Reading

1. P. Debye and E. Hückel, *Z. Physik*, **24**, 185 (1923).
2. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., Reinhold Publishing Corp., New York, 1958.
3. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworth's Publications, Ltd., London, 1959.

3.4. ACTIVITY COEFFICIENTS AND ION–ION INTERACTIONS

3.4.1. The Evolution of the Concept of Activity Coefficient

The existence of ions in solution, of interactions between these ions, and of a chemical-potential change $\Delta\mu_{i-I}$ arising from ion–ion interactions have all been taken to be self-evident in the treatment hitherto presented here. This, however, is a modern point of view. The thinking about electrolytic solutions actually developed along a different path.

Ionic solutions were at first treated in the same way as nonelectrolytic solutions, though the latter do not contain (interacting) charged species. The starting point was the classical thermodynamic formula for the chemical potential μ_i of a nonelectrolyte solute

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{3.52}$$

In this expression, x_i is the concentration[†] of the solute in mole fraction units, and μ_i^0 is its chemical potential in the standard state, i.e., when x_i assumes a standard or normalized value of unity

$$\mu_i = \mu_i^0 \qquad \text{when} \qquad x_i = 1 \tag{3.53}$$

Since the solute particles in a solution of a nonelectrolyte are uncharged, they do not engage in long-range coulombic interactions. The short-range interactions arising from dipole–dipole or dispersion forces become significant only when the mean distance between the solute particles is small, i.e., when the concentration of the solute is high. Thus, one can to a good approximation say that there are no interactions between solute particles in dilute nonelectrolyte solutions. Hence, if Eq. (3.52) for the chemical potential of a solute in a nonelectrolyte solution (with noninteracting particles) is used for the chemical potential of a ionic species i in an electrolytic solution, then it is tantamount to ignoring the long-range coulombic interactions between ions. In an actual electrolytic solution, however, ion–ion interactions operate whether one ignores them or not. It is obvious, therefore, that measurements of the chemical potential μ_i of an ionic species—or, rather, measurements of any property which depends on the chemical potential—would reveal the error in Eq. (3.52), which is blind to ion–ion interactions. In other words, experiments show that, *even in dilute solutions,*

$$\mu_i - \mu_i^0 \neq RT \ln x_i$$

In this context, a frankly empirical approach was adopted by earlier workers, not yet blessed by Debye and Hückel's light. Solutions that obeyed Eq. (3.52) were characterized as *ideal* solutions since this equation applies to systems of noninteracting solute particles, i.e., ideal particles. Electrolytic solutions which do not obey the equation were said to be *nonideal.* In order to use an equation of the form of (3.52) to treat nonideal electrolytic solutions, an empirical correction factor f_i was introduced by Lewis as a modifier of the concentration term[‡]

$$\mu_i - \mu_i^0 = RT \ln x_i f_i \tag{3.54}$$

[†] The value of x_i^0 in the case of an electrolyte derives from the number of moles of ions in species i actually present in solution. This number need not be equal to the number of moles of i expected of dissolved electrolyte; if, for instance, the electrolyte is a potential one, then only a fraction of the electrolyte may react with the solvent to form ions, i.e., the electrolyte may be incompletely dissociated.

[‡] The standard chemical potential μ_i^0 has the same significance here as in Eq. (3.52) for ideal solutions. Thus, μ_i^0 can be defined either as the chemical potential of an *ideal*

It was argued that, in nonideal solutions, it was not just the analytical concentration x_i of species i, but its *effective* concentration x_if_i which determined the chemical-potential change $\mu_i - \mu_i^0$. This effective concentration x_if_i was also known as the *activity* a_i of the species i, i.e.,

$$a_i = x_if_i \tag{3.55}$$

and the correction factor f_i, as the *activity coefficient*. For ideal solutions, the activity coefficient is unity, and the activity a_i becomes identical to the concentration x_i, i.e.,

$$a_i = x_i \qquad \text{when} \qquad f_i = 1 \tag{3.56}$$

Thus, the chemical-potential change in going from the standard state to the final state can be written as

$$\mu_i - \mu_i^0 = RT \ln x_i + RT \ln f_i \tag{3.57}$$

Equation (3.57) summarizes the empirical or formal treatment of the behavior of electrolytic solutions. Such a treatment cannot furnish a theoretical expression for the activity coefficient f_i. It merely recognizes that expressions such as (3.52) must be modified if significant interaction forces exist between solute particles.

3.4.2. The Physical Significance of Activity Coefficients

For a hypothetical system of *ideal* (noninteracting) particles, the chemical potential has been stated to be given by

$$\mu_i\,(\text{ideal}) = \mu_i^0 + RT \ln x_i \tag{3.52}$$

For a real system of interacting particles, the chemical potential has been expressed in the form

$$\mu_i\,(\text{real}) = \mu_i^0 + RT \ln x_i + RT \ln f_i \tag{3.57}$$

Hence, to analyze the physical significance of the activity coefficient term in Eq. (3.57), it is necessary to compare this equation with Eq. (3.52). It is obvious that, when Eq. (3.52) is subtracted from Eq. (3.57), the differ-

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solution in its standard state of $x_i = 1$ or as the chemical potential of a solution in its state of $x_i = 1$ and $f_i = 1$, i.e., $a_i = 1$. No real solution can have $f_i = 1$ when $x_i = 1$; so, the standard state pertains to the same hypothetical solution as the standard state of an ideal solution.

ence, i.e., μ_i (real) $-$ μ_i (ideal), is the chemical-potential change $\Delta\mu_{i-I}$ arising from interactions between the solute particles (ions in the case of electrolyte solutions). That is,

$$\mu_i \text{ (real)} - \mu_i \text{ (ideal)} = \Delta\mu_{i-I} \tag{3.58}$$

and, therefore,

$$\Delta\mu_{i-I} = RT \ln f_i \tag{3.59}$$

Thus, the activity coefficient is a measure of the chemical-potential change arising from ion–ion interactions. There are several well-established methods of experimentally determining activity coefficients, and these methods are treated in adequate detail in standard treatises (*cf.* Further Reading at the end of this section).

Now, according to the Debye–Hückel theory, the chemical-potential change $\Delta\mu_{i-I}$ arising from ion–ion interactions has been shown to be given by

$$\Delta\mu_{i-I} = -\frac{N_A(z_i e_0)^2}{2\varepsilon\varkappa^{-1}} \tag{3.51}$$

Hence, by combining Eqs. (3.51) and (3.58), the result is

$$RT \ln f_i = -\frac{N_A(z_i e_0)^2}{2\varepsilon\varkappa^{-1}} \tag{3.60}$$

Thus, the Debye–Hückel ionic-cloud model for ion–ion interactions has permitted a theoretical calculation of activity coefficients resulting in Eq. (3.59).

The activity coefficient in Eq. (3.59) arises from the formula (3.57) for the chemical potential, in which the concentration of the species i is expressed in mole fraction x_i units. But one can also express the concentration in moles per liter of solution (molarity) or in moles per kilogram of solvent (molality). Thus, alternate formulas for the chemical potential of a species i in an *ideal* solution read

$$\mu_i = \mu_i^0(c) + RT \ln c_i \tag{3.61}$$

and

$$\mu_i = \mu_i^0(m) + RT \ln m_i \tag{3.62}$$

where c_i and m_i are the molarity and molality of the species i, respectively; and $\mu_i^0(c)$ and $\mu_i^0(m)$, the corresponding standard chemical potentials.

When the concentration of the ionic species in a *real* solution is expressed as a molarity c_i or a molality m_i, there are corresponding activity coefficients γ_c and γ_m and corresponding expressions for μ_i

$$\mu_i = \mu_i^0(c) + RT \ln c_i + RT \ln \gamma_c \tag{3.63}$$

and

$$\mu_i = \mu_i^0(m) + RT \ln m_i + RT \ln \gamma_m \tag{3.64}$$

3.4.3. The Activity Coefficient of a Single Ionic Species Cannot Be Measured

Before the activity coefficients calculated on the basis of the Debye–Hückel model can be compared with experiment, there arises a problem similar to one faced in the discussion of ion–solvent interactions (Chapter 2).

There, it was realized the heat of hydration of an individual ionic species could not be measured because such a measurement would involve the transfer of ions of only one species into a solvent instead of ions of two species with equal and opposite charges. Even if such a transfer were physically possible, it would result in a charged solution[†] and, therefore, an extra, undesired interaction between the ions and the electrified solution. The only way out was to transfer a neutral electrolyte (an equal number of positive and negative ions) into the solvent, but this meant that one could only measure the heat of interactions of a *salt* with the solvent and this experimental quantity could not be separated into the individual ionic heats of hydration.

Here, in the case of ion–ion interactions, the desired quantity is the activity coefficient f_i,[‡] which depends through Eq. (3.57) on $\mu_i - \mu_i^0$. This means that one seeks the free-energy change of an ionic solution per mole of ions of a single species *i*. To measure this quantity, one would have a problem similar to that experienced with ion–solvent interactions, namely, the measurement of the change of free energy of a solution, resulting from a change in the concentration of one ionic species only.

This change in free energy associated with the addition of one ionic species only would include an undesired work term representing the electrical work of interaction between the ionic species being added and the charged solution.[†] To avoid free-energy changes associated with interacting

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[†] The solution may not be initially charged but will become so once an ionic species is added to it.

[‡] The use of the symbol γ for the activity coefficients when the concentration is expressed in molarities and molalities should be noted. When the concentration is expressed as a mole fraction, f_i has here been used. For dilute solutions, the numerical values of activity coefficients for these different systems of units are almost the same.

with a solution, it is necessary that, after changing the concentration of the ionic species, the electrolytic solution should end up uncharged and electroneutral. This aim is easily accomplished by adding an electroneutral electrolyte containing the ionic species *i*. Thus, the concentration of sodium ions can be altered by adding sodium chloride. The solvent, water, maintains its electroneutrality when the uncharged ionic lattice (containing two ionic species of opposite charge) is dissolved in it.

When ionic lattices, i.e., salts, are dissolved instead of individual ionic species, one eliminates the problem of ending up with charged solutions but another problem emerges. If one increases the concentration of sodium ions by adding the salt sodium chloride, one has perforce to produce a simultaneous increase of the concentration of chloride ions. This means, however, that there are two contributions to the change in free energy associated with a change in salt concentration: (1) the contribution of the positive ions, and (2) the contribution of the negative ions.

Since neither the positive nor the negative ions can be added separately, the individual contributions of the ionic species to the free energy of the system cannot be determined. Thus, the activity coefficients of individual ions, which depend by, e.g., (3.63) on the free-energy changes when the particular individual species alone is added to the solution, are inaccessible to experimental measurement. One can only measure the activity coefficient of the net electrolyte, i.e., of at least two ionic species together. It is necessary, therefore, to establish a conceptual link between the activity coefficient of an *electrolyte* in solution (that quantity accessible to experiment) and that of only one of its ionic species [*not* accessible to experiment, but calculable theoretically from (3.60)].

3.4.4. The Mean Ionic Activity Coefficient

Consider a uni-univalent electrolyte MA (e.g., NaCl). The chemical potential of the M^+ ions is [*cf.* (3.58)]

$$\mu_{M^+} = \mu^0_{M^+} + RT\ln x_{M^+} + RT\ln f_{M^+} \tag{3.65}$$

and the chemical potential of the A^- ions is

$$\mu_{A^-} = \mu^0_{A^-} + RT\ln x_{A^-} + RT\ln f_{A^-} \tag{3.66}$$

Adding the two expressions, one obtains

$$\mu_{M^+} + \mu_{A^-} = (\mu^0_{M^+} + \mu^0_{A^-}) + RT\ln(x_{M^+}x_{A^-}) + RT\ln(f_{M^+}f_{A^-}) \tag{3.67}$$

What has been obtained here is the change in the free energy of the system due to the addition of 2 moles of ions—1 mole of M^+ ions and 1 mole of A^- ions—which are contained in 1 mole of electroneutral salt MA.

Now, suppose that one is only interested in the *average* contribution to the free energy of the system from 1 mole of both M^+ and A^- ions. One has to divide Eq. (3.67) by 2

$$\frac{\mu_{M^+} + \mu_{A^-}}{2} = \frac{\mu^0_{M^+} + \mu^0_{A^-}}{2} + RT\ln(x_{M^+}x_{A^-})^{\frac{1}{2}} + RT\ln(f_{M^+}f_{A^-})^{\frac{1}{2}} \qquad (3.68)$$

At this stage, one can define several new quantities

$$\mu_{\pm} = \frac{\mu_{M^+} + \mu_{A^-}}{2} \qquad (3.69)$$

$$\mu^0_{\pm} = \frac{\mu^0_{M^+} + \mu^0_{A^-}}{2} \qquad (3.70)$$

$$x_{\pm} = (x_{M^+}x_{A^-})^{\frac{1}{2}} \qquad (3.71)$$

and

$$f_{\pm} = (f_{M^+}f_{A^-})^{\frac{1}{2}} \qquad (3.72)$$

What is the significance of these quantities $\mu_{\pm}$, $\mu_{\pm}{}^0$, $x_{\pm}$, and $f_{\pm}$? It is obvious they are all *average* quantities—the mean chemical potential $\mu_{\pm}$, the mean standard chemical potential $\mu_{\pm}{}^0$, the mean ionic mole fraction $x_{\pm}$, and the mean ionic-activity coefficient $f_{\pm}$. In the case of $\mu_{\pm}$ and $\mu_{\pm}{}^0$, the arithmetic mean (half the sum) is taken because free energies are additive; but, in the case of $x_{\pm}$ and $f_{\pm}$, the geometric mean (the square root of the product) is taken because the effects of mole fraction and activity coefficient on free energy are multiplicative.

In this notation, Eq. (3.68) for the *average* contribution of a mole of ions to the free energy of the system becomes

$$\mu_{\pm} = \mu_{\pm}{}^0 + RT\ln x_{\pm} + RT\ln f_{\pm} \qquad (3.73)$$

since a mole of ions is produced by the dissolution of half a mole of salt. In other words, $\mu_{\pm}$ is half the chemical potential μ_{MA} of the salt.†

$$\tfrac{1}{2}\mu_{MA} = \mu_{\pm} = \mu_{\pm}{}^0 + RT\ln x_{\pm} + RT\ln f_{\pm}. \qquad (3.74)$$

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† The symbol μ_{MA} should not be taken to mean that *molecules* of MA exist in the solution; μ_{MA} is the observed free-energy change of the system resulting from the dissolution of a mole of electrolyte.

Thus, a clear connection has been set up between observed free-energy changes μ_{MA} consequent upon the change from a state in which the two ionic species of a salt are infinitely far apart to a state corresponding to the given concentration, and its mean ionic-activity coefficient $f_\pm$. Hence the value of $f_\pm$ is experimentally measurable. This mean ionic-activity coefficient cannot, however, be *experimentally* split into the individual ionic-activity coefficients. All that can be obtained from $f_\pm$ is the *product* of the individual ionic-activity coefficients [Eq. (3.72)]. The theoretical approach must hence be to calculate the activity coefficients f_+ and f_- for the positive and negative ions [*cf.* Eq. (3.60)] and combine them through Eq. (3.72) into a mean ionic-activity coefficient $f_\pm$ which can be compared with the experimentally derived mean ionic-activity coefficient.

3.4.5. The Conversion of Theoretical Activity-Coefficient Expressions into a Testable Form

Individual ionic-activity coefficients are experimentally inaccessible (Section 3.4.3); hence, it is necessary to relate the theoretical individual activity coefficient f_i [Eq. (3.64)] to the experimentally accessible *mean* ionic-activity coefficient $f_\pm$ so that the Debye–Hückel model can be tested.

The procedure is to make use of the relation (3.72)

$$f_\pm = (f_{\mathrm{M}^+} f_{\mathrm{A}^-})^{\frac{1}{2}} \tag{3.72}$$

of which the general form for an electrolyte which dissolves to give ν_+ z_+-valent positive ions and ν_- z_--valent negative ions can be shown to be (*cf.* Appendix 3.3)

$$f_\pm = (f_+^{\nu_+} f_-^{\nu_-})^{1/\nu} \tag{3.75}$$

where f_+ and f_- are the activity coefficients of the positive and negative ions, and

$$\nu = \nu_+ + \nu_- \tag{3.76}$$

By taking logarithms of both sides of Eq. (3.75), the result is

$$\ln f_\pm = \frac{1}{\nu}(\nu_+ \ln f_+ + \nu_- \ln f_-) \tag{3.77}$$

At this stage, the Debye–Hückel expressions (3.60) for f_+ and f_- can be introduced into Eq. (3.77) to give

$$\ln f_\pm = -\frac{1}{\nu}\left[\frac{N_A e_0^2}{2\varepsilon RT}\varkappa(\nu_+ z_+^2 + \nu_- z_-^2)\right] \tag{3.78}$$

Since the solution as a whole is electroneutral, ν_+z_+ must be equal to ν_-z_-, and, therefore,

$$\begin{aligned}\nu_+z_+^2 + \nu_-z_-^2 &= \nu_-z_-z_+ + \nu_+z_+z_- \\ &= z_+z_-(\nu_+ + \nu_-) \\ &= z_+z_-\nu \end{aligned} \tag{3.79}$$

Using this relation in Eq. (3.78), one obtains

$$\ln f_\pm = -\frac{N_A(z_+z_-)e_0^2}{2\varepsilon RT}\varkappa \tag{3.80}$$

Now, one can substitute for $\varkappa$ from Eq. (3.43)

$$\varkappa = \left(\frac{4\pi}{\varepsilon kT}\sum n_i^0 z_i^2 e_0^2\right)^{\frac{1}{2}} \tag{3.43}$$

but, before this substitution is made, $\varkappa$ can be expressed in a different form. Since

$$n_i^0 = \frac{c_i N_A}{1000} \tag{3.81}$$

where c is the concentration in moles per liter, it follows that

$$\sum n_i^0 z_i^2 e_0^2 = \frac{N_A e_0^2}{1000}\sum c_i z_i^2 \tag{3.82}$$

Prior to the Debye–Hückel theory, $\frac{1}{2}\sum c_i z_i^2$ had been empirically introduced by Lewis as a quantity of importance in the treatment of ionic solutions. Since it quantifies the charge in an electrolytic solution, it was known as the *ionic strength* and given the symbol I

$$I = \tfrac{1}{2}\sum c_i z_i^2 \tag{3.83}$$

In terms of the ionic strength I, $\varkappa$ can be written as [*cf.* Eqs. (3.43), (3.82), and (3.83)]

$$\varkappa = \left(\frac{8\pi N_A e_0^2}{1000\varepsilon kT}\right)^{\frac{1}{2}} I^{\frac{1}{2}} \tag{3.84}$$

or as

$$\varkappa = BI^{\frac{1}{2}} \tag{3.85}$$

where

$$B = \left(\frac{8\pi N_A e_0^2}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{3.86}$$

TABLE 3.3

Value of the Parameter *B* for Water at Various Temperatures

Temperature, °C	$10^{-8}B$
0	0.3248
10	0.3264
20	0.3282
25	0.3291
30	0.3301
35	0.3312
40	0.3323
50	0.3346
60	0.3371
80	0.3426
100	0.3488

Values of B for water at various temperatures are given in Table 3.3.

On the basis of the expression (3.85) for $\varkappa$, Eq. (3.80) becomes

$$\ln f_{\pm} = -\frac{N_A(z_+z_-)e_0^2}{2\varepsilon RT}BI^{\frac{1}{2}} \tag{3.87}$$

or

$$\log f_{\pm} = -\frac{1}{2.303}\frac{N_Ae_0^2}{2\varepsilon RT}B(z_+z_-)I^{\frac{1}{2}} \tag{3.88}$$

For greater compactness, one can define a constant A given by

$$A = \frac{1}{2.303}\frac{N_Ae_0^2}{2\varepsilon RT}B \tag{3.89}$$

and write Eq. (3.88) in the form

$$\log f_{\pm} = -A(z_+z_-)I^{\frac{1}{2}} \tag{3.90}$$

For 1:1-valent electrolytes, $z_+ = z_- = 1$ and $I = c$, and, therefore,

$$\log f_{\pm} = -Ac^{\frac{1}{2}} \tag{3.91}$$

Values of the constant A for water at various temperatures are given in Table 3.4.

In Eqs. (3.90) and (3.91), the theoretical mean ionic-activity coefficients are in a form directly comparable with experiment. A quantitative compari-

TABLE 3.4

Values of Constant A for Water at Various Temperatures

Temperature, °C	Values of constant A
0	0.4918
10	0.4989
20	0.5070
25	0.5115
30	0.5161
40	0.5262
50	0.5373
60	0.5494
80	0.5767
100	0.6086

son of the experimentally observed activity coefficients with those calculated with the Debye–Huckel model can now be made.

Further Reading

1. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solution*, 3rd ed., Reinhold Publishing Corp., New York, 1958.
2. R. A. Robinson and R. H. Stokes, *Electrolytic Solutions*, Butterworth's Publications, Ltd., London, 1959.
3. G. Kortüm, *Treatise on Electrochemistry*, Elsevier, Amsterdam, 1965.

3.5. THE TRIUMPHS AND LIMITATIONS OF THE DEBYE–HÜCKEL THEORY OF ACTIVITY COEFFICIENTS

3.5.1. How Well Does the Debye–Hückel Theoretical Expression for Activity Coefficients Predict Experimental Values?

The approximate theoretical equation

$$\log f_{\pm} = -A(z_+z_-)I^{\frac{1}{2}} \tag{3.90}$$

indicates that the logarithm of the activity coefficient must decrease linearly with the square root of the ionic strength or, in the case of 1:1-valent electrolytes,[†] with $c^{\frac{1}{2}}$. Further, the slope of the $\log f_{\pm}$ versus $I^{\frac{1}{2}}$ straight line can be unambiguously evaluated from fundamental physical constants and

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[†] That is, $I = \frac{1}{2}\sum c_i z_i^2$. For a 1:1 electrolyte, $I = \frac{1}{2}(c_i 1^2 + c_j 1^2)$. As $c_i = c_j = c$, $I = c$.

TABLE 3.5

Experimental Values of Activity Coefficients of Various Electrolytes at Different Concentrations at 25°C

1:1 electrolyte, HCl					
Concentration, molal	0.0001	0.0002	0.0005	0.001	0.002
Mean activity coefficient	0.9891	0.9842	0.9752	0.9656	0.9521
2:1 electrolyte, $CaCl_2$					
Concentration, (moles per liter)	0.0018	0.0061	0.0095		
Mean activity coefficient	0.8588	0.7745	0.7361		
2:2 electrolyte, $CdSO_4$					
Concentration, molal	0.0005	0.001	0.005		
Mean activity coefficient	0.774	0.697	0.476		

from (z_+z_-). Finally, the slope does not depend on the particular electrolyte (i.e., whether it is NaCl or KBr, etc.) but only on its valence type, i.e., on the charges borne by the ions of the electrolyte, whether it is a 1:1-valent or 2:2-valent electrolyte, etc. These are clear-cut predictions.

Even before any detailed comparison with experiment, one can use an elementary spot check: At infinite dilution, where the interionic forces are negligible, does the theory yield the activity coefficient which one would expect from experiment, i.e., unity? At infinite dilution, c or $I \rightarrow 0$, which means that $\log f_{\pm} \rightarrow 0$ or $f_{\pm} \rightarrow 1$. The properties of an extremely dilute solution of ions should be the same as those of a solution containing nonelectrolyte particles. Thus, the Debye–Hückel theory comes out successfully from the infinite dilution test.

Further, if one takes the experimental values of the activity coefficient (Table 3.5) at extremely low electrolyte concentration and plots $\log f_{\pm}$ versus $I^{\frac{1}{2}}$ curves, it is seen that: (1) They are linear (*cf.* Fig. 3.19), and (2) they are grouped according to the valence type of the electrolyte (Fig. 3.20). Finally, when one compares the calculated and observed slopes, it becomes clear that there is excellent agreement to an error of $\pm 0.5\%$ (Table 3.6 and Fig. 3.21) between the results of experiment and the conclusions emerging from an analysis of the ionic-cloud model of the distribution of ions in an electrolyte. Since Eq. (3.90) has been found to be valid at limiting low electrolyte concentrations, it is generally referred to as the *Debye–Hückel limiting law.*

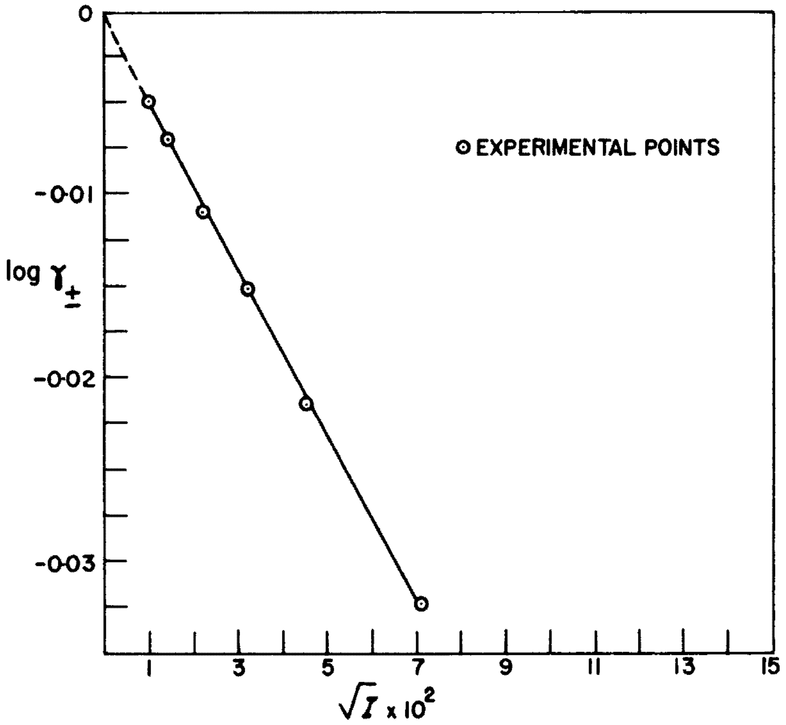

Fig. 3.19. The logarithm of the experimental mean activity coefficient of HCl varies linearly with the square root of the ionic strength.

The success of the Debye–Hückel limiting law is no mean achievement. One has only to think of the complex nature of the real system, of the presence of the solvent which has been recognized only through a dielectric

TABLE 3.6

Experimental and Calculated Values of the Slope of $\log f_\pm - \sqrt{I}$ for Alcohol Water Mixtures at 25°C

Solvent mole fraction water	Dielectric constant	Slope	
		Observed	Calculated
	1:1 *type of salt, Croceo tetranitro diamino cobaltiate*		
1.00	78.8	0.50	0.50
0.80	54.0	0.89	0.89
	1:2 *type of salt, Croceo sulfate*		
1.00	78.8	1.10	1.08
0.80	54.0	1.74	1.76
	3:1 *type of salt, Luteo iodate*		
1.00	78.8	1.52	1.51

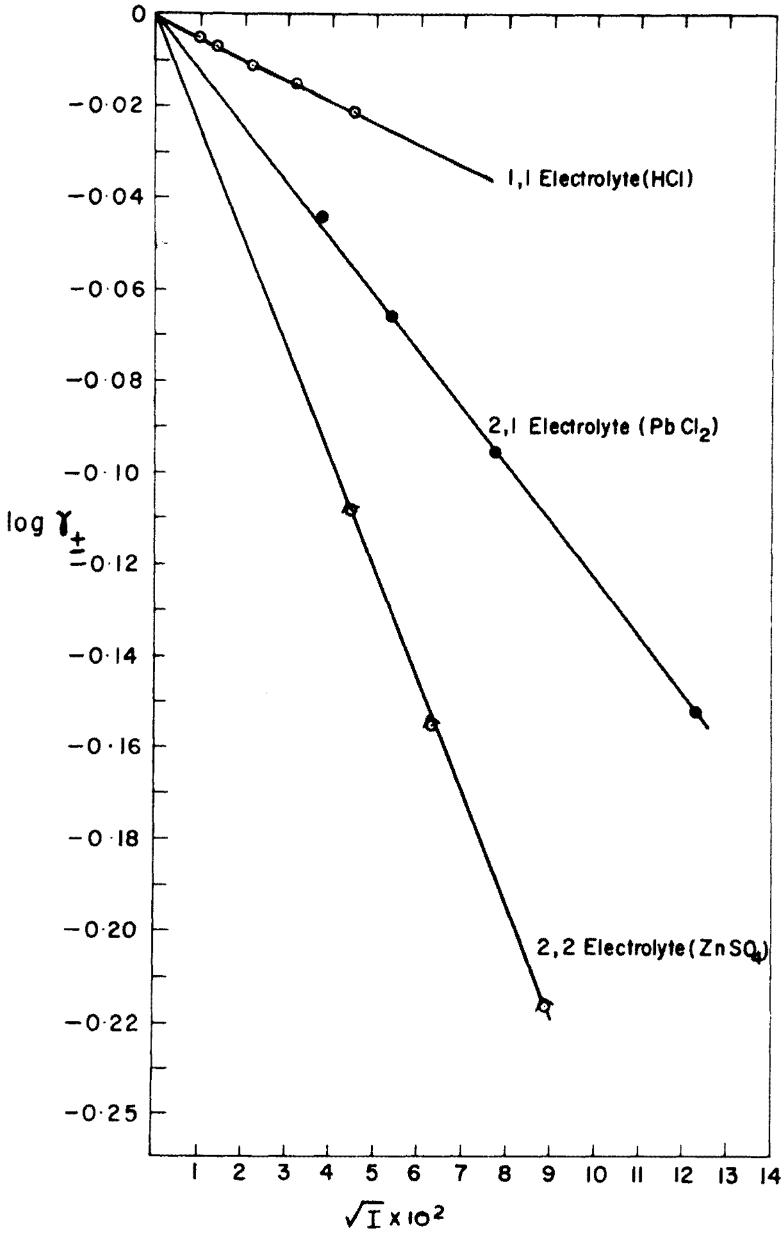

Fig. 3.20. The experimental log $f_{\pm}$ versus $I^{\frac{1}{2}}$ straight-line plots for different electrolytes can be grouped according to valence type.

constant, of the simplicity of the coulomb force law used, and, finally, of the fact that the ions are not point charges, to realize (*cf.* Table 3.6) that the simple ion-cloud model has been brilliantly successful—almost unexpectedly so. It has grasped the essential truth about electrolytic solutions, albeit about solutions of extreme dilution. The success of the model is so remarkable and the implications so wide (see Section 3.5.6), that the Debye–Hückel approach is to be regarded as one of the most significant pieces of theory in the ionics part of electrochemistry.

It is a theme of this book that model-oriented electrochemistry is to a

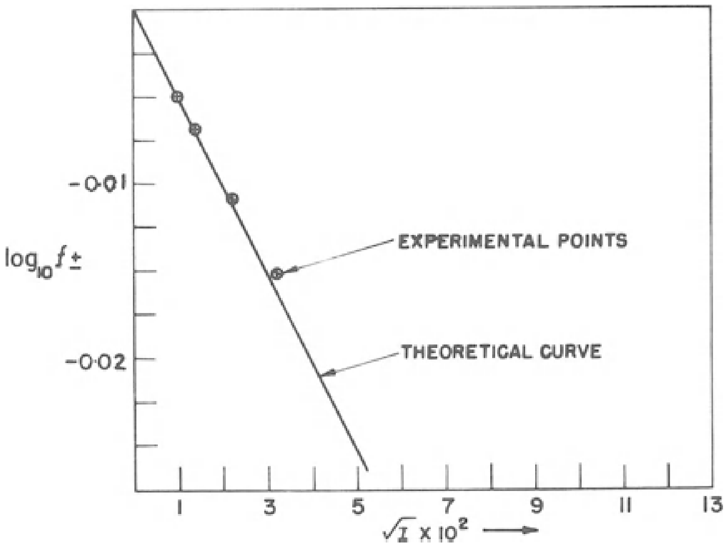

Fig. 3.21. The comparison of the experimentally observed mean activity coefficients of HCl and those that are calculated from the Debye–Hückel limiting law.

great extent the result of the application of electrostatics to chemistry. From this point of view, the Debye–Hückel approach is an excellent example of electrochemical theory. Electrostatics is introduced into the problem in the form of Poisson's equation, and the chemistry is contained in the Boltzmann distribution law and the concept of true electrolytes (Section 3.2). The union of the electrostatic and chemical modes of description to give the linearized Poisson–Boltzmann equation illustrates therefore a characteristic development of electrochemical thinking.

It is hence not surprising that the Poisson–Boltzmann approach has been used frequently in computing interactions between charged entities. Mention may be made of the Gouy theory (Fig. 3.22) of the interaction

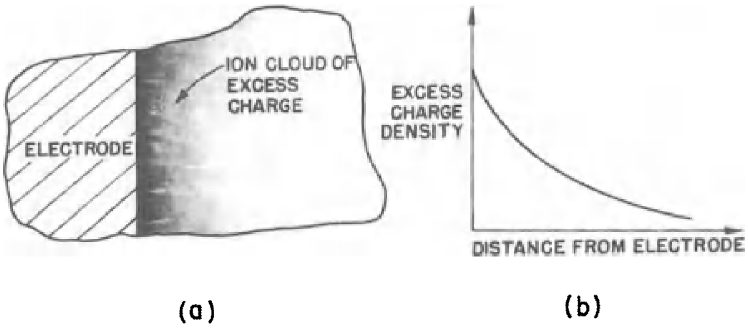

Fig. 3.22. An electrode immersed in an ionic solution is often enveloped by an ionic cloud [see Fig. 3.22 (a)] in which the excess charge density varies with distance as shown in Fig. 3.22 (b).

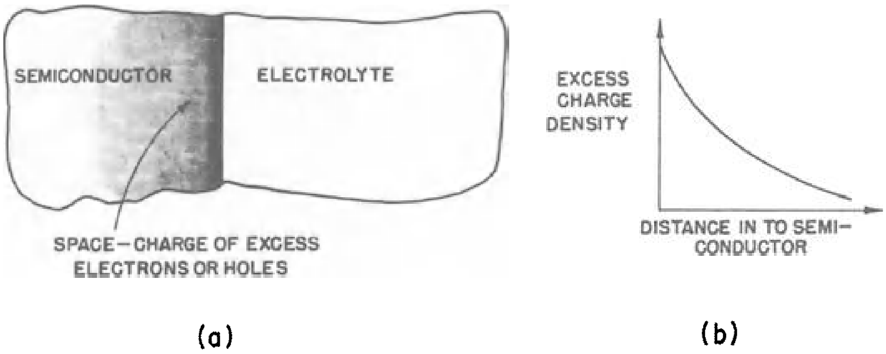

Fig. 3.23. (a) A space charge produced by excess electrons or holes often exists inside the semiconductor. **(b)** The space charge density varies with distance from the semiconductor–electrolyte interface.

between a charged electrode and the ions in a solution (see Section 7.4). Other examples are the distribution (Fig. 3.23) of electrons or holes inside a semiconductor and in the vicinity of the semiconductor electrolyte interface (see Section 7.7), and the distribution (Fig. 3.24) of charges near a polyelectrolyte molecule or a colloidal particle (see Section 7.8).

However, one must not overstress the triumphs of the Debye–Hückel limiting law [Eq. (3.90)]. Models are always simplifications of reality. They never treat all its complexities, and, thus, there can never be a *perfect* fit between experiment and the predictions based on a model.

What, then, are the inadequacies of the Debye–Hückel limiting law? One does not have to look far. If one examines the experimental $\log f_\pm$ versus $I^{\frac{1}{2}}$ curve, not just in the extreme dilution regions, but at higher concentrations, it turns out that the simple Debye–Hückel limiting law falters. The plot of $\log f_\pm$ versus $I^{\frac{1}{2}}$ is a curve (Fig. 3.25 and Table 3.7)

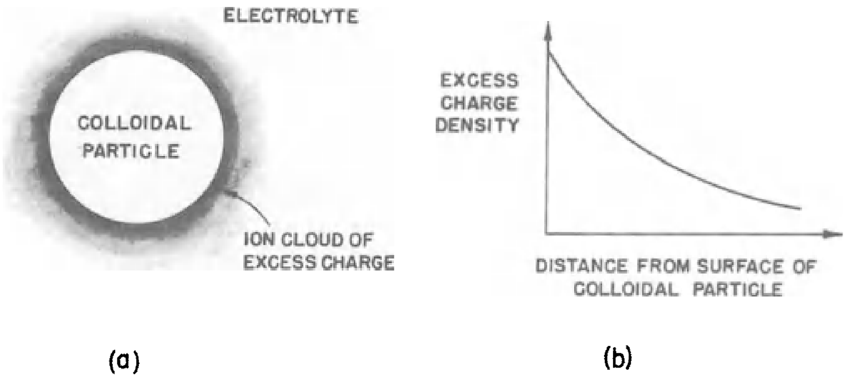

Fig. 3.24. (a) A colloidal particle is surrounded by an ionic cloud of excess charge density. **(b)** The excess charge density in the cloud varies with distance from the surface of the colloidal particle.

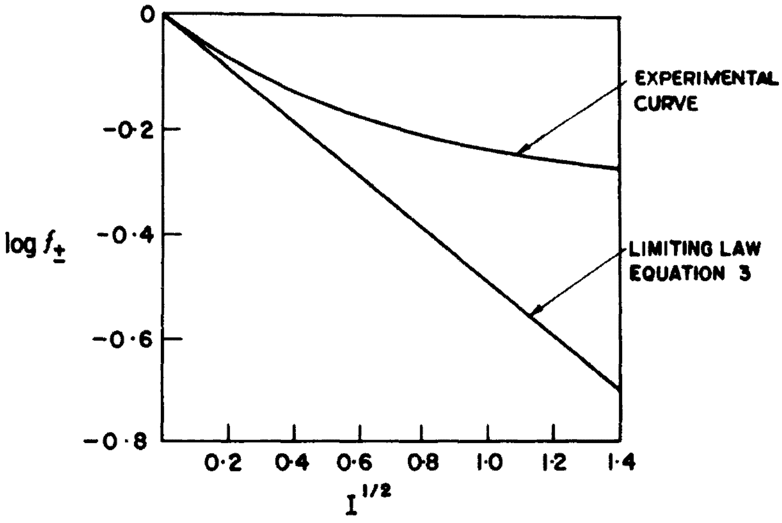

Fig. 3.25. The experimental log $f_\pm$ versus $I^{\frac{1}{2}}$ curve is a straight line only at extremely low concentrations.

and not a straight line as promised by Eq. (3.90). Further, the curves depend not only on valence type (e.g., 1:1 or 2:2) but also (Fig. 3.26) on the particular electrolyte (e.g., NaCl or KCl).

It appears that the Debye–Hückel law is the law for the tangent to the log $f_\pm$ versus $I^{\frac{1}{2}}$ curve at very low concentrations, say, up to 0.01N for 1:1 electrolytes in aqueous solutions. At higher concentrations, the model must be improved. What refinements can be made?

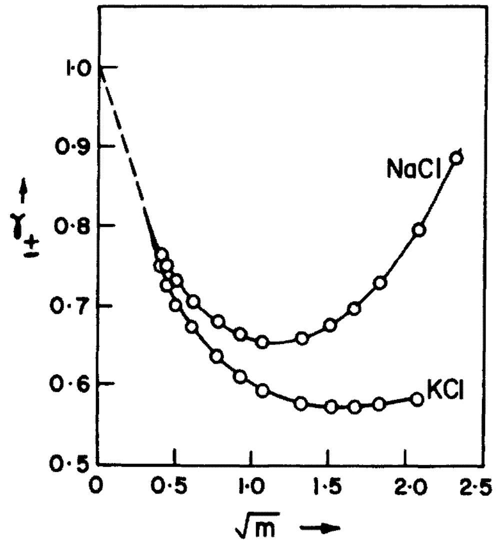

Fig. 3.26. Even though NaCl and KCl are 1 : 1 electrolytes, their activity coefficients vary in different ways with concentration directly one examines to higher concentrations.

TABLE 3.7

Comparison of Calculated [Eq. (3.90)] and Experimental Values of log $f_\pm$ for NaCl at 25°C

Concentration, molal	$-\log f_\pm$ experimental	$-\log f_\pm$ calculated
0.001	0.0155	0.0162
0.002	0.0214	0.0229
0.005	0.0327	0.0361
0.01	0.0446	0.0510
0.02	0.0599	0.0722

3.5.2. Ions Are of Finite Size, Not Point Charges

One of the general procedures for refining a model which has been successful in an extreme situation is to liberate the theory from its approximations. So one has to recall what approximations have been used to derive the Debye–Hückel limiting law. The first one that comes to mind is the point-charge approximation.[†] One now asks: Is it reasonable to consider ions as point charges?

It has been shown (*cf.* Section 3.3.8) that the mean thickness $\varkappa^{-1}$ of the ionic cloud depends on the concentration. As the concentration of a 1:1 electrolyte increases from $0.001N$ to $0.01N$ to $0.1N$, $\varkappa^{-1}$ decreases from about 100 to 30 to about 10 Å. This means that the relative dimensions of the ion cloud and of the ion change with concentration. Whereas the radius of the cloud is 100 times the radius of the ion at $0.001N$, it is only about 10 times the dimensions of an ion at $0.1N$. Obviously, under these latter circumstances, an ion cannot be considered a geometrical point charge in comparison with a dimension only 10 times its size (Fig. 3.27). The more concentrated the solution, i.e., the smaller the size $\varkappa^{-1}$ of the ion cloud (Section 3.3.8), the less valid is the point-charge approximation.

If, therefore, one wants the theory to be applicable to $0.1N$ solutions or to solutions of even higher concentration, the finite size of the ions must be introduced into the mathematical formulation.

To remove the assumption that ions can be treated as point charges,

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[†] Another approximation in the Debye–Hückel model involves the use of Poisson's equation, which is based on the smearing-out of the charges into a continuously varying charge density. At high concentrations, the mean distance between charges is low, and the ions see each other as discrete point charges, not as smoothed-out charges. Thus, the use of Poisson's equation becomes less and less justified as the solution becomes more and more concentrated.

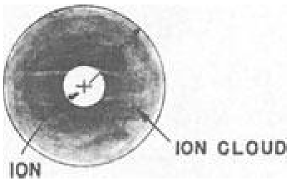

Fig. 3.27. At 0.1*N*, the thickness of the ion cloud is only 10 times the radius of the central ion.

it is necessary, at first, to recall at what stage in the derivation of the theory the assumption was invoked.

The linearized P–B equation involved neither the point-charge approximation nor any considerations of the dimensions of the ions. Hence, the basic differential equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_r}{dr}\right)=\varkappa^2\psi_r \tag{3.21}$$

and its general solution, i.e.,

$$\psi_r=A\frac{e^{-\varkappa r}}{r}+B\frac{e^{+\varkappa r}}{r} \tag{3.28}$$

can be taken as the basis for the generalization of the theory for finite-sized ions.

As before (*cf.* Section 3.3.7), the integration constant B must be zero because, otherwise, one cannot satisfy the requirement of physical sense that, as $r\rightarrow\infty$, $\psi\rightarrow 0$. Hence, Eq. (3.28) reduces to

$$\psi_r=A\frac{e^{-\varkappa r}}{r} \tag{3.29}$$

In evaluating the constant A, a procedure different from that used after (3.29) is adopted. The charge dq in any particular spherical shell (of thickness dr) situated at a distance r from the origin is, as argued earlier,

$$dq=\varrho_r 4\pi r^2\,dr \tag{3.36}$$

The charge density ϱ_r is obtained thus

$$\varrho_r=-\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right]=-\frac{\varepsilon}{4\pi}\varkappa^2\psi_r \tag{3.34}$$

and, inserting the expression for ψ_r from Eq. (3.29), one obtains

$$\varrho_r=-\frac{\varepsilon}{4\pi}\varkappa^2 A\frac{e^{-\varkappa r}}{r} \tag{3.92}$$

Fig. 3.28. For a finite-sized ion, the ion atmosphere starts at a distance *a* from the center of the reference ion.

Thus, by combining Eqs. (3.36) and (3.92),

$$dq = -A\kappa^2\varepsilon(e^{-\kappa r}r\,dr) \tag{3.93}$$

The total charge in the ion cloud q_{cloud} is, on the one hand, equal to $-z_i e_0$ [*cf.* Eq. (3.41)] as required by the electroneutrality condition and, on the other hand, the result of integrating dq. Thus,

$$q_{\text{cloud}} = -z_i e_0 = \int_?^\infty dq\,dr = -A\kappa^2\varepsilon \int_?^\infty e^{-\kappa r}r\,dr \tag{3.94}$$

What lower limit should be used for the integration? In the point-charge model, one used a lower limit of zero, meaning that the ion cloud commences from zero (i.e., from the surface of a zero-radius ion) and extends to infinity. But now the ions are taken to be of finite size, and a lower limit of zero is obviously wrong. The lower limit should be a distance corresponding to the distance from the ion center at which the ionic atmosphere starts (Fig. 3.28).

As a first step, one can use for the lower limit of the integration a distance parameter which is greater than zero. Then, one can go through the mathematics and later worry about the physical implications of the ion-size parameter. Let this procedure be adopted and symbol *a* be used for the ion-size parameter.

One has, then,

$$\int_a^\infty dq\,dr = -A\varkappa^2\varepsilon \int_a^\infty e^{-\varkappa r} r\,dr$$

$$= -A\varepsilon \int_a^\infty \varkappa r e^{-(\varkappa r)}\,d\varkappa r \tag{3.95}$$

As before (*cf.* Appendix 3.2), one can integrate by parts, thus,

$$\int_a^\infty \varkappa r e^{-(\varkappa r)}\,d\varkappa r = -[\varkappa r e^{-\varkappa r}]_a^\infty + \int_a^\infty e^{-\varkappa r}\,d\varkappa r$$

$$= \varkappa a e^{-\varkappa a} - [e^{-\varkappa r}]_a^\infty \tag{3.96}$$

Hence, inserting Eq. (3.96) in Eq. (3.95), one obtains

$$\int_a^\infty dq\,dr = -A\varepsilon e^{-\varkappa a}(1 + \varkappa a) = -z_i e_0 \tag{3.97}$$

from which

$$A = \frac{z_i e_0}{\varepsilon}\,\frac{e^{\varkappa a}}{1 + \varkappa a} \tag{3.98}$$

Using this value of A in Eq. (3.30), one obtains a new and less approximate expression for the potential ψ_r at a distance r from a finite-size central ion,

$$\psi_r = \frac{z_i e_0}{\varepsilon}\,\frac{e^{\varkappa a}}{1 + \varkappa a}\,\frac{e^{-\varkappa r}}{r} \tag{3.99}$$

3.5.3. The Theoretical Mean Ionic-Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions

Once again (*cf.* Section 3.3.9), one can use the law of superposition of potentials to obtain the ionic-atmosphere contribution ψ_{cloud} to the potential ψ_r at a distance r from the central ion. From Eq. (3.46), i.e.,

$$\psi_{\text{cloud}} = \psi_r - \psi_{\text{ion}} \tag{3.46}$$

it follows by substitution of the expression (3.99) for ψ_r and Eq. (3.44) for ψ_{ion} that

$$\psi_{\text{cloud}} = \frac{z_i e_0}{\varepsilon r}\,\frac{e^{\varkappa(a-r)}}{1 + \varkappa a} - \frac{z_i e_0}{\varepsilon r}$$

$$= \frac{z_i e_0}{\varepsilon r}\left[\frac{e^{\varkappa(a-r)}}{1 + \varkappa a} - 1\right] \tag{3.100}$$

It will be recalled, however, that, in order to calculate the activity coefficient from the expressions

$$RT \ln f_i = \Delta\mu_{i-I} \tag{3.59}$$

and

$$\Delta\mu_{i-I} = \frac{N_A z_i e_0}{2} \psi \tag{3.3}$$

i.e., from

$$\ln f_i = \frac{N_A z_i e_0}{2RT} \psi \tag{3.101}$$

it is necessary to know ψ, which is the potential at the surface of the ion due to the surrounding ions, i.e., due to the cloud. Since, in the finite-ion-size model, the ion is taken to have a size a, it means that ψ is the value of ψ_{cloud} at $r = a$,

$$\psi = \psi_{\text{cloud}} \qquad r = a \tag{3.102}$$

The value of ψ_{cloud} at $r = a$ is got by setting $r = a$ in Eq. (3.100). Hence,

$$\psi = \psi_{\text{cloud}(r=a)} = -\frac{z_i e_0}{\varepsilon \varkappa^{-1}} \frac{1}{1 + \varkappa a} \tag{3.103}$$

By substitution of the expression (3.103) for $\psi = \psi_{\text{cloud}(r=a)}$ in Eq. (3.101), one obtains

$$\ln f_i = -\frac{N_A (z_i e_0)^2}{2\varepsilon RT \varkappa^{-1}} \frac{1}{1 + \varkappa a} \tag{3.104}$$

This individual ionic-activity coefficient can be transformed into a mean ionic-activity coefficient by the same procedure as for the Debye–Hückel limiting law (*cf.* Section 3.4.12). On going through the algebra, one finds that the expression for $\log f_\pm$ in the finite-ion-size model is

$$\log f_\pm = -\frac{A(z_+ z_-) I^{\frac{1}{2}}}{1 + \varkappa a} \tag{3.105}$$

It will be recalled, however, that the thickness $\varkappa^{-1}$ of the ionic cloud can be written as [Eq. (3.85)]

$$\varkappa = B I^{\frac{1}{2}} \tag{3.85}$$

Using this notation, one ends up with the final expression

$$\log f_\pm = -\frac{A(z_+ z_-) I^{\frac{1}{2}}}{1 + B a I^{\frac{1}{2}}} \tag{3.106}$$

If one compares Eq. (3.105) of the finite-ion-size model with Eq. (3.90) of the point-charge approximation, it is clear that the only difference between the two expressions is that the former contains a term $1/(1 + \varkappa a)$ in the denominator. Now, one of the tests of a more general version of a theory is the *correspondence principle*, i.e., the general version of a theory must reduce to the approximate version under the conditions of applicability of the latter. Does the Eq. (3.105) from the finite-ion-size model reduce to Eq. (3.90) from the point-charge model?

Rewrite Eq. (3.105) in the form

$$\log f_{\pm} = -A(z_+z_-)I^{\frac{1}{2}} \frac{1}{1 + a/\varkappa^{-1}} \tag{3.107}$$

and consider the term $a/\varkappa^{-1}$. As the solution becomes increasingly dilute, the radius $\varkappa^{-1}$ of the ionic cloud becomes increasingly large compared with the ion size, and, simultaneously, $a/\varkappa^{-1}$ becomes increasingly small compared with unity, or

$$\frac{1}{1 + a/\varkappa^{-1}} \sim 1 \tag{3.108}$$

Thus, directly the solution is sufficiently dilute to make $a \ll \varkappa^{-1}$, i.e., to make the ion size insignificant in comparison with the radius of the ion atmosphere, the finite-ion-size model Eq. (3.105) reduces to the corresponding Eq. (3.90) of the point-charge model because the extra term $1/(1 + a/\varkappa^{-1})$ tends to unity

$$-\left[\frac{A(z_+z_-)I^{\frac{1}{2}}}{1 + \varkappa a}\right]_{a \ll \varkappa^{-1}} = -A(z_+z_-)I^{\frac{1}{2}} \tag{3.109}$$

The physical significance of $a/\varkappa^{-1} \ll 1$ is that, at very low concentrations, the ion atmosphere has such a large radius compared with that of the ion that one need not consider the ion as having a finite size a. Considering $a/\varkappa^{-1} \ll 1$ is tantamount to reverting to the point-charge model.

One can now proceed rapidly to compare this theoretical expression for $\log f_{\pm}$ with experiment; but what value of the ion-size parameter should be used? The time has come to worry about the precise physical meaning of the parameter a which was introduced to allow for the finite size of ions.

3.5.4. The Ion-Size Parameter *a*

One can at first try to speculate on what value of the ion-size parameter is appropriate. A lower limit is the sum of the *crystallographic* radii of the

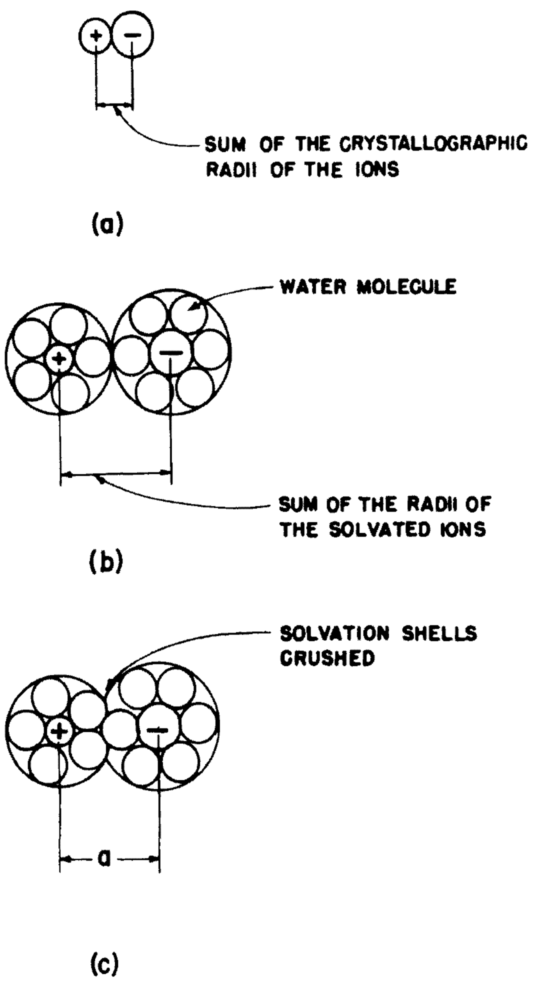

Fig. 3.29. The ion-size parameter cannot be (a) less than the sum of the crystallographic radii of the ions or (b) more than the sum of the radii of the solvated ions and is most probably (c) less than the sum of the radii of the solvated ions because the solvation shells may be crushed.

positive and negative ions present in solution; ions cannot come closer than this distance [Fig. 3.29(a)]. But, in a solution, the ions are generally solvated (*cf.* Chapter 2). So perhaps the sum of the solvated radii should be used [Fig. 3.29(b)]. However, when two solvated ions collide, is it not likely [Fig. 3.29(c)] that their hydration shells are crushed to some extent? This means that the ion-size parameter a should be greater than the sum of the crystallographic radii and perhaps less than the sum of the solvated radii. It should best be called the *mean distance of closest approach*, but, beneath the apparent wisdom of this term, there lies a measure of ignorance. For example, an attempted calculation of just how crushed together two solvated ions are would involve many difficulties.

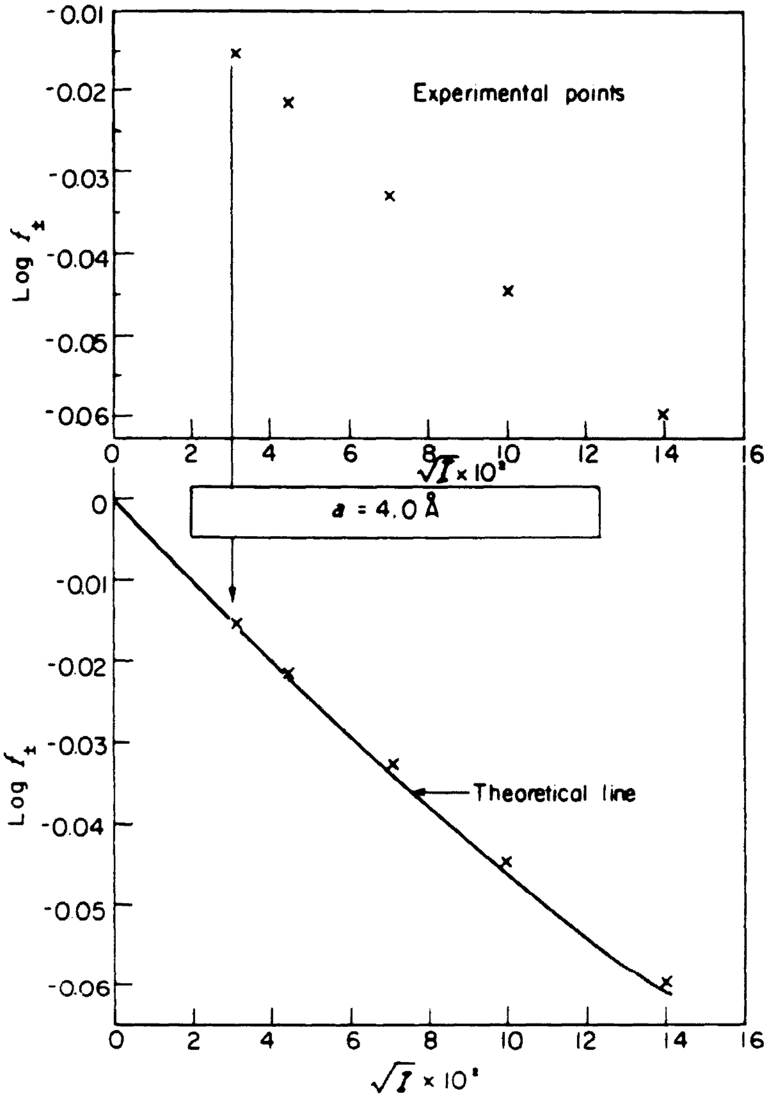

Fig. 3.30. Procedure for recovering the ion-size parameter from experiment and then using it to produce a theoretical log $f_\pm$ versus $I^{\frac{1}{2}}$ curve which can be compared with an experimental curve.

To circumvent the uncertainty in the quantitative definition of a, it is best to regard it as a *parameter* in Eq. (3.106), i.e., a quantity, the numerical value of which is left to be calibrated or adjusted on the basis of experiment. The procedure (Fig. 3.30) is to assume that the expression for $\log f_\pm$ [Eq. (3.106)] is correct at one concentration, then to equate this theoretical expression to the experimental value of $\log f_\pm$ corresponding to that concentration, and to solve the resulting equation for a. Once the ion-size parameter, or mean distance of closest approach, is thus obtained at one concentration, the value can be used for the calculation of values of the activity coefficient over a range of other and higher concentrations. Then, the situation is regarded as satisfactory if the value of a obtained from experiments at one concentration can be used in Eq. (3.106) to reproduce the results of experiments over a range of concentrations.

3.5.5. Comparison of the Finite-Ion-Size Model with Experiment

After taking into account the fact that ions have finite dimensions and cannot therefore be treated as point charges, the following expression has been derived for the logarithm of the activity coefficient:

$$\log f_{\pm} = -\frac{A(z_{+}z_{-})I^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} \tag{3.106}$$

How does the general form of this expression compare with the Debye–Hückel limiting law as far as agreement with experiment is concerned? To see what the extra term $(1 + BaI^{\frac{1}{2}})^{-1}$ does to the shape of the $\log f_{\pm}$ versus $I^{\frac{1}{2}}$ curve, one can expand it in the form of a binomial series

$$\frac{1}{1+x} = (1 + x)^{-1} = 1 - x + \frac{x^2}{2!} - \cdots \tag{3.110}$$

and use only the first two terms. Thus,

$$\frac{1}{1 + BaI^{\frac{1}{2}}} = 1 - BaI^{\frac{1}{2}} \tag{3.111}$$

and, therefore,

$$\log f_{\pm} \sim -A(z_{+}z_{-})I^{\frac{1}{2}}(1 - BaI^{\frac{1}{2}}) \tag{3.112}$$

$$\sim -A(z_{+}z_{-})I^{\frac{1}{2}} + \text{constant}(I^{\frac{1}{2}})^2 \tag{3.113}$$

This result is encouraging. It shows that the $\log f_{\pm}$ versus $I^{\frac{1}{2}}$ curve give values of $\log f_{\pm}$ higher than those given by the limiting law, the deviation increasing with concentration. In fact, the general shape of the predicted curve (Fig. 3.31) is very much on the right lines.

The values of the ion-size parameter, or closest distance of approach, which are recovered from experiment are physically reasonable for many electrolytes. They lie around 3 to 5 Å, which is greater than the sum of the crystallographic radii of the positive and negative ions and pertains more to the solvated ion (Table 3.8).

By picking on a reasonable value of the ion-size parameter a, independent of concentration, it is found that, in many cases, Eq. (3.112) gives a very good fit with experiment, often for ionic strengths up toward 0.1. For example, on the basis of $a = 4.0$ Å, Eq. (3.112) gives an almost exact

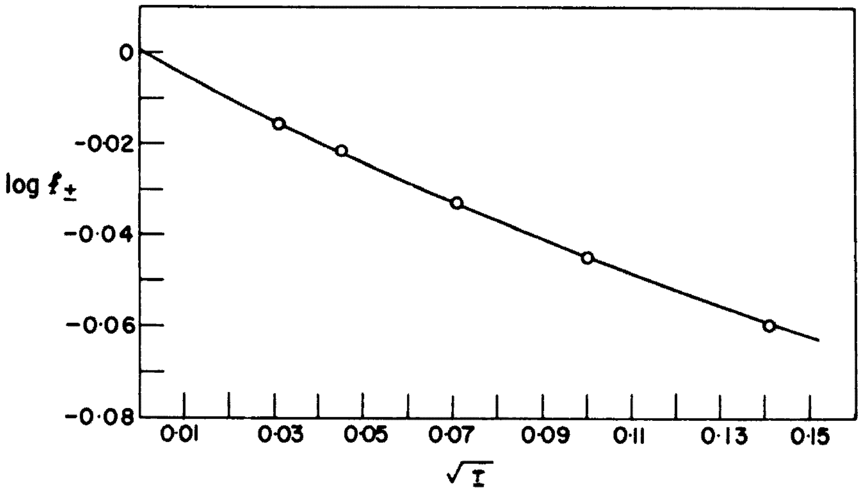

Fig. 3.31. Comparison of the experimental mean activity coefficients with theory for Eq. (3.112).

agreement up to 0.02*M* in the case of sodium chloride (Fig. 3.32 and Table 3.9).

The ion-size parameter *a* has done part of the job of extending the range of concentration in which the Debye–Hückel theory of ionic clouds agrees with experiment. But has it done the whole job? One must therefore start looking for discrepancies between theory and fact and for the less satisfactory features of the model.

The most obvious drawback of the finite-ion-size version of the Debye–Hückel theory lies in the fact that *a* is an *adjustable parameter.* When parameters which have to be taken from experiment enter a theory, they imply that the physical situation has been incompletely comprehended or is too complex to be mathematically analyzed. In contrast, the constants of the limiting law were calculated without recourse to experiment.

The best illustration of the fact that *a* has to be adjusted is its concentration dependence. As the concentration changes, the ion-size para-

TABLE 3.8

Values of Ion-Size Parameter for a Few Electrolytes

Salt	*a*, Å
HCl	4.5
HBr	5.2
LiCl	4.3
NaCl	4.0
KCl	3.6

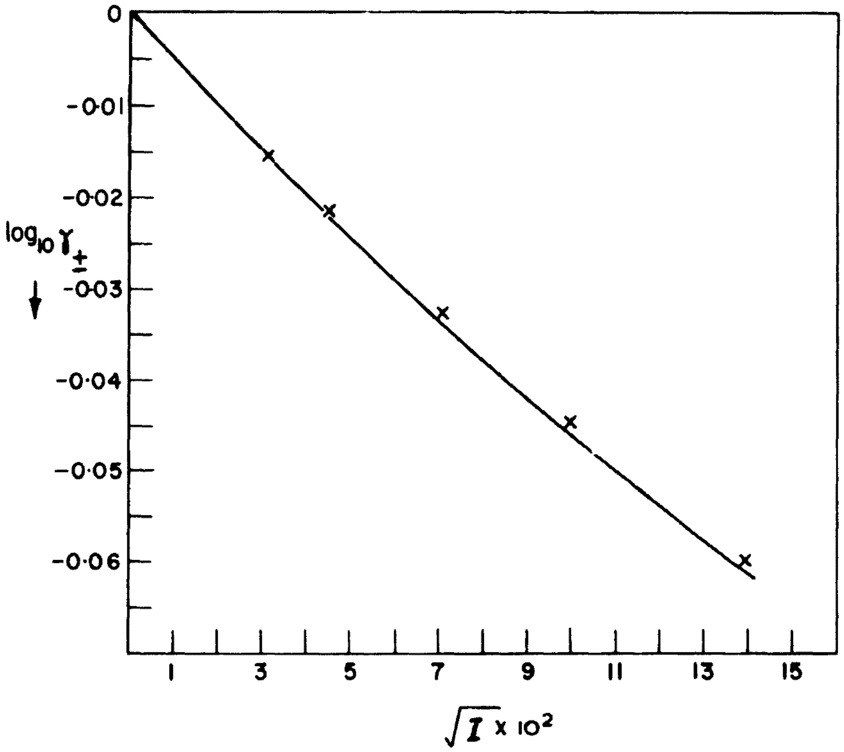

Fig. 3.32. Comparison of the experimental mean activity coefficients for sodium chloride with the theoretical log $f_{\pm}$ versus $I^{\frac{1}{2}}$ curve based on Eq. (3.112) with a = 4.0 Å.

meter has to be modified (Fig. 3.33). Further, for some electrolytes at higher concentrations, a has to assume quite impossible (i.e., large negative, irregular) values to fit the theory to experiment (Table 3.10).

Evidently, there are factors at work in an electrolytic solution which have not yet been reckoned with, and the ion-size parameter is being asked to include the effects of all these factors simultaneously, even though these other factors probably have little to do with the size of the ions and

TABLE 3.9

Experimental Mean Activity Coefficients and Those Calculated from Eq. (3.112) with a = 4.0 Å at 25°C at Various Concentrations of NaCl

Molality	Experimental mean activity coefficient $-\log f_{\pm}$	Calculated
0.001	0.0155	0.0155
0.002	0.0214	0.0216
0.005	0.0327	0.0330
0.01	0.0446	0.0451
0.02	0.0599	0.0609

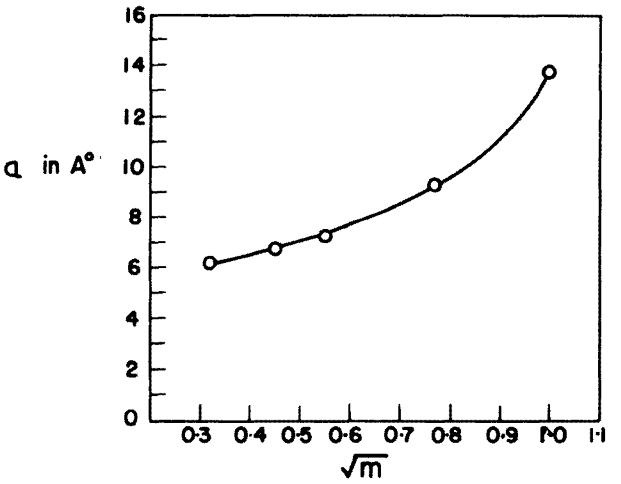

Fig. 3.33. The variation of the ion-size parameter with concentration of NaCl.

may vary with concentration. If this were so, the ion-size parameter *a*, calculated back from experiment, would indeed have to vary with concentration. The problem, therefore, is: What factors, forces, and interactions were neglected in the Debye–Hückel theory of ionic clouds?

3.5.6. The Debye–Hückel Theory of Ionic Solutions: An Assessment

It is appropriate at this stage to register the achievement in the theory of ionic solutions described thus far.

Starting with the point of view that ion–ion interactions are bound to operate in an electrolytic solution, the chemical-potential change $\Delta\mu_{i-I}$, in going from a hypothetical state of noninteracting ions to a state in which the ions of species *i* interact with the ionic solution, was considered a quantitative measure of these interactions. As a first approximation, the

TABLE 3.10

Values of Parameter *a* at Higher Concentrations

Concentration, molality	Value of *a* for HCl, Å	Concentration, molality	Value of *a* for LiCl, Å
1	13.8	2	41.3
1.4	24.5		
1.8	85.0	2.5	−141.9
2	−411.2		
2.5	− 27.9	3	− 26.4
3	− 14.8		

ion–ion interactions were assumed to be purely coulombic in origin. Hence, the chemical-potential change arising from the interactions of species i with the electrolytic solution is given by the Avogadro number times the electrostatic work W resulting from taking a discharged reference ion and charging it up in the solution to its final charge. In other words, the charging work is given by the same formula as that used in the Born theory of solvation, i.e.,

$$W = \frac{z_i e_0}{2} \psi \tag{3.3}$$

where ψ is the electrostatic potential at the surface of the reference ion, contributed by the other ions in the ionic solution. The problem, therefore, was to obtain a theoretical expression for the potential ψ. This involved an understanding of the distribution of ions around a given reference ion.

It was in tackling this apparently complicated task that appeal was made to the Debye–Hückel simplifying model for the distribution of ions in an ionic solution. This model treats only one ion—the central ion—as a discrete charge, the charge of the other ions being smoothed out to give a continuous charge density. Because of the tendency of negative charge to accumulate near a positive ion, and *vice versa*, the smoothed-out positive and negative charge densities do not cancel out; rather, their imbalance gives rise to an excess local charge density ϱ_r, which of course dies away toward zero as the distance from the central ion is increased. Thus, the calculation of the distribution of ions in an electrolytic solution reduces to the calculation of the variation of excess charge density ϱ_r with distance r from the central ion.

The excess charge density ϱ_r was taken to be given, on the one hand, by Poisson's equation of electrostatics

$$\varrho_r = -\frac{\varepsilon}{4\pi} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) \tag{3.17}$$

and, on the other, by the linearized Boltzmann distribution law

$$\varrho_r = -\sum \frac{n_i^0 z_i^2 e_0^2 \psi_r}{kT} \tag{3.18}$$

The result of equating these two expressions for the excess charge density is the fundamental partial differential equation of the Debye–Hückel model, the linearized P–B equation (*cf.* Fig. 3.34)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = \varkappa^2 \psi_r \tag{3.21}$$

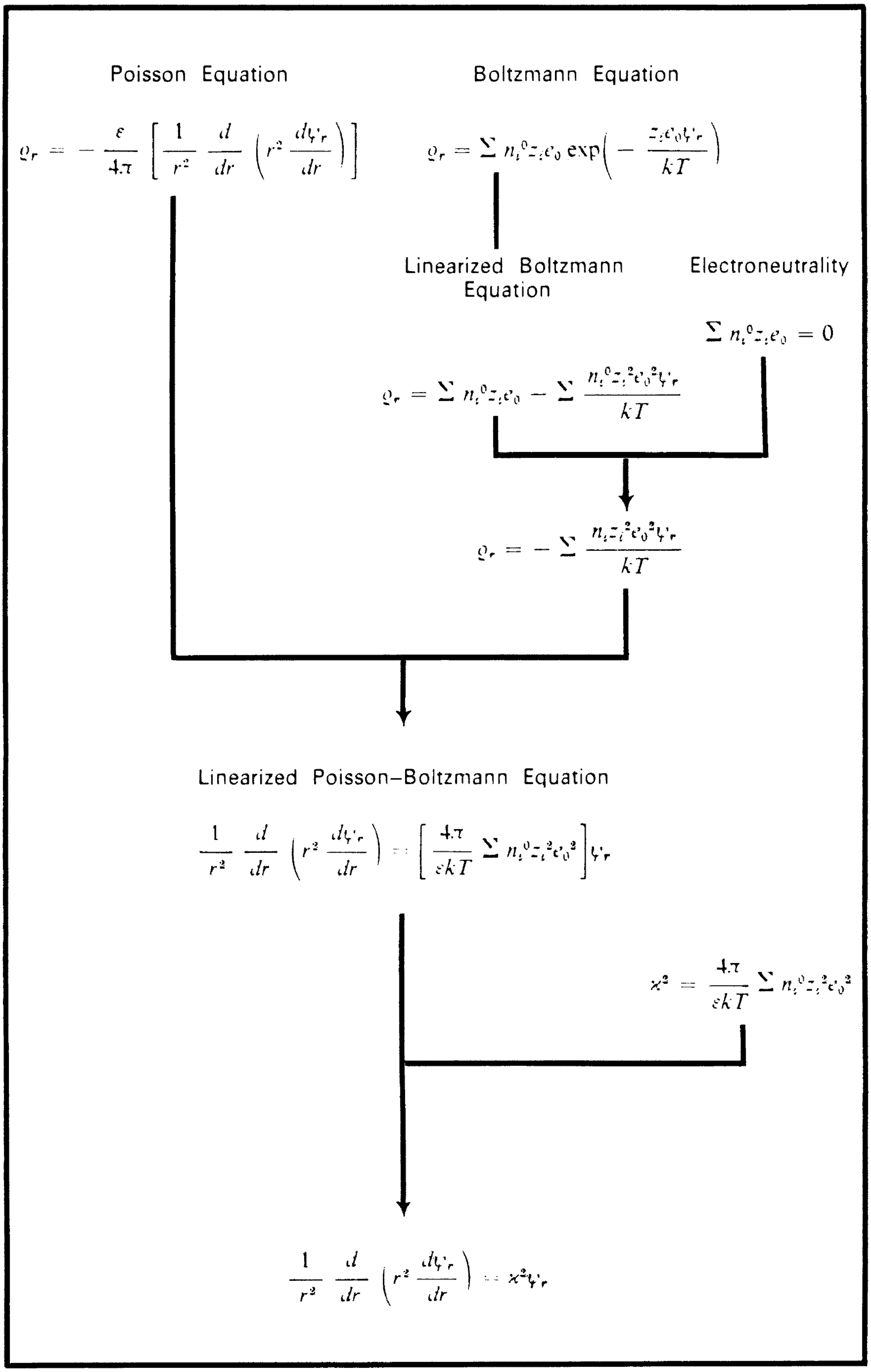

Fig. 3.34. Steps in the derivation of the linearized Poisson–Boltzmann equation.

where

$$\varkappa^2 = \frac{4\pi}{\varepsilon kT} \sum n_i^0 z_i^2 e_0^2 \tag{3.20}$$

By assuming that ions can be regarded as point charges, the solution of the linearized P–B equation turns out to be (*cf.* Fig. 3.35)

$$\psi_r = \frac{z_i e_0}{\varepsilon} \frac{e^{-\varkappa r}}{r} \tag{3.33}$$

Such a variation of potential with distance from a typical (central or reference) ion corresponded to a charge distribution which can be expressed as a function of distance r from the central ion by

$$\varrho_r = -\frac{z_i e_0}{4\pi} \varkappa^2 \frac{e^{-\varkappa r}}{r} \tag{3.35}$$

This variation of the excess charge density with distance around the central or typical ion yielded a simple physical picture. A reference positive ion can be thought of as being surrounded by a cloud of negative charge of radius $\varkappa^{-1}$. The charge density in this ionic atmosphere, or ionic cloud, decays in the manner indicated by Eq. (3.35). Thus, the interactions between a reference ion and the surrounding ions of the solution is equivalent to the interactions between the reference ion and the ionic cloud which, in the point-charge model, sets up at the central ion a potential ψ_{cloud} given by

$$\psi_{\text{cloud}} = -\frac{z_i e_0}{\varepsilon \varkappa^{-1}} \tag{3.49}$$

The magnitude of central ion–ionic-cloud interactions is given by introducing the expression for ψ_{cloud} into the expression (3.3) for the work of creating the ionic cloud, i.e., setting up the ionic interaction situation. Thus, one obtains for the energy of such interactions

$$\Delta\mu_{i-I} = -\frac{N_A (z_i e_0)^2}{2\varepsilon \varkappa^{-1}} \tag{3.51}$$

In order to test these predictions, attention was drawn to an empirical treatment of ionic solutions. For solutions of noninteracting particles, the chemical-potential change in going from a solution of unit concentration to one of concentration x_i is described by the equation

$$\mu_i - \mu_i^0 = RT \ln x_i \tag{3.52}$$

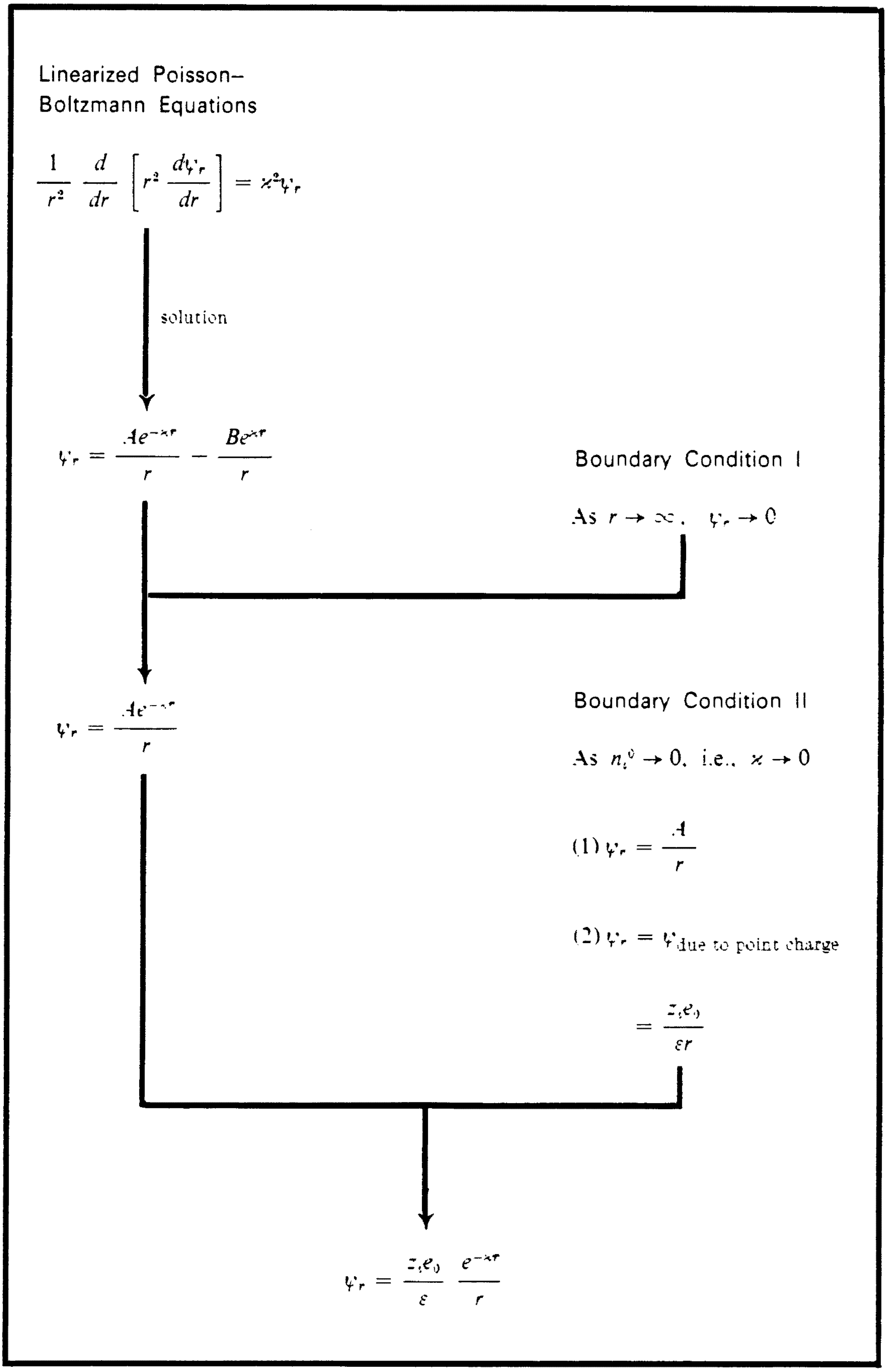

Fig. 3.35. Steps in the solution of the linearized Poisson–Boltzmann equation for point-charge ions.

However, in the case of an electrolytic solution in which there are ion–ion interactions, it is experimentally observed that

$$\mu_i - \mu_i^0 \neq RT \ln x_i$$

If one is unaware of the nature of these interactions, one can write an empirical equation to compensate for one's ignorance

$$RT \ln f_i = (\mu_i - \mu_i^0) - RT \ln x_i \tag{3.58}$$

and say that solutions behave ideally if the so-called activity coefficient f_i is unity, i.e., $RT \ln f_i = 0$, and, in real solutions, $f_i \neq 1$. It is clear that f_i corresponds to a coefficient to account for the behavior of ionic solutions, which differs from those in which there are no charges. Thus, f_i accounts for the interactions of the charges, so that

$$RT \ln f_i = \Delta\mu_{i-I} = -\frac{N_A(z_i e_0)^2}{2\varepsilon\varkappa^{-1}} \tag{3.60}$$

Thus arose the Debye–Hückel expression for the experimentally inaccessible individual ionic-activity coefficient. This expression could be transformed into the Debye–Hückel limiting law for the experimentally measurable mean ionic-activity coefficient

$$\log f_{\pm} = -A(z_+ z_-)I^{\frac{1}{2}} \tag{3.90}$$

which would indicate that the logarithm of the mean activity coefficient falls linearly with the square root of the ionic strength $I(= \frac{1}{2} \sum c_i z_i^2)$, which is a measure of the total number of electric charges in the solution.

The agreement of the Debye–Hückel limiting law with experiment improved with decreasing electrolyte concentration and became excellent for the limiting tangent to the $\log f_{\pm}$ versus $I^{\frac{1}{2}}$ curve. With increasing concentration, however, experiment deviated more and more from theory, and, at concentrations above $1N$, even showed an *increase* in $f_{\pm}$ with increase of concentration, whereas theory indicated a continued decrease.

An obvious improvement of the theory consisted in removing the assumption of point-charge ions and taking into account their finite size. With the use of an ion-size parameter a, the expression for the mean ionic-activity coefficient became

$$\log f_{\pm} = -\frac{A(z_+ z_-)I^{\frac{1}{2}}}{1 + \varkappa a} \tag{3.105}$$

However, the value of the ion-size parameter a could not be theor-

3.8. TEMPORARY ION ASSOCIATION IN AN ELECTROLYTIC SOLUTION: FORMATION OF PAIRS, TRIPLETS, ETC.

3.8.1. Positive and Negative Ions Can Stick Together: Ion-Pair Formation

The Debye–Hückel model assumed the ions to be in *almost* random thermal notions and therefore in *almost* random positions. The slight deviation from randomness was pictured as giving rise to an ionic cloud around a given ion, a positive ion (of charge $+ze_0$) being surrounded by a cloud of excess negative charge $(-ze_0)$. However, the possibility was not considered that some negative ions in the cloud would get sufficiently close to the central positive ion in the course of their quasi-random solution movements so that their thermal translational energy would not be sufficient for them to continue their independent movements in the solution. Bjerrum suggested that a pair of oppositely charged ions may get trapped in each other's coulombic field. An *ion pair* may be formed.

The ions of the pair together form an ionic dipole on which the net charge is zero. Within the ionic cloud, the locations of such uncharged ion pairs are completely random, since, being uncharged, they are not acted upon by the coulombic field of the central ion. Further, on the average, a certain fraction of the ions in the electrolytic solution will be stuck together in the form of ion pairs. This fraction must now be evaluated.

3.8.2. The Probability of Finding Oppositely Charged Ions near Each Other

Consider a spherical shell of thickness dr and of radius r from a reference positive ion (Fig. 3.41). The probability P_r that a negative ion is in the spherical shell is proportional, firstly, to the ratio of the volume $4\pi r^2\,dr$ of the shell to the total volume V of the solution; secondly, to the total number N_- of negative ions present; and, thirdly, to the Boltzmann factor $\exp(-U/kT)$, where U is the potential energy of a negative ion at a distance r from a cation, i.e.,

$$P_r = 4\pi r^2\,dr\,\frac{N_-}{V}\,e^{-U/kT} \tag{3.122}$$

Since N_-/V is the concentration n_-^0 of negative ions in the solution and

$$U = \frac{-z_- z_+ e_0^2}{\varepsilon r} \tag{3.123}$$

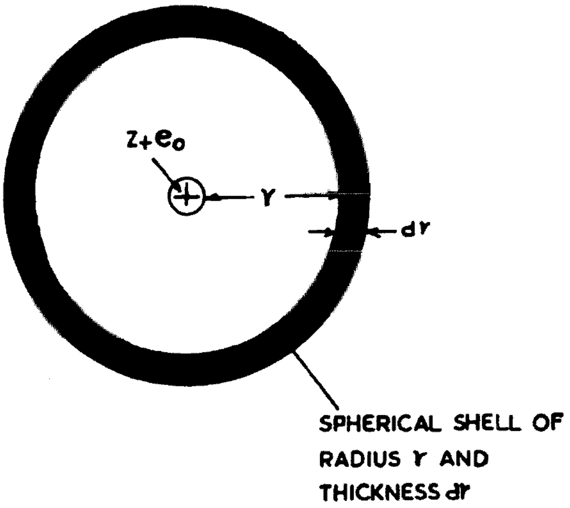

Fig. 3.41. The probability P_r of finding an ion of charge z_-e_0 in a dr-thick spherical shell of radius r around a reference ion of charge z_+e_0.

it is clear that

$$P_r = (4\pi n_-^0)r^2 e^{z_-z_+e_0^2/\varepsilon rkT}\,dr \tag{3.124}$$

or, writing

$$\lambda = \frac{z_-z_+e_0^2}{\varepsilon kT} \tag{3.125}$$

one has

$$P_r = (4\pi n_-^0)e^{\lambda/r}r^2\,dr \tag{3.126}$$

A similar equation is valid for the probability of finding a positive ion in a dr-thick shell at a radius r from a reference negative ion. Hence, in general, one may write for the probability of finding an i type of ion in a dr-thick spherical shell at a radius r from a reference ion k of opposite charge

$$P_r = (4\pi n_i^0)e^{\lambda/r}r^2\,dr \tag{3.127}$$

where

$$\lambda = \frac{z_iz_ke_0^2}{\varepsilon kT} \tag{3.128}$$

This probability of finding an ion of one type of charge near an ion of the opposite charge varies in an interesting way with distance (Fig. 3.42). For small values of r, the function P_r is dominated by $e^{\lambda/r}$ rather than by r^2, and, under these conditions, P_r *increases with decreasing* r; for large values of r, $e^{\lambda/r} \rightarrow 1$ and P_r *increases with increasing* r because the volume $4\pi r^2\,dr$ of the spherical shell increases as r^2. It follows from these considerations

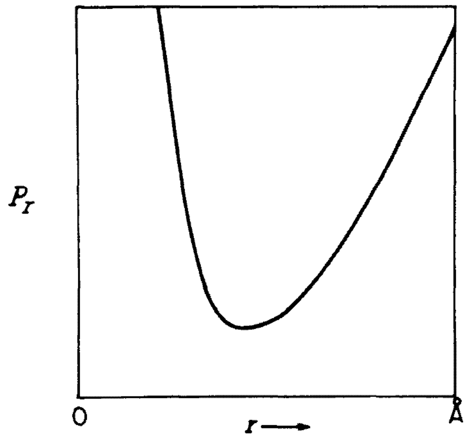

Fig. 3.42. The probability P_r of finding an ion of one type of charge as a function of distance.

that P_r goes through a minimum for a particular, critical value of r. This conclusion may also be reached by computing the number of ions in a series of shells, each of an arbitrarily selected thickness of 0.1 Å (Table 3.14).

3.8.3. The Fraction of Ion Pairs, According to Bjerrum

If one integrates P_r between a lower and an upper limit, one gets the probability P_r of finding a negative ion within a distance from the reference positive ion, defined by the limits. Now, for two oppositely charged ions to stick together to form an ion pair, it is necessary that they should be close enough for the coulombic attractive energy to overcome the thermal energy which scatters them apart. Let this "close-enough" distance be q. Then, one can say that an ion pair will form when the distance r between a

TABLE 3.14

Number of Ions in Spherical Shells at Various Distances

r, Å	Number of ions in shell × 10^{22}	
	Of opposite charge	Of like charge
2	$1.77n_i$	$0.001n_j$
2.5	$1.37n_i$	$0.005n_j$
3	$1.22n_i$	$0.01n_j$
3.57	$1.18n_i$	$0.02n_j$
4	$1.20n_i$	$0.03n_j$
5	$1.31n_i$	$0.08n_j$

positive and negative ion becomes less than q. Thus, the probability of ion-pair formation is given by the integral of P_r between a lower limit of a, the closest distance of approach of ions, and an upper limit of q.

Now, the probability of any particular event is the number of times that the particular event is expected to be observed divided by the total number of observations. Hence, the probability of ion-pair formation is the number of ions of species i which are associated into ion pairs divided by the total number of i ions, i.e., the probability of ion-pair formation is the fraction θ of ions which are associated into ion pairs. Thus,

$$\theta = \int_a^q P_r \, dr = \int_a^q 4\pi n_i^0 e^{\lambda/r} r^2 \, dr \tag{3.129}$$

It is seen from Figure 3.43 that the integral in Eq. (3.129) is the area under the curve between the limits $r = a$ and $r = q$. But it is obvious that, as r increases past the minimum , the integral becomes greater than unity. Since, however, θ is a fraction, this means that the integral diverges.

In this context, Bjerrum took the arbitrary step of cutting off the integral at the value of $r = q$ corresponding to the minimum of the P_r versus r curve. This minimum can easily be shown (Appendix 3.4) to occur at

$$q = \frac{z_- z_+ e_0^2}{2\varepsilon kT} = \frac{\lambda}{2} \tag{3.130}$$

Bjerrum justified this step by arguing that it is only short-range coulombic interactions that lead to ion-pair formation and, further, when a pair of oppositely charged ions are situated at a distance apart of $r > q$, it is more appropriate to consider them free ions.

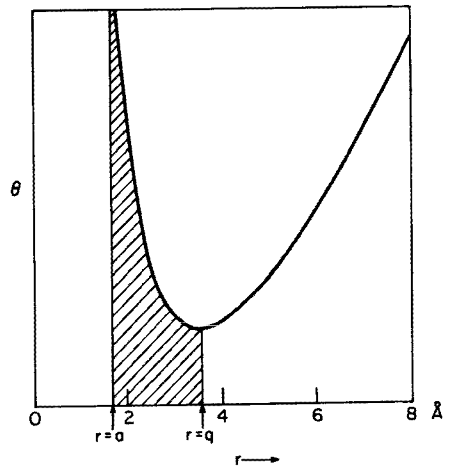

Fig. 3.43. The integral in Eq. (3.129) is the area under the curve between the limits $r = a$ and $r = q$.

Bjerrum concluded, therefore, that ion-pair formation occurs when an ion of one type of charge, e.g., a negative ion, enters a sphere of radius q drawn around a reference ion of the opposite charge, e.g., a positive ion. But it is the ion-size parameter which defines the closest distance of approach of a pair of ions. The Bjerrum hypothesis can therefore be stated as follows: If $a < q$, then ion-pair formation can occur; if $a > q$ the ions remain free (Fig. 3.44).

Now that the upper limit of the integral in Eq. (3.129) has been taken to be $q = \lambda/2$, the fraction of ion pairs is given by carrying out the integration. It is

$$\theta = 4\pi n_i^0 \int_a^{q=\lambda/2} e^{\lambda/r} r^2\, dr \tag{3.131}$$

For mathematical convenience, a new variable y is defined as

$$y = \frac{\lambda}{r} = \frac{2q}{r} \tag{3.132}$$

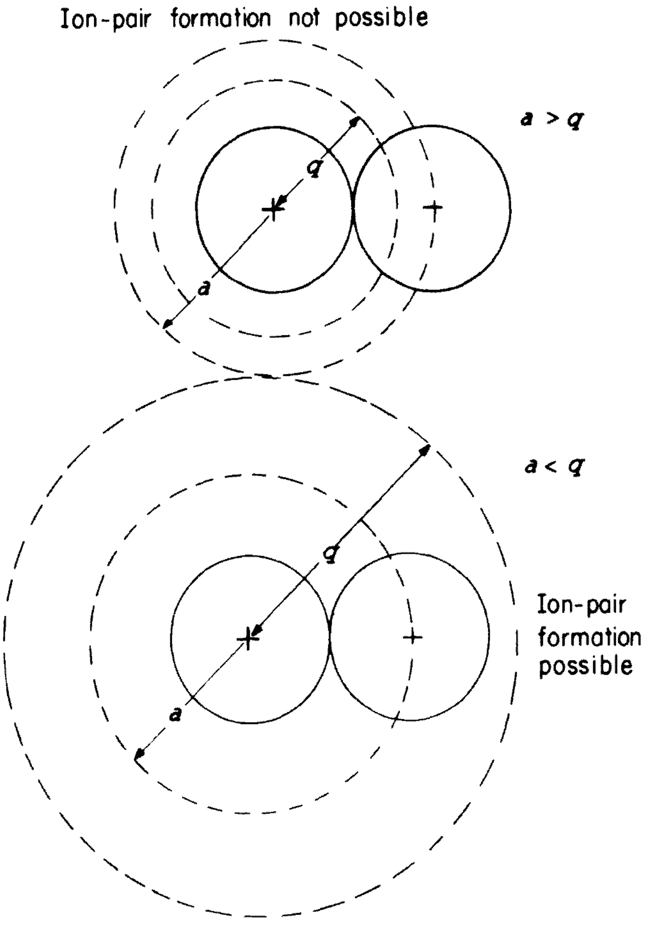

Fig. 3.44. (a) Ion-pair formation occurs if $a \leq q$; (b) ion-pair formation does not occur if $a > q$.

TABLE 3.15

Value of the Integral $\int_2^b e^y y^{-4}\, dy$

b	$\int_2^b e^y y^{-4}\, dy$	b	$\int_2^b e^y y^{-4}\, dy$	b	$\int_2^b e^y y^{-4}\, dy$
2.0	0	3	0.326	10	4.63
2.1	0.0440	3.5	0.442	15	93.0
2.2	0.0843	4	0.550		
2.4	0.156	5	0.771		
2.6	0.218	6	1.041		
2.8	0.274				

Hence, in terms of the new variable y, Eq. (3.131) becomes (*cf.* Appendix 3.5)

$$\theta = 4\pi n_i^0 \left(\frac{z_+ z_- e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \tag{3.133}$$

where

$$b = \frac{\lambda}{a} = \frac{z_+ z_- e_0^2}{\varepsilon a kT} = \frac{2q}{a} \tag{3.134}$$

Bjerrum has tabulated the integral $\int_2^b e^y y^{-4}\, dy$ for various values of b (Table 3.15). This means that, by reading off the value of the corresponding

TABLE 3.16

Fraction of Association, θ, of Univalent Ions in Water at 18°C

$a \times 10^8$ cm:	2.82	2.35	1.76	1.01	0.70	0.47
q/a:	2.5	3	4	7	10	15
c[†], moles liter^{-1}						
0.0001	—	—	—	—	0.001	0.027
0.0002	—	—	—	—	0.002	0.049
0.0005	—	—	—	0.002	0.006	0.106
0.001	—	0.001	0.001	0.004	0.011	0.177
0.002	0.002	0.002	0.003	0.007	0.021	0.274
0.005	0.002	0.004	0.007	0.016	0.048	0.418
0.01	0.005	0.008	0.012	0.030	0.030	0.529
0.02	0.008	0.013	0.022	0.053	0.137	0.632
0.05	0.017	0.028	0.046	0.105	0.240	0.741
0.1	0.029	0.048	0.072	0.163	0.336	0.804
0.2	0.048	0.079	0.121	0.240	0.437	0.854

[†] c in moles liter^{-1} = $1000 n_i^0/N$.

integral and substituting for the various other terms in (3.133), the degree of association of an electrolyte may be computed if the ion sizes, the dielectric constant, and the concentrations are known (Table 3.16).

3.8.4. The Ion-Association Constant K_A of Bjerrum

The quantity θ yields a clear idea of the fraction of ions which are associated in ion pairs in a particular electrolytic solution, at a given concentration. It would, however, be advantageous if each electrolyte, e.g., NaCl, $BaSO_4$, and $La(NO_3)_3$, were assigned a particular number which would reveal, without going through the calculation of θ, the extent to which the ions of that electrolyte associate in ion pairs. The quantitative measure chosen to represent the tendency for ion-pair formation was guided by historical considerations.

Arrhenius in 1887 had suggested that many properties of electrolytes could be explained by a *dissociation* hypothesis: The neutral molecules AB of the electrolyte dissociate to form ions A^+ and B^-, and this dissociation is governed by an equilibrium

$$AB \rightleftharpoons A^+ + B^- \tag{3.135}$$

Applying the law of mass action to this equilibrium, one can define a dissociation constant

$$K = \frac{a_{A^+}a_{B^-}}{a_{AB}} \tag{3.136}$$

By analogy,[†] one can define an *association* constant K_A for ion-pair formation. Thus, one can consider an equilibrium between free ions (the positive M^+ ions and the negative A^- ions) and the associated ion pairs (symbolized IP)

$$M^+ + A^- \rightleftharpoons \mathrm{IP} \tag{3.137}$$

The equilibrium sanctions the use of the law of mass action

$$K_A = \frac{a_{\mathrm{IP}}}{a_{M^+}a_{A^-}} \tag{3.138}$$

[†] The analogy must not be carried too far because it is only a formal analogy. Arrhenius's hypothesis can now be seen to be valid for ionogens (i.e., potential electrolytes), in which case the neutral ionogenic molecules (e.g., acetic acid) consist of aggregates of atoms held together by covalent bonds. What is under discussion here is ion association, or ion-pair formation, of ionophores (i.e., true electrolytes). In these ion pairs, the positive and negative ions retain their identity as ions and are held together by electrostatic attraction.

where the a's are the activities of the relevant species. From (3.138), it is seen that K_A is the reciprocal of the ion pair's dissociation constant.

Since θ is the fraction of ions in the form of ion pairs, θc is the *concentration* of ion pairs, and $(1 - \theta)c$ is the concentration of free ions. If the activity coefficients of the positive and negative free ions are f_+ and f_-, respectively, and that of the ion pairs is f_{IP}, one can write

$$\begin{aligned} K_A &= \frac{\theta c f_{\text{IP}}}{(1-\theta)cf_+(1-\theta)cf_-} \\ &= \frac{\theta}{(1-\theta)^2} \frac{1}{c} \frac{f_{\text{IP}}}{f_+f_-} \end{aligned} \tag{3.139}$$

or, using the definition of the mean ionic-activity coefficient [*cf.* Eq. (3.72)],

$$K_A = \frac{\theta}{(1-\theta)^2} \frac{1}{c} \frac{f_{\text{IP}}}{f_\pm^2} \tag{3.140}$$

Some simplifications can now be introduced. The ion-pair activity coefficient f_{IP} is assumed to be unity because deviations of activity coefficients from unity are ascribed in the Debye-Hückel theory to electrostatic interactions. But ion pairs are not involved in such interactions owing to their zero charge, and, hence, they behave ideally like uncharged particles, i.e., $f_{\text{IP}} = 1$.

Further, in very dilute solutions: (1) The ions rarely come close enough together (i.e., to within a distance q) to form ion pairs, and one can consider $\theta \ll 1$ or $1 - \theta \sim 1$; (2) activity coefficients tend to unity, i.e., f_i or $f_\pm \to 1$.

Hence, under these conditions of very dilute solutions, Eq. (3.140) becomes

$$K_A \sim \frac{\theta}{c} \tag{3.141}$$

and, substituting for θ from Eq. (3.133), one has

$$K_A = \frac{4\pi n_i^0}{c} \left(\frac{z_+z_-e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \tag{3.142}$$

But

$$n_i^0 = \frac{cN_A}{1000} \tag{3.143}$$

and, therefore,

$$K_A = \frac{4\pi N_A}{1000} \left(\frac{z_+z_-e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \tag{3.144}$$

TABLE 3.17

Ion Association Constant K_A: Extent to Which Ion-Pair Formation Occurs

Salt	Solvent	Temperature, °C	ε	K
KBr	Acetic acid	30	6.20	9.09×10^6
KBr	Ammonia	−34	22	5.29×10^2
CsCl	Ethanol	25	24.30	1.51×10^2
KI	Acetone	25	20.70	1.25×10^2
KI	Pyridine	25	12.0	4.76×10^3

The value of the association constant provides an indication of whether ion-pair formation is significant. The higher the value of K_A, the more extensive is the ion-pair formation (Table 3.17).

What are the factors which increase K_A and therefore increase the degree of ion-pair formation? From Eq. (3.144), it can be seen that the factors which increase K_A are (1) low dielectric constant ε; (2) small ionic radii, which lead to a small value of a and hence [*cf.* Eq. (3.134)] to a large value of the upper limit b of the integral in Eq. (3.144); and (3) large z_+ and z_-.

These ideas based on Bjerrum's picture of ion-pair formation have received considerable experimental support. Thus, in Fig. 3.45, the association constant is seen to increase markedly with decrease of dielectric con-

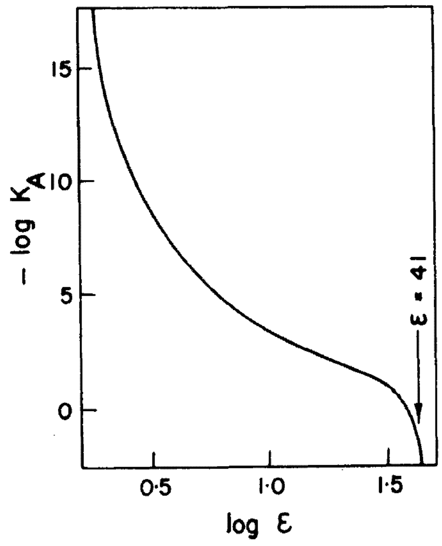

Fig. 3.45. Variation of the association constant K_A with dielectric constant for 1:1 salts.

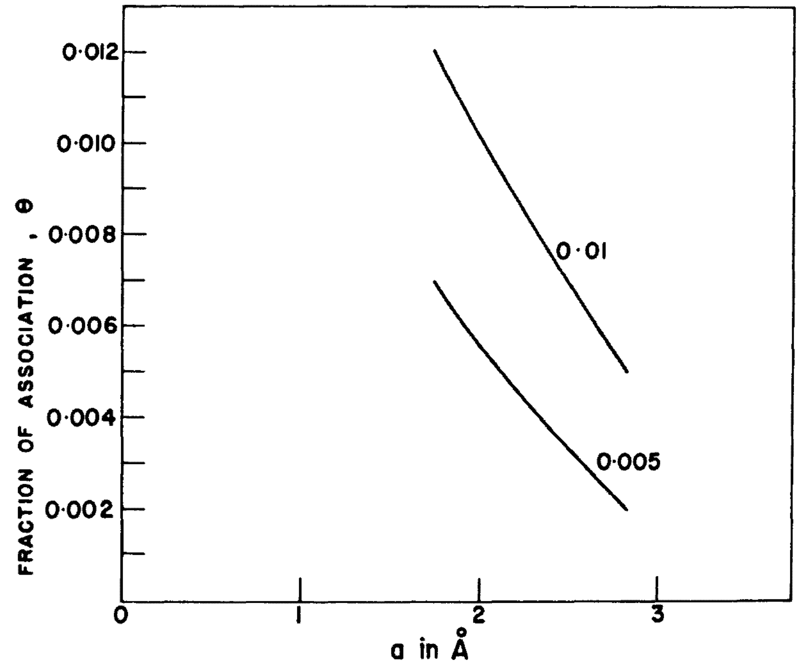

Fig. 3.46. Variation of θ, the fraction of associated ions, with a, the closest distance of approach (i.e., the ion-size parameter).

stant.[†] The dependence of ion-pair formation on the distance of closest approach is seen in Fig. 3.46.

When numerical calculations are carried out with these equations, the essential conclusion which emerges is that, in aqueous media, ion association in pairs scarcely occurs for 1:1-valent electrolytes but can be of importance for 2:2-valent electrolytes. The reason is that K_A depends on z_+z_- through Eq. (3.142). In nonaqueous solutions, most of which have dielectric constants much less than that of water ($\varepsilon = 80$), ion association is extremely important.

3.8.5. Activity Coefficients, Bjerrum's Ion Pairs, and Debye's Free Ions

What direct role do the ion pairs have in the Debye–Hückel electrostatic theory of activity coefficients? The answer simply is: None. Since ion pairs carry no net charge,[‡] they are ineligible for membership in the

---

[†] But the critical dielectric constant above which there is no more ion-pair formation (as indicated by Fig. 3.45) is really a result of the arbitrary cutting off of ion-pair formation at the distance q [see (3.8.6)].

[‡] Remember that the equations for the Bjerrum theory, as presented here, are correct only for electrolytes yielding ions of the same valency z, i.e., only for symmetrical 1:1- or 2:2-valent electrolytes.

ion cloud where the essential qualification is *charge*. Hence, ion pairs are dismissed from a direct consideration in the Debye–Hückel theory.

This does not mean that the Debye–Hückel theory gives the right answer when there is ion-pair formation. The extent of ion-pair formation decides the value of the concentration to be used in the ionic-cloud model. By removing a fraction θ of the total number of ions, only a fraction $1 - \theta$ of the ions remain for the Debye–Hückel treatment which interests itself only in the *free* charges. Thus, the Debye–Hückel expression for the activity coefficient [Eq. (3.106)] is valid for the free ions with two important modifications: (1) Instead of there being a concentration c of ions, there is only $(1 - \theta)c$; the remainder θc is not reckoned with owing to association. (2) The closest distance of approach of *free* ions is q and not a. These modifications yield

$$\log f_\pm = -\frac{A(z_+z_-)\sqrt{(1-\theta)c}}{1 + Bq\sqrt{(1-\theta)c}} \tag{3.145}$$

This calculated mean activity coefficient is related to the measured mean activity coefficient of the electrolyte $(f_\pm)_{\text{obs}}$ by the relation (for the derivation, see Appendix 3.6)

$$(f_\pm)_{\text{obs}} = (1 - \theta)f_\pm \tag{3.146}$$

or

$$\begin{aligned}\log (f_\pm)_{\text{obs}} &= \log f_\pm + \log (1 - \theta)\\ &= -\frac{A(z_+z_-)\sqrt{(1-\theta)c}}{1 + Bq\sqrt{(1-\theta)c}} + \log (1 - \theta)\end{aligned} \tag{3.147}$$

This equation indicates how the activity coefficient depends on the extent of ion association. In fact, this equation constitutes the bridge between the treatment of solutions of true electrolytes and solutions of potential electrolytes. More will be said on this matter in the chapter on protons in solution (Chapter 5), part of which deals with potential electrolytes.

3.8.6. The Fuoss Approach to Ion-Pair Formation

Despite a considerable agreement with experiment, there are several unsatisfactory features of the Bjerrum picture of ion-pair formation.

The first and most important defect of the Bjerrum picture is that it identifies, as ion pairs, ions which are not in physical contact; the pair is counted as an ion pair as long as $r < q$.

A second defect is the arbitrary way in which the probability integral [*cf.* Eq. (3.129)] is terminated at q, i.e., the distance r at which P_r is a minimum. The physical reasons supporting this choice of a condition for the maximum distance between ion centers at which pairing can occur are not clear. In practice, however, the value of the ion-association constant K_A is not very sensitive to the actual numerical value chosen for the upper limit of the integral.

It is these considerations that led Fuoss to present an alternative picture of ion pairs and a derivation of the ion-association constant.

An ion pair is defined in a straighforward manner. For the period of time (irrespective of its magnitude) that two oppositely charged ions are in contact and, therefore, at a distance apart of $r = a$, the two ions function as neutral dipole and can be defined as an ion pair.

To get an idea of the fraction of ion pairs in a solution, the following thought experiment is a useful device. Let the motion of all the ions in a solution be frozen and the number of oppositely charged pairs of ions *in contact* be counted. If this thought experiment is repeated many times, then one can determine N_{IP}, the average number of ion pairs. The fraction of ion pairs is then obtained by dividing N_{IP} by N_i, the average number of ions.

The calculation of the fraction $\theta = N_{\mathrm{IP}}/N_i$ is done as follows. Suppose Z positive ions and an equal number of negative ions exist in a volume V of solution. Let there be Z_{IP} ion pairs; then there will be $Z_{\mathrm{FI}} = Z - Z_{\mathrm{IP}}$ free ions of each species. Now, suppose one adds δZ positive ions and a similar number of anions. Since some of these will form ion pairs and some will remain free,

$$\delta Z = \delta Z_{\mathrm{FI}} + \delta Z_{\mathrm{IP}} \tag{3.148}$$

The number δZ_{FI} of added negative ions that remain free is proportional, firstly, to the number δZ of negative ions added to the solution and, secondly, to the free volume $V - v_+Z$ not occupied by positive ions of volume v_+

$$\delta Z_{\mathrm{FI}} = (V - v_+Z)\,\delta Z \tag{3.149}$$

The number δZ_{IP} of negative ions that form pairs with positive ions is proportional, firstly, to the number δZ of negative ions added; secondly, to the volume v_+Z_{FI} occupied by free positive ions; and, finally, to the Boltzmann factor $e^{-U/kT}$, where U is the potential energy of a negative ion in contact with a positive ion[†]

$$\delta Z_{\mathrm{IP}} = 2v_{+} Z_{\mathrm{FI}} e^{-U/kT}\,\delta Z \tag{3.150}$$

By dividing (3.150) by (3.149), the result is

$$\frac{\delta Z_{\mathrm{IP}}}{\delta Z_{\mathrm{FI}}} = 2v_{+}\frac{Z_{\mathrm{FI}} e^{-U/kT}\,\delta Z}{(V - v_{+}Z)\,\delta Z} \tag{3.151}$$

or

$$\delta Z_{\mathrm{IP}} = 2v_{+}\frac{e^{-U/kT}}{(V - v_{+}Z)} Z_{\mathrm{FI}}\,\delta Z_{\mathrm{FI}} \tag{3.152}$$

If dilute solutions are considered, one can neglect the total volume $v_{+}Z$ occupied by positive ions in comparison with the volume V of the solution, and, therefore,

$$\delta Z_{\mathrm{IP}} = \frac{2v_{+}e^{-U/kT}}{V} Z_{\mathrm{FI}}\,\delta Z_{\mathrm{FI}} \tag{3.153}$$

Now suppose that one adds increments δZ of positive and negative ions until a total of N positive and N negative ions are present in the volume V; this process is equivalent to integrating Eq. (3.153). The result is

$$N_{\mathrm{IP}} = \frac{N_{\mathrm{FI}}^{2}}{V} v_{+}e^{-U/kT} \tag{3.154}$$

or

$$\frac{N_{\mathrm{IP}}}{V} = \left(\frac{N_{\mathrm{FI}}}{V}\right)^{2} v_{+}e^{-U/kT} \tag{3.155}$$

As a model of an ion pair, one can consider the positive ions to be charged spheres of radius a and the negative ions point charges; this gives a contact distance of a. Then, the volume of the cations is given by

$$v_{+} = \tfrac{4}{3}\pi a^{3} \tag{3.156}$$

With regard to U, the potential energy of a negative ion in contact with a positive ion, the following argument is adopted. It has been shown that the potential ψ_r at a distance r from a central positive ion [*cf.* Eq. (3.99)] is

$$\psi_r = \frac{z_{+}e_0}{\varepsilon r}\,\frac{1}{1 + \varkappa a}\,e^{\varkappa(a-r)} \tag{3.157}$$

[†] The factor of 2 comes in because, when one adds δZ negative ions, one must also add δZ positive ions, which also form ion pairs.

Hence, at the surface of the positive ion of radius $r = a$, the potential is

$$\psi_{r=a} = \frac{z_+ e_0}{\varepsilon a} \frac{1}{1 + \varkappa a} \tag{3.158}$$

It follows therefore that

$$U = -z_- e_0 \psi_{r=a} = -\frac{z_+ z_- e_0^2}{\varepsilon a} \frac{1}{1 + \varkappa a} \tag{3.159}$$

or

$$\frac{U}{kT} = -\frac{z_+ z_- e_0^2}{\varepsilon akT} \frac{1}{1 + \varkappa a} = -\frac{b}{1 + \varkappa a} \tag{3.160}$$

where, as stated earlier,

$$b = \frac{z_+ z_- e_0^2}{\varepsilon akT} \tag{3.134}$$

By substituting for U/kT and v_+ from (3.160) and (3.156) in (3.155), the result is

$$\frac{N_{\text{IP}}}{V} = \left(\frac{N_{\text{FI}}}{V}\right)^2 \frac{4}{3} \pi a^3 e^{b/(1+\varkappa a)} \tag{3.161}$$

But

$$\frac{N_{\text{IP}}}{V} = n_{\text{IP}} = \frac{c_{\text{IP}} N_A}{1000} = \frac{\theta c N_A}{1000} \tag{3.162}$$

where c_{IP} and c are the concentration of ion pairs and electrolyte, respectively, and

$$\frac{N_{\text{FI}}}{V} = n_{\text{FI}} = \frac{(1 - \theta) c N_A}{1000} \tag{3.163}$$

where c_{FI} is the concentration of free ions. Hence, from (3.161), (3.162), and (3.163).

$$\theta c = \frac{(1 - \theta)^2 c^2 N_A}{1000} \left(\frac{4}{3} \pi a^3\right) e^{b/(1+\varkappa a)} \tag{3.164}$$

If the solution is considered dilute, $1 - \theta \sim 1$, and, since $\varkappa^{-1} \rightarrow \infty$ (i.e., $\varkappa \rightarrow 0$),

$$e^{b/(1+\varkappa a)} \sim e^b \tag{3.165}$$

in which case, Eq. (3.164) becomes

$$\frac{\theta}{c} = \frac{4\pi N_A}{3000} a^3 e^b \tag{3.166}$$

But, according to (3.141),

$$K_A = \frac{\theta}{c} \tag{3.141}$$

Hence, according to the Fuoss approach, the ion-association constant is given by

$$K_A = \frac{4\pi N_A}{3000} a^3 e^b \tag{3.167}$$

in contrast to the following expression (3.144) from the Bjerrum approach,

$$K_A = \frac{4\pi N_A}{1000} \left(\frac{z_+ z_- e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \tag{3.144}$$

Now, the Bjerrum theory was tested in solutions with dielectric constants such that $b = z_+ z_- e_0^2/\varepsilon akT = 2q/a$ was significantly larger than 2. Under these conditions, the following approximation to the integral in Bjerrum's equation can be made

$$\left(\frac{z_+ z_- e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \sim a^3 \frac{e^b}{b} \tag{3.168}$$

in which case, the ion association constant of Bjerrum reduces to

$$K_A = \frac{4\pi N_A a^3}{1000} \frac{e^b}{b} \tag{3.169}$$

As the dielectric constant of the solution is changed, $b = z_+ z_- e_0^2/\varepsilon akT$ changes, but this change is overshadowed by the e^b term. In other words, the experimental results do not permit a distinction between the Fuoss dependence of K_A on e^b [*cf.* Eq. (3.167)] and the Bjerrum dependence of K_A on e^b/b [*cf.* Eq. (3.169)]. However, the Fuoss approach is to be preferred because it is on a simpler and less arbitrary conceptual basis.

3.8.7. From Ion Pairs to Triple Ions to Clusters of Ions...

The coulombic attractive forces given by $z_+ z_- e_0^2/\varepsilon r^2$ are large when the dielectric constant is small. When nonaqueous solvents of low dielectric constant are used, the values of dielectric constant are small. In such solutions of electrolytes, therefore, it has already been stated that ion-pair formation is favored.

Suppose that the electrostatic forces are sufficiently strong; then, it may well happen that the ion-pair "dipoles" may attract ions and *triple ions* are formed thus

$$M^+ + (A^-M^+)_{\text{ion pair}} = [M^+A^-M^+]_{\text{triple ion}} \tag{3.170}$$

or

$$A^- + (M^+A^-)_{\text{ion pair}} = [A^-M^+A^-]_{\text{triple ion}} \tag{3.171}$$

From uncharged ion pairs, charged triple ions have been formed. These charged triple ions play a role in determining activity coefficients. Triple-ion formation has been suggested in solvents for which $\varepsilon < 15$. The question of triple-ion formation can be treated on the same lines as has been done for ion-pair formation.

Further decrease of dielectric constant below a value of about 10 may make possible the formation of still larger clusters of four, five, or more ions. In fact, there is some evidence for the clustering of ions into groups containing four ions in solvents of low dielectric constant.

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