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IONIC PROCESSES IN SOLUTION

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IONIC PROCESSES IN SOLUTION

by RONALD W. GURNEY, Ph.D.

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PREFACE

The study of ions in gases is a part of physics, while the study of ions in solution is classed as chemistry. Although this division seems somewhat arbitrary, the experimental investigation of ionic solutions is carried on almost entirely by electrochemists. The present book is therefore primarily addressed to students of electrochemistry and research workers in this field. To make the book as useful as possible for teaching purposes, problems have been inserted at the ends of many of the chapters. The author hopes that the work will be found suitable for graduate courses and seminars, as well as for individual study.

Although they contain some experimental data, the first six chapters are mainly concerned with setting forth the fundamental ideas and principles on which a study of ions in solution should be based. Chapters 7 to 16 deal with experimental data, and attempt to give a unified interpretation of ionic behavior embracing a wide variety of experimental results obtained by more than a hundred investigators. This section contains the hitherto unpublished results of original research by the author, which will be of interest to physicists as well as to chemists.

While writing the first chapters, the author discovered that there existed no book giving a full yet elementary treatment of solutions from the point of view of statistical mechanics. Feeling the need of such a book to refer to, he set aside the present project and proceeded to write one. It was published in 1949 by McGraw-Hill under the title, "Introduction to Statistical Mechanics." Some familiarity with Chapter 7 of that book will be found helpful by the reader of this one.

Several years earlier "Ions in Solution," a small book by the author, had been published by the Cambridge University Press. In the present work an entirely fresh approach is adopted, and thus this book is not in any sense a revision or an extension of the former.

Most of this work was done during a tenure of a senior fellowship of the Commonwealth Fund, and the author takes pleasure in expressing his sincere gratitude to the directors of the Commonwealth Fund. He would also like to acknowledge editorial assistance from his wife, and the encouragement that he received from various friends, especially, in the early stages, from Dr. J. E. Mayer and Dr. R. E. Gibson.

New York, N.Y. RONALD W. GURNEY
February, 1953

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1. The Electrical Analogue of Magnetic Cooling. All the common solvents consist of polar molecules; that is to say, each molecule in the liquid has a permanent electric moment. The behavior of electric dipoles in an external electric field is similar to that of magnetic dipoles in a magnetic field. It is well known that, if a paramagnetic substance has been placed in a magnetic field, and if the field is then shut off or reduced in its intensity, the substance shows a marked cooling. This forms, in fact, the basis of the familiar method which has been used in recent years to obtain the lowest temperatures, near the absolute zero (temperatures below 0.01°K).

The behavior of a polar dielectric in an electric field is of the same kind. If the dielectric is exposed to an external electric field of intensity X, and this field is reduced in intensity by an amount δX, the temperature of the dielectric will not remain constant, unless a certain amount of heat enters the substance from outside, to compensate for the cooling which would otherwise occur. Alternatively, when the field is increased in intensity by an amount δX, we have the converse effect. In ionic solutions these effects are very important in any process which involves a change in the intensity of the ionic fields to which the solvent is exposed—that is to say, in almost all ionic processes. When, for example, ions are removed from a dilute solution, the portion of the solvent which was adjacent to each ion becomes free and no longer subject to the intense electric field of the ion. In the solution there is, therefore, for each ion removed, a cooling effect of the kind mentioned above. If the temperature is to remain constant, a certain amount of heat, per ion removed, will have to enter the solution from outside; this amount of heat will have a characteristic value for each species of ion. The removal of ions from solution occurs in various different processes; and it is convenient to recognize at once that, for any species of ion, the cooling effect will have exactly the same value per ion, whatever the nature of the process by which this ion has been removed from this solvent.

Conversely, when ions of a certain species are introduced into a solvent, the amount of heat generated, per ion introduced, will have the same value, by whatever process these ions have been brought into the solvent. A systematic treatment of ionic solutions thus demands that we make a list of the chief processes whereby ions are introduced into or removed from solutions, and that we then give a unified discussion of the effects which are common to them all.

2. Three Processes by Which Ions Are Introduced into Solution. We may distinguish three chief processes: (1) When an ionic crystal is in contact with a solvent, positive and negative ions leave their positions on the surface and go into solution. (2) When a piece of soluble metal, such as zinc or silver, is in contact with a solvent, metallic positive ions leave their positions on the surface and go into solution; this process or its converse especially accompanies the passage of an electric current. (3) Some species of neutral molecules, when in solution, tend to break up into positive and negative ions, giving a solution which contains ions of both signs in addition to neutral solute molecules (molecules of a so-called "weak electrolyte"). We may regard these as the three chief ways in which ions are brought into a solvent. The converse processes whereby ions are removed from solution are thus: when positive and negative ions are deposited from solution to build up an additional layer on the surface of an ionic crystal; when positive ions are deposited on the surface of a piece of metal; and when ions recombine to form a neutral molecule in solution.

We have mentioned the cooling and heating effects as *one* reason why these three processes should be given a parallel treatment; but the advantage of such a unified procedure is much wider and extends to nearly all the aspects of these three processes. In this book one of the chief aims will be to make use of our detailed knowledge of the properties of ions in a vacuum, and to apply this knowledge to ions in solution. We may then notice that to each of these processes there is a corresponding process whereby, in the absence of solvent, we can obtain the same species of ions in a vacuum. Corresponding to (1), (2), and (3), described above, we may denote these three processes by (1_{vac}), (2_{vac}), and (3_{vac}), respectively (see Fig. 1). The first process, (1_{vac}), is the removal of a pair of ions from the surface of an ionic crystal, leaving the separate ions at rest in a vacuum. The second process, (2_{vac}), corresponding to (2) above, is the removal of a positive atomic core from a metal surface, leaving the positive ion at rest in a vacuum. The third process, (3_{vac}), corresponding to (3), is the ionic dissociation of a molecule, leaving the separate ions at rest in a vacuum. The relations between these processes are shown schematically in Fig. 1.

Let us choose now a particular solvent and a particular ionic crystal. If by the process (1_{vac}) we obtain in a vacuum the ions from this crystal, and if we then imagine that we plunge these ions into the chosen solvent, as indicated by the *vertical* dotted arrow in Fig. 1*a*, it is clear that the final state is the same as if these same ions had been introduced directly into the solvent by the process (1). In the same way, if in a vacuum we have obtained certain species of ions, either by the process (2_{vac}) or by the process (3_{vac}), and if we now plunge these separate ions into a solvent, the final result will be the same as if these ions had been introduced directly into this solvent by process (2) or by process (3). When an ion of a certain species has been brought into a solvent at temperature T, the final result is of course the same, whether this ion has been brought into the solute from a vacuum or from some other source.

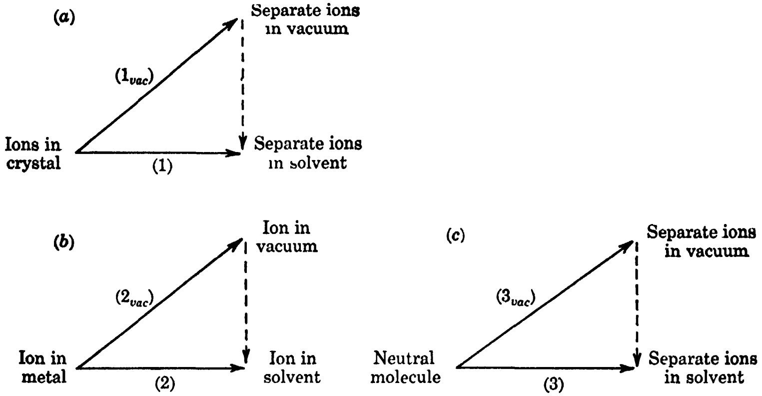

FIG. 1

Each of the vertical arrows in Fig. 1 represents the process of plunging one or more ions from a vacuum into a certain solvent. We want to know in detail what takes place in this process. For each ion in the final state a little portion of solvent is subject to the intense field of the ionic charge and is slightly modified. Thus each ion determines to some extent the character of its own environment in the solvent. In comparing different species of ions in the same solvent, the environment of each species will depend on the charge, the size, and perhaps to a less extent on the electronic structure, of the ion. Even apart from molecular ions, we have among atomic ions a great variety. Not only have we singly charged and multiply charged ions, but the largest atomic ions have radii about three times that of the smallest species.

When studying ions in a vacuum, we are mainly interested in the electronic structure of each species of ion. In dilute solution, the center of interest is largely shifted to the little region of modified solvent immediately surrounding each ion. Strangely enough, no technical term is in use for referring to this important region. In this book, for each species of atomic ion in a very dilute solution, we shall use the term *co-sphere of the ion* to refer to the little spherical portion of solvent which encloses the ion and which is somewhat modified by the presence of the ion.

The picture of a very dilute solution that we must adopt is shown schematically in Fig 2 Each ion is enclosed in its own co-sphere, while the remainder of the solvent between the ions does not differ in any way from ordinary pure solvent. As a result of recent progress in atomic physics, we now know in great detail the structure and properties of different species of atomic ions in a vacuum; and at the same time we know the physical properties of the pure solvent. In order to understand the properties of a very dilute solution, we need to discuss the portions of solvent that lie in the co-spheres of the ions.

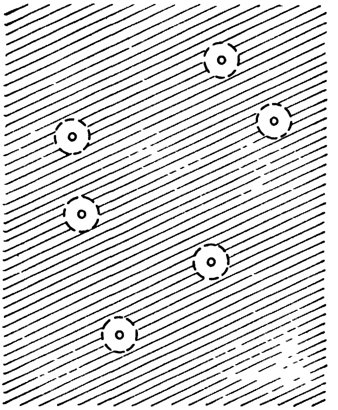

FIG. 2

The term "Brownian motion" was originally introduced to refer to the random thermal motion of visible particles. There is no reason why we should not extend its use to the random motion of the molecules and ions themselves. Even if the ion itself were stationary, the solvent molecules in the outer regions of the co-sphere would be continually changing; furthermore, the ion itself executes a Brownian motion. We must use the term *co-sphere* to refer to the molecules which at any time are momentarily in that region of solvent which is appreciably modified by the ion. In this book we are primarily interested in solutions that are so dilute that the co-spheres of the ions do not overlap, and we are little concerned with the size of the co-spheres. In studying any property to which the co-spheres contribute, there would, however, be no difficulty in deciding where we must place the boundary of the co-sphere. We ask what is the highest accuracy with which we can measure the said property of interest, and we define the volume of the co-sphere as including the solvent molecules which make an appreciable contribution. All the molecules of the solvent lying outside the boundaries will together make a contribution which is smaller than the experimental error with which the property is measured. That is to say, all the liquid not included in the co-spheres is to be regarded as having the properties of pure solvent.

3. A Polar Dielectric in an Electrostatic Field. When a solvent is subjected to the electrostatic field of an ion, the behavior of the molecules near any distant point (in this field) is similar to the behavior of the same molecules in a *uniform* electrostatic field; and we may recall what is usually said in textbooks about the polarization of a dielectric in a uniform field. A molecule consists of positive and negative particles (electrons and nuclei); and, when this structure is subjected to an external field, the positive and negative parts of the molecule tend to be moved slightly in opposite directions. If the molecule has no permanent electric moment, the applied field leads only to a temporary distortion of the molecule. On the other hand, when the molecule is a permanent electric dipole, it leads, in addition, to a tendency for the dipole to be aligned by the field, or rather, to be rotated slightly in the direction of alignment. In the common solvents the total effect due to the partial alignment of the molecular dipoles is large compared with the total effect arising from the distortion of the molecules themselves by the field. In any case, the slight displacement of the oppositely charged parts of each molecule implies a loss of potential energy by the molecules of the dielectric.

Let us consider now the amount of work required in the familiar problem of the charging of a parallel-plate condenser. Between the plates of the condenser there may be either a vacuum or a dielectric; we shall first consider the case of a vacuum. With insulated parallel plates A and B we may imagine that electrons removed from A are conveyed across the gap to the parallel plate B, so that A acquires a positive and B a negative charge. When, at any stage of this process, a field of intensity X has been set up between the plates, the work required to convey the next installment of charge dq across the gap will be $Xl\,dq$, if l is the distance between the plates. Thus the work to set up charges $+q$ and $-q$ on the plates is

$$\int_0^q Xl\,dq \tag{1}$$

Throughout this chapter we shall use the symbol X to denote the intensity of the field in a vacuum. When there is a dielectric between the plates, the work to convey an installment of charge dq is again given by the product of $l\,dq$ with the intensity of the field; but the intensity of the field associated with given charges $\pm q$ is smaller than in a vacuum. Each additional element of charge dq is conveyed through a weaker field, and consequently less work is done in charging the condenser than in a vacuum.

When this process has been completed, the dielectric has become polarized, to a certain degree. It is useful to notice that the same final situation may be reached as a result of the two steps; first, with the parallel plates A and B separated by a distance l in a *vacuum*, we set up the charges $+q$ and $-q$ on the plates; and later we fill the space between the plates with the dielectric. If this has been carried out isothermally, the final state that we reach by these two steps is of course the same as the final state which would be reached if these plates were charged, in a single process, with the dielectric between, as described above. As will be seen from Fig. 3, on page 10, the set of three steps is quite analogous to each set of three steps depicted in Figs. 1*a* to *c*. We shall find that the cycles are not merely analogous, but that in the physical process there is a basic correspondence.

Consider the processes (1), (2), and (3) of Fig. 1. In each case, initially no electrostatic field exists. When we bring ions into the solvent, we have to do the electrostatic work required to set up their fields in the dielectric. These ionic fields are weak compared with the fields which would be set up in a vacuum—which are, in fact, set up in processes (1_{vac}), (2_{vac}), and (3_{vac}) where the same ions are brought into a vacuum.

In Sec. 2 we saw that the vertical arrows in Fig. 1 denote the process of plunging ions from a vacuum into a solvent. Initially the ionic field exists in the vacuum, and we may say that, in this process, solvent molecules are introduced into this field. In fact, starting with the ion in a vacuum, the final state could equally well be reached by placing molecules in contact with the ion, and continuing to add more and more molecules until the ion is situated in a drop of liquid. In either case each vertical arrow in Fig. 1 denotes a process where solvent molecules are introduced into an intense ionic field and therefore corresponds to the process of introducing a dielectric into the gap between the plates of a condenser which already bears charges $\pm q$.

4. The Concepts of Faraday and Maxwell. We shall find that the most useful method for estimating the energy of electrostatic charges is to make use of the concepts of Maxwell and Faraday, in which the energy is regarded as belonging to the medium which is subject to the electrostatic field of the charges. Faraday imagined "tubes of force" between the charges and regarded the energy as belonging to these tubes of force. If in a vacuum there is a uniform field of intensity X, the energy associated with the field has everywhere the value

$$\frac{X^2}{8\pi} \tag{2}$$

per unit volume. Modern books on electrostatics say very little about Faraday's tubes of force, but they derive the quantity $X^2/8\pi$ from the energy of a charged condenser or conductor. Consider, for example, a parallel-plate condenser, in which plates each of area A are separated by a distance l. When there is a vacuum between the plates, the capacity of the condenser is given by $C = A/4\pi l$. When charges $+q$ and $-q$ have been placed on the plates, the potential difference is given by $V = q/C$. The work that has been done to charge the condenser is

$$\frac{1}{2}CV^2 = \frac{1}{2}C(Xl)^2 = \left(\frac{X^2}{8\pi}\right)Al$$

Now Al is the volume, between the plates, that is occupied by the uniform field X. Hence, if the energy of the charged condenser is to be regarded as associated with the field, the energy density has to be $X^2/8\pi$ per unit volume. The same result may be reached for a condenser or conductor of any shape. Consider any element of volume dv in a nonuniform field. Since (2) applies to unit volume, if (2) is multiplied by dv, we may take

$$\frac{X^2}{8\pi}\,dv \tag{3}$$

to be the amount of energy in a volume dv where the field has the intensity X. The total energy in the field is to be obtained by integrating (3) over the whole field.

When we deal with any spherical atomic ion in a vacuum, we may regard it as a charge sphere of radius a bearing a charge $+q$ or $-q$. We shall find that the correct expression for the total energy in the field is obtained by integrating (3) over all space outside the sphere. The electrical capacity of any spherical conductor is equal to its radius. The work to place a charge $+q$ or $-q$ on this sphere is

$$\frac{q^2}{2C} = \frac{q^2}{2a}$$

We may verify that the same result is obtained by integrating (3). Anywhere outside the sphere, at a distance r from the center, the intensity of the field is $X = q/r^2$. The volume of a spherical shell of thickness dr is $4\pi r^2\,dr$. Substituting this for dv, and integrating from a to infinity, we have

$$\int \frac{X^2}{8\pi}\,dv = \frac{q^2}{8\pi}\int_a^\infty \frac{4\pi r^2}{r^4}\,dr = \frac{q^2}{2a} \tag{4}$$

If we introduce numerical values for q and a, we can estimate in ergs the energy associated with the fields of atomic ions. But first let us, from a different point of view, ask what order of magnitude we expect. Consider an electrically neutral spherical atom in a vacuum, and fix attention on a valence electron. Within the atom this electron is surrounded by its own intense field. In the space outside the atom, however, there is zero field, since the atom is electrically neutral. If we now remove the electron from the atom to a great distance, this leaves a positively charged ion. The space surrounding the ion is filled with radial lines of force, and the lines of force of the electron are no longer confined in a small volume. In removing the electron from the neutral atom, work must have been done in setting up these additional fields—an amount of work equal to $X^2/8\pi$ per unit volume of the final fields. Now we know that the first ionization potential of a neutral atom amounts to at least a few electron-volts; we may regard this as the work that must have been done to set up the additional fields in the vacuum.

Let us proceed now with the evaluation of (4), substituting

$$q = 4.8 \times 10^{-10} \text{ e.s.u.}$$

and $a = 1.5 \times 10^{-8}$ cm. We find

$$\frac{q^2}{2a} = \frac{(4.8 \times 10^{-10})^2}{2 \times 1.5 \times 10^{-8}} = 8 \times 10^{-12} \text{ erg} \tag{5}$$

Now 1 electron-volt is equivalent to 1.6×10^{-12} erg. Hence for an ion of this size the value turns out to be 5 electron-volts. We shall obtain smaller values for larger ions, and larger values for smaller ions. In general, we find, as predicted above, that the values of (4) agree roughly with the ionization potentials of neutral atoms.

At the same time it will be useful to look at the way in which this energy is distributed in the space around an ion in a vacuum. It follows from (4) that, if we imagine a concentric sphere of any radius R, larger than a, drawn round the ion, and if we integrate from R to infinity, we find that the amount of energy associated with the field outside this sphere is equal to

$$\frac{q^2}{2R} \tag{6}$$

Consider two such concentric spheres of radii R_1 and R_2, such that $R_2 = 2R_1$. On substituting these radii in the denominator of (6), the energy lying outside the smaller sphere is *twice* the energy lying outside the larger sphere. In other words, there is as much energy in the spherical shell between the two spheres as there is in the whole of space outside the larger sphere. We shall refer to this result later.

5. The Electrostatic Energy in the Fields of Ions. These concepts may now be applied to the processes (1_{vac}), (2_{vac}), and (3_{vac}) of Fig. 1. Let us consider an ionic crystal such as sodium chloride. Each positive ion in the crystal lattice is surrounded by negative ions; most of the lines of force from any positive ion do not stretch out through the crystal but come to an end on the negative ions immediately adjacent; similarly, the lines of force from a negative ion in the lattice come to an end on the adjacent positives. If, however, we split up the crystal into its component ions and leave the separate ions at long distances apart in a vacuum, lines of force will radiate from each spherical ion, with energy everywhere equal to $X^2/8\pi$ per unit volume. In splitting up the crystal, work must have been done. In the original crystal, if the ions are to be treated as spheres packed together, there are, of course, void spaces between these spheres with a certain amount of energy per unit volume there. To break up the crystal into its component ions, the electrostatic work is equal to the work required to set up the *additional* electrostatic fields. For singly charged ions, this must obviously, according to (3), amount to a few electron-volts per ion. In the alkali halides and similar crystals the contribution from non-electrostatic forces (exchange forces of repulsion and attraction) is rather small compared with the electrostatic work. The lattice energy of crystalline potassium chloride amounts to 7.17 electron-volts per ion pair.

The same ideas may be applied to the other processes of Fig. 1. The work required to dissociate a diatomic molecule into two *electrically neutral* atoms may be quite small; the dissociation energy of the bromine molecule Br_2 in a vacuum, for example, is only 1.96 electron-volts. On the other hand, the work to dissociate a molecule into two atomic ions in a vacuum cannot be as small as this, since work must be done to set up the full electrostatic field of the positive ion, and the full electrostatic field of the negative ion; and this must amount to at least a few electron-volts.[1] In addition, the non-electrostatic forces may make a small or large contribution.

In the same way, if we remove a positive atomic core from a piece of

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[1] The work to dissociate an NaCl molecule into Na^+ and Cl^- ions in a vacuum is said to be 5.5 electron-volts; see O. K. Rice, "Electronic Structure and Chemical Binding," p. 253, McGraw-Hill, 1940.

metal into a vacuum—for example, Ag^+ from metallic silver, we know that the ionic field of the Ag^+ in the vacuum must contain the same amount of energy ($X^2/8\pi$ per unit volume) as it would contain if this ion had been brought into the vacuum from a silver salt, or from an ionic solution, or from elsewhere.

6. The Charging of a Condenser. Returning now to the question of a parallel-plate condenser, let us now examine the polarization of a dielectric at temperature T in a uniform field. Figure 3 has already been referred to in Sec. 3. We shall have to ask in what way the steps labeled B and C in Fig. 3 are together equivalent to A. Suppose that considerable charges of opposite sign have been placed on rigid parallel plates in a vacuum. If we now bring up a slab of dielectric, to introduce it between the plates, it experiences a strong attraction; moving under this attraction, it could be made to raise a weight or to perform other useful work. The amount of work that can be obtained in this isothermal process is equal to the loss of free energy by the molecules of the dielectric during the process. Initially, when the dielectric is remote from the plates, the whole of it is in zero field. When the slab is slowly introduced between the plates (process C in Fig. 3), the molecules in each element of volume δv inside the dielectric are subject to a field which slowly increases from zero to the final value. But this is exactly the same as that which happens in process A: the molecules in any element of volume δv experience a field which increases from zero to the same final value. The change in the free energy of the dielectric is the same in process C as in process A; the only difference is that in C it takes place *after* the plates have been charged, while in A it takes place *during* the charging of the plates.

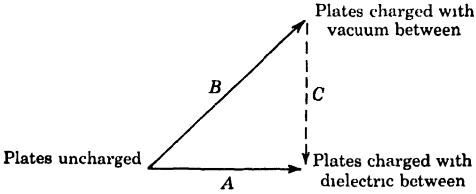


FIG. 3

Let us next ask how the changes of energy will depend on the type of dielectric. The vertical arrows labeled A, B, and C in Fig. 4 are intended to indicate the changes in free energy for the steps A, B, and C, respectively, of Fig. 3. The length of the arrow B represents the work done in charging a condenser that has a vacuum between the plates. If a gaseous dielectric is now introduced between the charged plates (process

C in Fig. 3), the loss of free energy will be small (arrow *C* in Fig. 4*a*). In this case the length of the vertical arrow *A* in Fig. 4*a* is nearly as great as *B*; the work to charge the condenser with the gas between the plates would be almost as great as in a vacuum.

On the other hand, all the solvents with which we deal in this book have large electrostatic susceptibilities. In Fig. 4*b* the length of the vertical arrow *C* is almost as great as *B*. That is to say, the amount of free energy lost by the dielectric is almost as large as the whole of the energy initially associated with the field *X* in the vacuum.

If the dielectric is already between the plates when the plates are charged, we must regard the two processes *B* and *C* as taking place simultaneously; in this case, the work required to charge the condenser (vertical arrow *A*) is much smaller than in vacuum. If the dielectric is pure water near room temperature with dielectric constant equal to 80, *C* will be $\frac{79}{80}$ of *B*. We may begin to examine the mechanism by which the dielectric loses this amount of free energy.

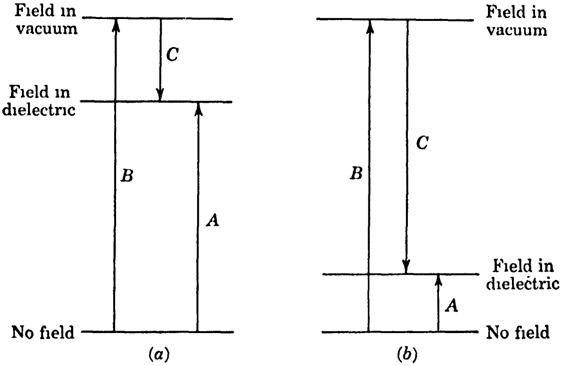


FIG. 4

At the opening of this chapter we mentioned the electric analogue of magnetic cooling. It is essential to have an understanding of this process if one wishes to obtain a clear understanding of ionic processes in solution. For this purpose we may begin to speak of the polarization of the dielectric. This, at first, scarcely amounts to more than a change in terminology, the polarization being the rate of change of the free energy with field strength. In a dielectric consisting of polar molecules, nearly the whole of the polarization arises from the partial alignment of the dipoles by the field; only a small contribution comes from the distortion of the electronic cloud of each molecule. In fields of ordinary intensity the polarization (which is the electric moment per unit volume) is proportional to the intensity of the field in the dielectric. But at higher intensities the polarization will increase less rapidly, as shown qualitatively in Fig. 5. The theory of this effect in a dilute polar gas, given by Langevin, is described in many textbooks. The similar tendency toward saturation in liquid dielectrics has not been treated. The total amount of free energy lost by the dielectric (during the application of the field), corresponding to the arrow C in Fig. 4, will be represented per unit volume by the area under the curve in Fig. 5.

Consider next a homogeneous dielectric exposed to a non-uniform field. The above considerations may be applied to any element of volume dv. Since the polarization is the moment per unit volume, the total amount of free energy lost by the dielectric is to be obtained by integrating over its whole volume

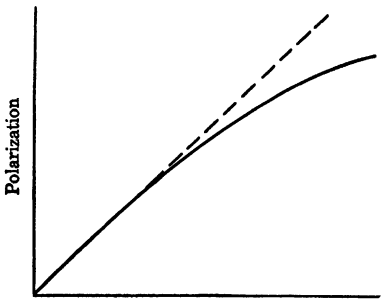


FIG. 5

When a dielectric is introduced into a field X due to the presence of certain fixed charges in a vacuum, the amount of free energy lost by the dielectric cannot exceed the amount of energy originally associated with the field X in the vacuum, though, for a medium of high electrical susceptibility, it may be *nearly* as large. In the case of water at room temperature, introduced into an ordinary weak field, it will be as much as $\frac{79}{80}$ of the original energy.

When the dielectric is a substance consisting of polar molecules, the charging of the condenser is accompanied by a change of entropy in the dielectric. The constraint exerted on the molecular dipoles by the field introduces a certain degree of order. This is obvious if we first imagine a field which is so strong that it aligns most of the dipoles; such an arrangement would be a state with a very high degree of order; the application of an ordinary weak external field takes the dielectric a short way in this direction—it introduces a small degree of order. Thus, when the charging of the condenser takes place, the polarization of the dielectric is accompanied by a loss of entropy.

With rise of temperature, the polarization produced by given electrostatic charges decreases, because the thermal agitation maintains, in opposition to the field, a higher degree of disorder. At a higher temperature the *loss* of free energy by the dielectric is smaller; that is to say, $\frac{d}{dT}\Delta F$ is positive. Since the change of entropy ΔS is equal to $-\frac{d}{dT}\Delta F$, there is a loss of entropy, which corresponds to an increment in the degree of order, as described above.

7. The Amount of Free Energy Lost by a Dielectric. The above considerations apply to fields of any intensity. When we are dealing only with ordinary weak fields, for which the polarization is proportional to the field (the straight part of the curve in Fig. 5), the substance under discussion is said to possess a *dielectric constant.* This will be denoted by ϵ. In a vacuum ϵ is set equal to unity; and in a dielectric the polarization is proportional to $(\epsilon - 1)$. The loss of free energy by the dielectric may be expressed in terms of ϵ. In Note 1 of the Appendix at the end of this book it is shown that, when a homogeneous slab is introduced into a uniform field of initial intensity X, the free energy lost per unit volume amounts to

$$\left(\frac{\epsilon - 1}{\epsilon}\right)\frac{X^2}{8\pi} \tag{7}$$

When, for example, ϵ is equal to 80, the quantity $(\epsilon - 1)/\epsilon$ has the value $\frac{79}{80}$, mentioned above.

In Fig. 3 we saw that the process A is to be regarded as equivalent to the processes B and C taking place simultaneously. In Sec. 4 we obtained in (3) an expression for the amount of work required to set up charges $\pm q$ on the plates of a condenser, when there is a vacuum between the plates. We can now find the work required to set up the same charges $\pm q$, where there is a slab of dielectric between the plates; clearly this will be obtained per unit volume by subtracting (7) from (2), thus

$$\frac{X^2}{8\pi} - \left(\frac{\epsilon - 1}{\epsilon}\right)\frac{X^2}{8\pi} = \frac{X^2}{8\pi\epsilon} \tag{8}$$

Let us next consider a non-uniform field, where the intensity X is a function of position. The expression (7) applies to unit volume; if then (7) is multiplied by dv, the expression will give the amount of free energy lost in an element of volume dv, where the field has an intensity X. The total loss of free energy will be obtained by integrating over the whole volume of the homogeneous dielectric:

$$\Delta F = -\frac{1}{8\pi}\left(1 - \frac{1}{\epsilon}\right)\int X^2\,dv \tag{9}$$

In Fig. 4*b* we saw that the length of the arrow A is to be obtained by subtracting the length of the arrow C from that of the arrow B. To obtain an expression for this amount of free energy associated with the field in the dielectric, the amount of free energy lost must be subtracted from the integral of (3). In other words, the negative quantity (9) must be added to the integral of (3), thus

$$\frac{1}{8\pi}\int X^2\,dv - \frac{\epsilon - 1}{8\pi\epsilon}\int X^2\,dv = \frac{1}{8\pi\epsilon}\int X^2\,dv \tag{10}$$

The expressions (9) and (10) can of course be used for both uniform and non-uniform fields. In the case of a uniform field, the X^2 can be taken outside the integral sign; the value of (10) will then reduce to (8) multiplied by the volume under consideration.

Comparing (10) with (3), we see that, if the intensity of the field nowhere exceeds the value at which the polarization ceases to be proportional to the field, the whole of the free energy remaining associated with the resultant field will be $1/\epsilon$ times the energy associated with the field which the same charges would set up in a vacuum, irrespective of whether the field is uniform or non-uniform. This corresponds to the familiar fact that the work required to charge a condenser at any given temperature T is $1/\epsilon$ times the work required to set up the same charges on the plates of the condenser when there is a vacuum between the plates, irrespective of the geometrical form of the condenser.

Turning next to the changes of entropy in Fig. 3, the change of entropy in process A must be equal to the sum of the changes in processes B and C. But when there is a vacuum between the plates, the charging of the condenser is not accompanied by any change of entropy. It follows then that the ΔS for the process A must be identical with the ΔS for the process C. The latter quantity is obtained by differentiating (9) with respect to the temperature, and changing the sign; the former quantity is obtained by differentiating (10) with respect to the temperature, and changing the sign. The only quantity in (9) and (10) that varies with temperature is ϵ; hence we may verify that from (9) or (10) we get the same result, namely,

$$\Delta S = -\left(\int \frac{X^2}{8\pi}\,dv\right)\frac{d}{dT}\left(\frac{1}{\epsilon}\right) \tag{11}$$

For all common substances the temperature coefficient of ϵ is negative; that is to say, the temperature coefficient of $1/\epsilon$ is positive; hence (11) represents a loss of entropy on subjecting the homogeneous dielectric to the field.

When a molecule is dissociated into a pair of ions, the work done is stored as the mutual potential energy of the ions. In deriving equation (3), we considered a similar process, in which charges of one sign were separated and conveyed across from one condenser plate to the other; the work done in this process is stored as the mutual potential energy of the equal and opposite charges; the situation is similar to that which results from the dissociation of molecules into ions. In both cases, if the charges are later allowed to come together under their mutual attraction, the potential energy (if not used to do work) will be converted into kinetic energy, and eventually into energy of thermal motion, that is to say, into heat. In a charged condenser of any form that has a dielectric between the plates, the amount of energy stored is given by (10); when the condenser is discharged this amount of energy becomes available. At the same time the dielectric becomes free from the applied field. If this dielectric consists of polar molecules, the liberation of the dipoles from the controlling field must be accompanied by the cooling effect mentioned in Sec. 1; that is to say, if the temperature of the dielectric is to remain constant, a certain amount of heat must be supplied. The question immediately arises, which of these two amounts of heat is the larger. Does the release of potential energy generate an amount of heat which is sufficient to prevent a lowering of temperature? Or is it more than sufficient or less than sufficient? Writing

$$\Delta H = \Delta F + T\,\Delta S$$

we found that, whether the condenser is being charged or discharged, the terms $T\,\Delta S$ and ΔF are of opposite sign; and we are asking whether the magnitude of ΔF is greater or less than that of $T\,\Delta S$. The equations (10) and (11) at once enable us to answer this important question in the case of ordinary weak fields. To obtain $T\,\Delta S$, equation (11) must be multiplied by the absolute temperature, thus

$$T\,\Delta S = -\left(\int \frac{X^2}{8\pi}\,dv\right) T\frac{d}{dT}\left(\frac{1}{\epsilon}\right) \tag{12}$$

Since (10) gives the amount of work done in charging the condenser, we compare (12) with (10) and find that the problem resolves itself into the question whether, at the temperature considered, the reciprocal of the dielectric constant is greater, or less, than the quantity

$$T\frac{d}{dT}\left(\frac{1}{\epsilon}\right) \tag{13}$$

8. The Behavior of Solvents in an Electrostatic Field. The dielectric constant of water falls from 88 at 0°C to the value 55 at 100°C, while that of methyl alcohol falls from 47.5 at -60°C to the value 29 at $+40$°. Careful measurements on various common solvents near room temperature have shown that, over the whole range of temperature covered, the value in each case falls exponentially; the value at any temperature T

may be obtained from the empirical formula

$$\epsilon = \epsilon_0 e^{-T/\vartheta} \tag{14}$$

where the characteristic constants ϵ_0 and ϑ have the values listed in Table 1. It will be seen that for each liquid except water the value of the characteristic temperature ϑ lies quite near the normal freezing point; in the case of water it lies well below the freezing point. We may note then that, in practice, the value of the quantity T/ϑ in (14) is always greater than unity.

TABLE 1. DIELECTRIC CONSTANTS OF SOLVENTS

Solvent	ϵ_0	ϑ	Freezing point, °K
H_2O	305.7	219[a]	273.1
D_2O	306.7	218[a]	273.1
Methanol	157.1	185.4[b]	175.3
Ethanol	148.5	164.5[b]	155.8
n-Propanol	150.4	148[b]	146

[a] J. Wyman and E. N. Ingalls, *J. Am. Chem. Soc.*, **60,** 1184 (1938).
[b] G. Akerlof, *J. Am. Chem. Soc.*, **54,** 4125 (1932).

From (13) we obtain

$$T\frac{d}{dT}\left(\frac{1}{\epsilon}\right) = T\frac{d}{dT}\left(\frac{e^{T/\vartheta}}{\epsilon_0}\right) = \frac{Te^{T/\vartheta}}{\vartheta\epsilon_0} = \frac{T}{\vartheta\epsilon} \tag{15}$$

We can now answer the question whether the value of (10) will be greater than (12). We find that this will be so, if $1/\epsilon$ is greater than $T/\vartheta\epsilon$; that is to say, if unity is greater than T/ϑ. We have seen, however, that for the common solvents in the range covered by experiments T/ϑ is greater than unity. For water at 25°C, T/ϑ has the value of $\frac{298}{219}$, or 1.36. We conclude that, in the discharge of any condenser that has water or another of these liquids in the gap between the plates, the energy released is not sufficient to supply the amount of heat required to maintain constant the temperature of the dielectric. An amount of heat must flow in from the surroundings; in the case of water at 25°C it amounts to an additional 36 per cent. This is the *electrical analogue* of the well-known magnetic cooling that was mentioned at the beginning of this chapter. We shall find that it often plays an important role in ionic solutions.

In Sec. 6 we saw that, if a dielectric is introduced into the gap between condenser plates that already bear charges $\pm q$, the amount of free energy lost during this process is the same as that which would be lost by the dielectric if it were already between the plates during the process of charging the condenser. A similar remark may be made about the amount of entropy lost by the dielectric; the amount will be the same in the two cases. Consequently the $T\,\Delta S$ term will be the same in the two processes, although the ΔF term (represented by the short arrow A in Fig. 4*b*) is, of course, quite different.

Consider a condenser in which the gap is completely filled with a dielectric whose dielectric constant ϵ is large; and suppose that we gradually build up large charges $+q$ and $-q$ on the plates. During this process no intense field comes into being, because at all stages of the process the dielectric reduces the intensity to a small value. Consequently, we do not have any large amount of free energy to deal with. In Fig. 3 this is because the processes B and C are taking place simultaneously; and the final result is that in Fig. 4*b* the length of the arrow A is quite small, since it is merely the difference between the arrows B and C.

It should be noticed that in discussing (12) and (15) the comparison between ΔF and $T\,\Delta S$ was made for the process whose ΔF is represented by the small arrow A in Fig. 4*b*. If we make a similar comparison between ΔF and $T\,\Delta S$ for the process whose ΔF is represented by the much longer arrow C, the result will be very different. In this case, the terms ΔF and $T\,\Delta S$ are of the same, not of opposite, sign, and the magnitude of $T\,\Delta S$ is small compared with ΔF. In this case there would be nothing unusual about the behavior; potential energy would be converted into heat in the usual way. It is in the process A that we find the cooling effect; and this must be clearly grasped, because, as we shall see, it is process A that is of practical importance in dealing with ionic fields.

9. A Dielectric in the Field of a Charged Sphere. In equation (4) we obtained the value of the energy in the field of a charged sphere in a vacuum; and at the same time we noticed in (6) that the energy associated with the field outside any radius R, greater than a, amounts to $q^2/2R$. We can likewise obtain an expression for the free energy associated with the field of a charged sphere that is situated in a dielectric. In this way we can construct a set of three steps, depicted in Fig. 6, that will be more directly useful for our purpose than those for the parallel-plate condenser with which we started. When subjected to the electrostatic field, the behavior of the dielectric in any element of volume will be no different from that which we have been describing. We shall find that Figs. 4*a* and 4*b* will apply to the three steps of Fig. 6. To put the expressions (9) and (12) into the form applicable to a field with spherical symmetry, we substitute $4\pi r^2\,dr$ for dv, and integrate from R to infinity. If the radius R is chosen such that the intensity of the field in the region outside is sufficiently small (so that the polarization is everywhere proportional to the intensity), the amount of free energy lost by the dielectric that lies outside the sphere of radius R will be

$$\frac{\epsilon - 1}{8\pi\epsilon} \int_R^\infty 4\pi X^2 r^2 \, dr \tag{16}$$

If the field is due to a charge $+q$ or $-q$ at the origin, (16) becomes

$$\frac{\epsilon - 1}{2\epsilon} \int \frac{q^2}{r^4} r^2 \, dr = \left(1 - \frac{1}{\epsilon}\right) \frac{q^2}{2R} \tag{17}$$

To find an expression for the free energy associated with the field in the dielectric lying outside any radius R, (17) must be subtracted from the original energy in a vacuum, $q^2/2R$, thus

$$\frac{q^2}{2R} - \left(1 - \frac{1}{\epsilon}\right) \frac{q^2}{2R} = \frac{q^2}{2R\epsilon} \tag{18}$$

The free energy associated with the field is reduced to $1/\epsilon$ of its original value in a vacuum; and Figs. 4*a* and 4*b* show the resultant behavior.

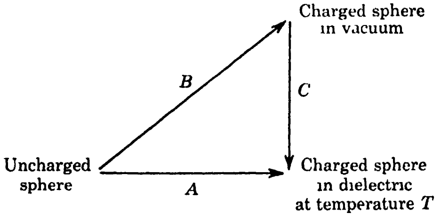


FIG. 6

Since ϵ is the only quantity in (17) that varies with temperature, we obtain from (17)

$$\Delta S = -\frac{q^2}{2R} \frac{d}{dT} \left(\frac{1}{\epsilon}\right) \tag{19}$$

This is the amount of entropy lost by the dielectric that lies outside any radius R. If we use (15) the expression for $T \, \Delta S$ takes the form

$$T \, \Delta S = -\frac{T}{\vartheta} \frac{q^2}{2R\epsilon} \tag{20}$$

10. Two Types of Process Contrasted. Although the discussion of a parallel-plate condenser has been useful, it will be obvious, if Fig. 6 is compared with Fig. 1, that in the processes A, B, and C of Fig. 6 we have found something directly comparable with the ionic processes of Fig. 1. We may conclude this chapter by drawing attention to the very important distinction that was made at the end of Sec. 8 between the type of process where the ΔF and the $T\,\Delta S$ are comparable in magnitude and of opposite sign, and the type of process where $T\,\Delta S$ is small compared with ΔF and is of the same sign; the processes A and C of Fig. 6 are examples of the two types. It is important to grasp the fact that the former type is the one that is characteristic of ionic fields as they occur in actual experiments. The latter type occurs in imaginary experiments—for example, where we plunge ions from a vacuum into a solvent and measure the heat evolved; this is never done in practice, but it is a necessary theoretical concept.

In this connection let us now discuss Fig. 6, paying attention always to the region outside any sphere of radius R. The entropy lost by the solvent in the electrostatic field will be the same whether the sphere is already in the infinite dielectric during the charging process, or whether an already charged sphere is slowly introduced into the liquid. But the value of ΔF in the two cases is quite different. In a vacuum the initial energy $q^2/2R$ will be reduced to $q^2/2\epsilon R$ when the sphere is introduced into the liquid; here ΔF will have the large negative value

$$\Delta F = -\frac{q^2}{2R}\left(\frac{\epsilon - 1}{\epsilon}\right) \tag{21}$$

while the term $T\,\Delta S$ will have the small negative value given by (20). On the other hand, when an uncharged sphere is in the dielectric, a small amount of work is required to set up the electrostatic field; the value of ΔF given by (18) is thus small and positive. The term $T\,\Delta S$, again given by (20), is of opposite sign and in practice is somewhat larger than ΔF, since T/ϑ is greater than unity. In water at 25°C, as we have seen, the magnitude of (20) will be 1.36 times as great as (18). On the other hand, for the process C of Fig. 6, dividing (20) by (21), the ratio of $T\,\Delta S$ to ΔF will be

$$\frac{T}{\vartheta(\epsilon - 1)} \tag{22}$$

which is small when ϵ is large. In water at 25°C the ratio will be $1.36/78 = 0.017$; in this case we find

$$\begin{aligned}\Delta H &= \Delta F + T\,\Delta S\\ &= 1.017\Delta F\end{aligned} \tag{23}$$

Here the value of ΔH is of the same sign as ΔF and is less than 2 per cent greater. On the other hand, for process A in Fig. 6, adding (20) to (18), we have

$$\begin{aligned}\Delta H &= \Delta F + T\,\Delta S \\ &= \frac{q^2}{2R\epsilon} - 1.36\,\frac{q^2}{2R\epsilon} \\ &= -0.36\Delta F\end{aligned} \tag{24}$$

Here ΔH and ΔF are of opposite sign, and quite different in magnitude. As emphasized above, it is this kind of relation that is characteristic of ionic fields under experimental conditions. These numerical values are for water at 25°C. Similar results for other solvents may be obtained by using the values given in Table 1.

In Fig. 1 we considered three processes by which certain species of ions may be introduced into a solvent; and at the same time we considered the processes by which these same ions may be introduced into a vacuum. In the following chapter we shall examine each of these three processes in greater detail; and in Fig. 12 we shall obtain a diagram quite analogous to Fig. 4*b*.

Problems

1. Using the method described in Note 1 of the Appendix at the end of this book, complete the derivation of the expressions (7) and (16).

2. The numerical values in (23) and (24) refer to water. After checking these values, obtain the corresponding expressions for methyl and ethyl alcohols, taking the necessary quantities from Table 1.

CHAPTER 2

The Dissociation of a Molecule into Ions. The Removal of Ions from a Metal Surface. The Removal of Ions from the Surface of an Ionic Crystal. The Solvation Energy of an Ion. Work Done against Electrostatic Forces. Molecules and Molecular Ions Containing One or More Protons. Proton Transfers. The Quantities **D**, **L**, **Y**, and **J**. *Two Spherical Conductors.*

11. The Dissociation of a Molecule into Ions. It was pointed out at the beginning of Sec. 8 that, whether we charge a condenser or dissociate a molecule into two ions, in either case a separation of positive and negative charges is effected; the work done may be regarded as converted into the mutual potential energy of the charges, and as stored in this form. Although attention has been focused mainly on electrostatic forces, the presence of non-electrostatic forces of attraction has been mentioned in Sec. 5 in the case of both crystals and molecules.

Before discussing in detail the dissociation of a molecule into a pair of ions, let us first examine the dissociation of a diatomic molecule into a pair of neutral atoms. This process is usually studied with the aid of a plot of the mutual potential energy of the two atoms—a plot which has the familiar form shown by the curve of Fig. 7. In this diagram the horizontal line represents the energy of the separate atoms at rest in a vacuum. Between these two atoms only short-range forces are present, and the value of the mutual potential energy does not differ appreciably from this horizontal line except at very small distances (a few angstroms); here the curve falls, passes through a minimum, and then rises steeply when the intense repulsion between the electronic shells of the two atoms becomes predominant.

On the other hand, when a molecule in a vacuum is broken up into a positive ion and a negative ion, the mutual attraction, instead of disappearing rapidly, falls off slowly. At large separations of the ions the mutual potential energy $-e^2/r$ approaches zero as $1/r$. In Fig. 8a the curve approaches the horizontal line varying as $1/r$. The slope of the curve at any point, of course, represents the force of attraction.

The name "dissociation energy" is given to the work required to break up a diatomic molecule which is in its lowest rotation-vibrational state, and to leave the two particles (either atoms or ions) at rest in a vacuum. This quantity, which will be denoted by $\mathbf{D}_{vac}$, corresponds to the length of the arrow in Fig. 7 or Fig. 8*a*, where the length is the vertical distance between the lowest level of the molecule and the horizontal line which the potential energy approaches for large values of r.

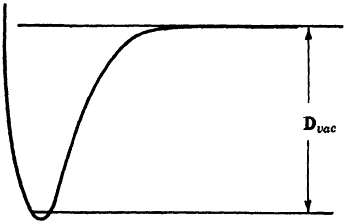
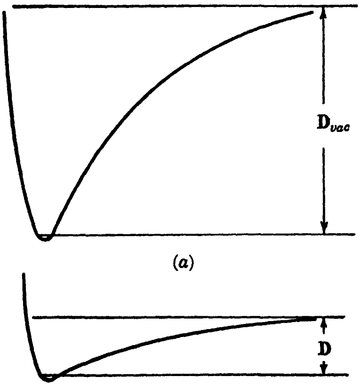


FIG. 7



(*a*)

(*b*)

FIG. 8

Let us now consider the same species of molecule situated in a particular solvent and dissociated into a pair of ions. The potential-energy curve will be similar but will have a much shallower minimum, as in Fig. 8*b*, because in a medium of high dielectric constant the electrostatic attraction is much weaker. Let the dissociation energy in solution be denoted by **D**, in contrast to the larger $\mathbf{D}_{vac}$, the value in a vacuum.

At large distances the curve of Fig. 8*b* is a plot of $-(e^2/\epsilon r)$, where ϵ is the macroscopic dielectric constant of the solvent at the temperature considered. For small values of r the curve deviates from this value; but at every point the slope of the curve must represent the mean intensity of the mutual attraction or repulsion at the particular temperature considered. If the curve of Fig. 8*b* for dissociation in solution is to be useful, every point on this curve must belong to the same temperature T. That is to say, when we consider any change in the distance r between the ions, we are interested in an *isothermal* change in r.

In Fig. 8*a* the dissociation energy $\mathbf{D}_{vac}$ is the work required to break up one molecule and leave the ions at rest in a vacuum. In Fig. 8*b* the dissociation energy **D** is the work required to break up one molecule and to separate the ions isothermally in a solvent at temperature T. Although we have mentioned only electrostatic forces of attraction between the two ions, short-range quantum-mechanical forces of attraction may also be present; see Sec. 29.

12. The Removal of Ions from a Metal Surface. Now that we have considered one of the processes by which ions are produced either in a vacuum or in solution, we can pass on to the processes (2) and (2_{vac}), (3) and (3_{vac}). The appropriate treatment is so similar that it will not be necessary to give it in detail.

The atoms of any metal adhere together to form a crystal because of the forces of attraction between them; to remove an atom from the surface requires a definite amount of work, characteristic of the metal; this is called the "sublimation energy." To detach a positive atomic core from the surface requires more work than to detach the corresponding neutral atom. For example, to detach an Ag^+ core from the surface of a crystal of metallic silver requires a greater amount of work than to detach a neutral Ag atom. When the ion has been removed and is in the vacuum, it is surrounded by its electrostatic field; and, in removing the ion from the metal, energy has been put into this field. Consider a straight line perpendicular to the surface of the metal, and passing through a surface lattice point, about which an atomic core can vibrate. If we plot the potential energy of the ion against the distance d from the metal surface, we obtain a curve similar in shape to the curve of Fig. 8a. When d is large compared with the radius of the ion, the ion is attracted to the surface by the so-called "electrical-image force," whose intensity is $e^2/4d^2$. The corresponding part of the potential-energy curve is therefore a plot of $-e^2/4d$. At smaller distances the quantum-mechanical forces of attraction and repulsion become more important, leading to a curve like that of Fig. 8a.

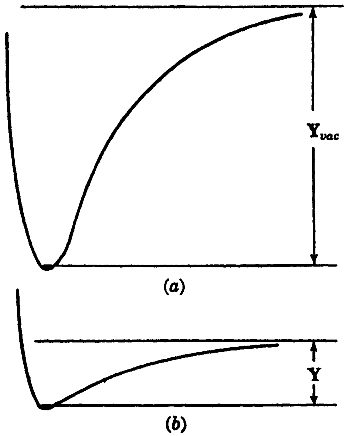


Fig. 9

The depth of this potential minimum will play a part similar to that of the depth of the minimum in Fig. 8a. The energy represented by the vertical arrow in Fig. 9a is the work required to detach a positive atomic core from the surface of the metallic lattice and to leave it at rest in a vacuum. No name for this quantity has come into general use. We shall denote it by $\mathbf{Y}_{vac}$, corresponding to the $\mathbf{D}_{vac}$ of Fig. 8a.

If a piece of metal, such as silver, is dipping into a solvent, and a positive atomic core is taken from the surface into the solvent, the ion is again surrounded by its electrostatic field; but free energy has been lost by the dielectric, and a relatively small amount of work has had to be done. The corresponding potential-energy curve (Fig. 9*b*) is therefore much less steep and has a much shallower minimum than that of Fig. 9*a*. For large distances d from a plane metal surface this curve is a plot of $-e^2/4\epsilon d$ where ϵ is the dielectric constant of the medium at the temperature considered The curve represents the work done in an isothermal removal of the positive core.

In Sec. 8 we took the point of view that, when a molecule has been dissociated into ions, energy equivalent to the work done may be regarded as stored in the form of potential energy, which will be liberated when the ions recombine. The same point of view can be adopted with regard to the quantities Y_{vac} and Y. The electrostatic part of this energy may be regarded as associated with the ionic field.

13. The Removal of Ions from the Surface of an Ionic Crystal. Turning next to an ionic crystal, we can imagine the process of systematically stripping a surface layer from the crystal, row by row, and ion by ion. If the ions are taken into a vacuum, we can draw for the positive ion a potential-energy curve similar to that of Fig. 9*a*, and likewise for the removal of the adjacent negative ion. Alternatively, if the ions are taken into a solvent, we can draw for the positive ion a curve similar to that of Fig. 9*b*, and likewise for the negative ion. For many purposes, however, it is more convenient not to deal with the positive and negative ions separately. Consider a uni-univalent or di-divalent crystal, and suppose that from adjacent lattice points we detach a positive and a negative ion, and take them simultaneously from the crystal, not along parallel lines, but along divergent lines, as indicated in Fig. 10, which represents the removal of a pair of ions from adjacent lattice points. During this simultaneous removal of two ions, let their common distance from the underlying layer of the lattice be denoted by d; and let the distance from one ion to the other be denoted by r. As we remove the ions from the crystal, so do we also separate the ions against their mutual attraction; r is proportional to d. Suppose now that the potential energy of the whole system is plotted against d. For removal of the two ions into a vacuum simultaneously, we thus obtain a single curve, which will be similar in shape to that of Fig. 9*a*. For large values of d the potential energy will again be proportional to $1/d$. This curve is shown in Fig. 11*a*; the depth of the minimum represents L_{vac}, the lattice energy per ion pair.

Let us next suppose that this same crystal is in contact with a certain solvent, and suppose that we again remove two adjacent ions along divergent paths. As we remove the ions from the crystal we shall, at the same time, separate them against their mutual attraction, which in this case is much weaker. If the potential energy is plotted against *d*, we obtain a diagram analogous to Fig. 9*b*. The depth of the potential minimum, labeled **L** in Fig. 11*b*, represents the amount of work required to take the pair of ions into the solvent at temperature *T*. Although we have mentioned only long-range electrostatic forces of attraction, short-range quantum-mechanical forces of attraction may also be present and make a contribution to **L** (compare Fig. 27).

At the end of Chapter 1 the discussion of a charged sphere led to the construction of Fig. 6, and to the recognition of the fact that the diagram

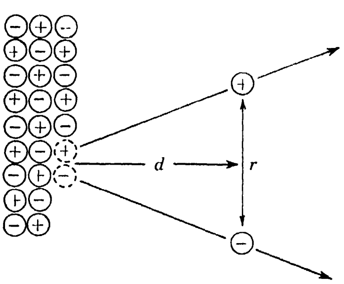
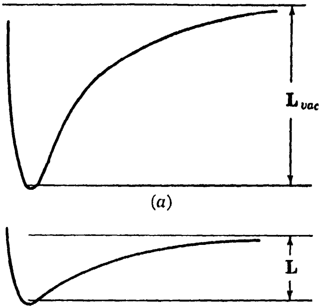


FIG. 10



(*a*)

(*b*)

FIG. 11

of Fig. 4*b* would apply to the charging of the sphere in a medium of large ϵ, because the dielectric loses free energy in the field of the charge. We shall find now that Fig 4*b* is likewise applicable to ionic processes, because the solvent loses free energy in the field of any ionic charge. Later, we shall make our discussion more precise, as we proceed. First, in order to show the relation between $\mathbf{L}_{vac}$ and **L** as represented in Figs. 11*a* and 11*b*, we may superimpose the minimum of one curve on the minimum of the other curve; the result is shown in Fig. 12. Similarly for the curves of Figs. 9*a* and 9*b*, if we superimpose the minimum of one curve on that of the other, we again obtain a diagram of the form shown in Fig. 12. Thirdly, for the curves of Figs. 8*a* and 8*b*, if we superimpose the minimum of one curve on that of the other, we obtain a diagram of the same form. The states represented by the three horizontal lines in Fig. 12 correspond to those in Fig. 4; and when the arrows *A*, *B*, and *C* have been drawn in Fig. 12, these three steps correspond to those of Fig. 4*b*.

The three arrows drawn in Fig. 12 correspond to any set of three steps in Fig. 1. In both cases we have hitherto avoided referring to the three steps as forming a cycle, though, if the two curves of Fig. 12 were drawn for the same temperature, they could be used for describing an isothermal cycle. Consider, for example, an ionic crystal at temperature T. The upper curve of Fig. 12 could be used for removing a pair of ions into a vacuum. Next plunge the separate ions into a solvent; and finally use the lower curve to replace the ions on the surface of the crystal. Conversely, the cycle could be carried out in the opposite direction. In either case the cycle will be equivalent to the three steps of Fig. 1*a*.

We shall, however, wish to make use of the lattice energies which are tabulated for ionic crystals at the absolute zero of temperature. Now the free energy of a crystal at room temperature has a value which is negative with respect to the free energy of the crystal at the absolute zero. For silver chloride, for example, the difference amounts to −0.175 electron-volts per ion pair, or −4020 cal/mole. If we are going to make use of the lattice energy at the absolute zero of temperature, the diagram of Fig. 12 must be replaced by one in which the minimum of one curve lies below the minimum of the other curve by the appropriate amount, as in Fig. 13. Here the lower curve corresponds to ions taken into a solvent from a crystal, both at room temperature, while the upper curve corresponds to ions taken from the same crystal at 0°K, and left at rest in a vacuum. Using Fig. 13, the cycle will now consist of four steps; in going round this cycle of four steps, the total change in the free energy will be zero.

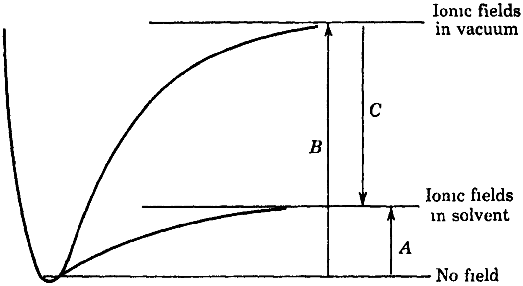


FIG. 12

14. The Solvation Energy of an Ion. The interaction that takes place when an ion is introduced into a solvent is called the *solvation* of the ion. In recent years the concept of solvation has gradually changed. Formerly, solvation was held to be the attachment of a large or small number of solvent molecules to an ion; and *heat of solvation* meant the heat evolved in the process of attachment. It is now felt that for most species one cannot properly distinguish between solvent molecules that are attached to an ion and those which remain unattached. It is much more useful to use the word *solvation* to denote the total interaction between an ion and a solvent.

It is the accepted practice to refer the lattice energy of a crystal to a state where the separated ions are at rest in a vacuum. It is convenient to use the same reference state when dealing with the same ions in a solvent. This has been done in Fig. 13; if the upper horizontal line refers to the state where two ions are at rest at distant points in a vacuum, the vertical arrow in Fig. 13 refers to the change in free energy when these ions are separately plunged into a solvent at temperature T. It will be very convenient to have a short name for the magnitude of this quantity. The expression "change in the free energy when ions initially at rest in a vacuum are introduced at distant points into a solvent at temperature T" is too long for general use. We shall therefore call the magnitude of this quantity the *solvation energy* of the ions. At the same time, the solvation energy for a pair of ions is the magnitude of the work required to remove the ions from the solvent and leave them at rest at distant points in a vacuum; the term here is analogous to the dissociation energy of a molecule, which is the work required to leave the separate ions at rest in a vacuum. During the process of plunging the ions into a solvent, or of removing them from a solvent, the ions are supposed to be remote from each other throughout. It must then be legitimate to speak separately of the solvation energy of a single positive or negative ion, even if this cannot be measured experimentally.

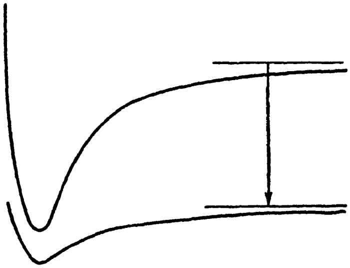


FIG. 13

Although Fig. 10 was drawn for a uni-univalent or di-divalent crystal, there is no reason why three or more ions should not be removed from the crystal along divergent lines, so that the ions are gradually separated from each other against their mutual attraction. In this way Fig. 11 can be constructed for uni-divalent or other types of crystal. In this case, when Fig. 13 is drawn the vertical arrow will represent the sum of the solvation energies of three or more ions.

In Sec. 2 it was pointed out that, when studying ions in a vacuum, we are mainly interested in the electronic structure of each species of ion; but in dilute solution the center of interest is largely shifted to the little region of solvent surrounding each ion—the region of solvent that we have called the co-sphere of the ion. From the beginning of Chapter 1 the whole discussion has been leading up to an inquiry into the state of affairs in the co-sphere of any species of ion. The solvation energy of any ion is, in fact, the magnitude of the change in free energy associated with the ion and its co-sphere.

In deriving (17) it was pointed out that we can expect to obtain a correct result only so long as (17) is used for a region in which the intensity X nowhere exceeds a certain limit. Equations (17) to (20) undoubtedly give correct results in the outer parts of the co-sphere of any ion, when the value of R has been taken sufficiently large. On the other hand, a calculation shows at once that in the central region, close to an atomic ion, the intensity X will be extremely high. Let us evaluate X at a distance of 2 angstroms from the center of a singly charged ion.

$$\frac{e}{r^2} = \frac{4.8 \times 10^{-10}}{(2 \times 10^{-8})^2} = 1.2 \times 10^{6} \text{ e.s.u.}$$

Now one electrostatic unit of potential is equal to 300 volts. We find then that the intensity of the field will amount to 360 million volts/cm; and when polar molecules are introduced into this field, we must expect the deviation depicted in Fig. 5.

There is an even more important aspect of the problem that we must next consider.

In Chapter 1 we drew attention to the fact that an ordinary weak electrostatic field produces only a small degree of alignment. Under these conditions, if we were to fix attention on any small group of molecules in the field, the total amount of free energy lost by them would be inconsiderable. The field in the neighborhood of an atomic ion has, as we have seen, a very high intensity, amounting to several million volts per centimeter. In such a field the free energy lost by even a small group of polar molecules will be considerable. We may say then that we obtain an appreciable loss of free energy, either (1) from the effect of a weak field on a large number of molecules, or (2) from the drastic effect of a strong field on a small group of molecules. We have summed up the situation in this way because, when we discuss an atomic ion in solution, both effects are present, and they are of about equal importance. The ionic field has a drastic effect on the few molecules that are in actual contact with the ion; and at the same time, it produces a low degree of alignment among the very large number of more distant molecules in its vicinity.

It is clear that the use of (18) would point toward the conclusion that, for an atomic ion in aqueous solution, the contributions from these two sources would be about equally large. In discussing a spherical field in a vacuum, it was pointed out in Sec. 4 that, if we consider any two spheres of radii such that $R_2 = 2R_1$, the amount of energy associated with the field in the region between the two spheres is equal to that associated with the whole of the region outside the larger sphere. This will be true likewise for a field in a dielectric to which (18) applies, since (18) differs from (6) only in the presence of ϵ in the denominator. If then we consider an atomic ion such as Cl^- (with radius a) in water, it is clear that a sphere of radius $2a$ will contain only those molecules which are actually in contact with the ion. We conclude then that these few molecules would make, according to (17), a contribution about as large as that from the whole of the rest of the solvent. This is the result that we should obtain if (16) were applicable to the region that contains the few molecules that are in immediate contact with the atomic ion. But of course it is not strictly applicable here. The occurrence of the macroscopic dielectric constant ϵ in (16) implies that we are discussing the over-all effect of a weak field on a large number of molecules. There is no physical basis for using (16) to predict the drastic effect of a strong field on a small number of molecules, though, as we shall find later, the predicted effect is of the right order of magnitude; the contribution from the few molecules in actual contact with an atomic ion is of the same order of magnitude as the total contribution from the whole of the rest of the solvent.

On referring to Chapter 1, it will be seen that, in discussing an ion of radius a in a vacuum, in (4) we integrated from a to infinity. On the other hand, when preparing to discuss the same ion in a solvent, we never inserted the ionic radius a but always considered the energy associated with the region outside some larger radius R. This was done deliberately because, if an atomic radius is inserted in equations (17) to (21), we cannot expect to obtain more than semiquantitative results. Nevertheless, a grasp of the significance of these expressions is extremely useful in understanding the state of affairs in the co-sphere of an ion. These equations provide a standard of comparison. When discussing the behavior of the solvent dipoles in an ionic field, we can put our question in the form: to what extent does the behavior of the dipoles in contact with the ion simulate the behavior of the more distant dipoles, to which the simple electrostatic theory is applicable? In later chapters we shall find that the degree of resemblance is very different for different species of ions. But in any case the above equations are useful as a starting point.

We should expect the solvation energy for a small ion to be greater than for a larger ion in the same solvent; for, when the ion is in a vacuum, the radius a occurs in the denominator of (4). When, therefore, the ions are plunged into a solvent, we expect that in the field of the smaller ion more free energy will be lost, simply because initially in the vacuum there is more energy to lose.

Consider also the numerical values obtained in (23) and (24) for a sphere in water at 25°C. These values will be correct when applied to the outer parts of an ionic co-sphere. If we next insert progressively smaller values of R, the numerical values will no longer be correct; but the whole argument as to the relative magnitudes of $T\,\Delta S$ and ΔF in the various processes will still be useful as a starting point. ·When, for example, inserting progressively smaller values of R, we reach a stage where the ΔH of the process (23) ceases to be equal to $1.017\Delta F$, it will still be true at this stage that the ΔH is of the same sign as ΔF and nearly equal in magnitude. Similarly, in the process (24), when we reach a stage where ΔH ceases to be equal to $-0.36\Delta F$, it will still be true, at this stage, that ΔH is of opposite sign to ΔF and considerably smaller in magnitude.

15. Work Done against Electrostatic Forces. In discussing Fig. 10 it was pointed out that, when the pair of ions is removed from the crystal surface, the positive and negative ions are, at the same time, separated against the electrostatic force of mutual attraction. By this process, or by that of Fig. 8*b*, we finally obtain a pair of solvated ions; and we may here examine the relation between the process of solvation and the strength of this Coulomb attraction. We shall again begin from the fact that, in a vacuum, any element of volume δv, where the field has the intensity X, contains an amount of energy $(X^2/8\pi)\,\delta v$.

Suppose now that this field X is due to the presence of two charges $+q$ and $-q$, separated by a distance r. These charges attract one another; that is to say, we have to do work if we wish to increase the separation to the value of $(r + \delta r)$. We shall say now that we have to do this amount of work, because the integral of $(X^2/8\pi)\,dv$, carried out over all space when the separation is $(r + \delta r)$, will yield a greater value than when the separation has the value r. In fact, the difference between these two integrals must be just $(q^2/r^2)\,\delta r$, the work that has to be done. We describe the process in this unfamiliar way, because we wish to add that, when the same two charges are in a dielectric, the molecules that happen to lie in any element of volume δv suffer a change in free energy when the separation of the ions is altered—a change appropriate to the local intensity X of the field; the total change of free energy in the dielectric is to be obtained by integrating over the whole volume of the dielectric. For two charges of opposite sign, whatever be the magnitude of these charges, or of their separation r, this total change in free energy in the dielectric is negative, when r is increased; owing to this loss of free energy, we have to do less work to separate the charges when they are in the dielectric than when they are in a vacuum; the force of mutual attraction between the charges is weaker. When the separation is increased isothermally from r to $(r + \delta r)$, the total loss of free energy by the dielectric can never be greater than $\left(\frac{q^2}{r^2}\right) \delta r$, but it will be very nearly as great in a solvent of high dielectric constant. For large values of r it is legitimate to make use of the macroscopic dielectric constant ϵ of the medium. In this case, when the separation of the charges is increased isothermally from r to $(r + \delta r)$ the loss of free energy by the dielectric amounts to

$$\frac{q^2}{r^2}\left(1 - \frac{1}{\epsilon}\right) \delta r$$

and consequently the work to increase the separation of the charges amounts to

$$\frac{q^2}{r^2}\,\delta r - \frac{q^2}{r^2}\left(1 - \frac{1}{\epsilon}\right) \delta r = \frac{q^2}{\epsilon r^2}\,\delta r \tag{25}$$

In water at room temperature, for example, the loss of free energy by the dielectric amounts to $\frac{79}{80}$ of the preceding term; hence the force of attraction between the charges has a value equal to only $\frac{1}{80}$ of the value in a vacuum.

At the same time, when we increase the separation of the charges from r to $(r + \delta r)$ isothermally, there is a change of entropy in the dielectric. For large values of r this amounts to

$$\delta S = -\frac{q^2}{r^2}\,\delta r\,\frac{d}{dT}\left(\frac{1}{\epsilon}\right) \tag{26}$$

Clearly the relation between (26) and (25) is precisely the same as the relation between (19) and (18). For charges in any solvent whose dielectric constant varies in accordance with (14), we shall have then from (26)

$$T\,\delta S = -\frac{T}{\vartheta}\,\frac{q^2}{\epsilon r^2}\,\delta r = -\frac{T}{\vartheta}\,\delta F \tag{27}$$

Thus in water at room temperature the work done in separating the charges against the forces of their mutual Coulomb attraction will be equal to 73 per cent of the quantity $-T\,\delta S$, since, in accordance with (24) the term $-T\,\delta S$ will be 1.36 times the increment in the free energy.

Now when we come to apply these considerations to ions that are not far apart, we can make remarks like those made at the end of Sec when (27) ceases to apply quantitatively, it will still, for a time, a qualitatively. When $T\ \delta S$ ceases to be equal to $-1.36\delta F$, it will sti of opposite sign to δF and greater in magnitude. We already have processes[1] to which this result can be applied in this form—namely separation of ions in the dissociation of a molecule, and secondly ir process of Fig. 10, where we separate two ions from each other v removing them from the surface of a crystal. When a contribution 1 short-range quantum-mechanical forces is present, the argument holds for the electrostatic forces, provided that δF denotes not the w work done, but the work done against the electrostatic forces.

From (25) we see clearly that, when a neutral molecule is broke into a pair of separate ions, the solvation of these ions is a gradual pro which becomes complete when the ions are far apart; only then doe solvation energy of each ion attain its full characteristic value at temperature considered.

The hydration or solvation of ions, on the one hand, and the Coul attraction between ions, on the other, are not usually regarded as ha any close connection with each other. Nevertheless, we have seen they are two aspects of the same phenomenon; and we may extenc discussion to include quantitatively their variation with tempera In the solvent at a higher temperature the dielectric constant wi smaller; the value of (17) will be smaller; and at the same time the c of Fig. 8*b* will be steeper. We have to do more work to increase separation of the charges from r to $(r + dr)$. This is because, at temperature, the solvent loses less free energy during the separation; finally, when the ions have been separated to a great distance from other and are fully solvated, less free energy has been lost by the sol —that is to say, the solvation energy arising from the partial alignr of solvent dipoles is smaller than it was at the lower temperature.

Figure 14 reproduces the two curves of Fig. 13, upon which we now make some further comments. The four quantities ΔF that n up the cycle are indicated in Fig. 14 by the four arrows a, b, c, d. From the form of the diagram it is obvious that, whatever qu ties these four arrows represent, it must be true in every case $(c + d) = (a + b)$. This must be so for any crystal dissolving in solvent at any temperature. Let us now recall what quantities denoted by the four arrows. Of these a is $\mathbf{L}_{vac}$, the work require split the crystal at 0°K into its component ions, while b represents free energy of the crystal at room temperature. Neither of these qu ties depends on the solvent into which the ions are going to be dissol

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[1] In Sec. 17 we shall introduce a third process, to which these remarks will app

Thus $(a + b)$ depends on the crystal only. On the other hand, the quantities represented by c and d in Fig. 14 depend on the solvent; for d is **L**, the work required to take a pair of ions from the surface of the crystal to distant points in the solvent, and c represents the sum of the solvation energies of these ions in the solvent at the given temperature.

Suppose now that we consider a crystal, such as KCl, that is to be dissolved in various solvents, all at the same temperature T. It is clear that the value of $(c + d)$ must be the same for the introduction of the ions $(K^+ + Cl^-)$ into each of these solvents, since $(c + d)$ in each case must be equal to $(a + b)$. In a solvent where c is smaller, d will be larger; that is to say, in a solvent where the solvation energies are smaller the value of **L** is necessarily larger *by an equal amount*, as indicated by the arrows d' and c' in Fig. 14.

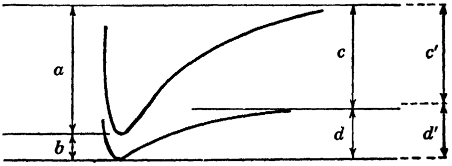

FIG 14

This agrees with, and illustrates, what was said above about the solvation of an ion being a gradual process. When ions are removed from a crystal by the process depicted in Fig. 10, the positive and negative ions are gradually separated from each other against their mutual attraction. The work that has to be done during this process depends upon the rate at which the solvent is losing free energy in the growing ionic field. Only when this process is complete will the amount of work done be equal to **L**, and only then will the ions have received their full solvation energy, with the result that $(c + d)$ for the ions in different solvents is equal to $(a + b)$.

16. Molecules and Molecular Ions Containing One or More Protons. The argon atom has 18 electrons moving round a nucleus with charge $+18e$. The hydrogen chloride molecule HCl likewise has 18 electrons moving round a total nuclear charge of $+18e$; within this electronic cloud, however, are two nuclei, the proton and the chlorine nucleus with a charge $+17e$. Consider an isolated HCl molecule in a vacuum. If the proton is removed, it leaves behind a negative ion Cl^-. A certain amount of work is required to remove the proton from HCl and leave both particles at rest in a vacuum. If the proton is put back into the Cl^- ion, to re-form an HCl molecule at rest in its state of lowest energy, an equal amount of energy is liberated. We can say that the negative Cl^- ion has a certain affinity for a proton, just as any neutral chlorine atom has an affinity for an additional electron. When we say that this electron affinity of the neutral chlorine atom is equal to 3.8 electron-volts, we refer to the difference between the energy of the normal quantized state of the negative ion and that of the neutral atom when the extra electron has been removed and left at rest in a vacuum. In the same way, the energy of a proton level in any molecule is determined by the quantization of the system. When we speak of the proton level in the HCl molecule, we are interested in the difference in energy between the lowest quantized state of the HCl molecule and the normal quantized state of the Cl^- ion, when the proton has been removed and left at rest in a vacuum; this difference is what we refer to when we speak of the energy of the proton level in the HCl molecule, or the energy of the vacant proton level in the Cl^- negative ion.

The neon atom has 10 electrons moving round a nucleus with a charge $+10e$ At the same time HF, H_2O, and NH_3 have 10 electrons moving round a total nuclear charge of $+10e$. Consider an isolated H_2O molecule in a vacuum. If we remove a proton from the H_2O molecule, we obtain the hydroxyl ion $(OH)^-$; the work to remove such a proton to a great distance has a certain value; in this way we assign a value to the energy of the proton level in the H_2O molecule. At the same time, the H_2O molecule has an affinity for an additional proton, to form the positive ion $(H_3O)^+$. This additional proton will be bound in a certain level, determined by the difference between the quantized energy of the $(H_3O)^+$ ion and that of the H_2O molecule.

In discussing the HCl molecule in a vacuum, we have spoken as if the Cl^- ion provides for a proton a single vibrational level. Actually the HCl molecule has, of course, a set of vibrational levels. At room temperature, however, only the lowest vibrational level is of interest. In molecules consisting of atoms of low atomic weight, the difference in energy between the lowest level and the next higher level is so great—the spacing of the levels is so wide—that at room temperature nearly all the molecules will be in the lowest vibrational level. This is especially true of molecules containing a proton, the lightest of all nuclei. In each molecule and molecular ion we shall be interested in the lowest vibrational level.

17. Proton Transfers. Now that we have examined the nature of proton levels, let us consider any two particles at rest in a vacuum, one of which contains a proton, while the other has a vacancy for a proton. Let the latter species be denoted by B, while the former species is denoted by AH. Let us examine the transfer of the proton from the molecule

AH to a distant B. This process, which may be written

$$\mathrm{AH} + \mathrm{B} \rightarrow \mathrm{A} \quad + (\mathrm{BH})^+$$

yields two ions, both at rest in the vacuum. The particle B, on receiving the proton, has become the positive ion $(\mathrm{BH})^+$, while the removal of the proton from AH has left behind a negative ion A^-. Near any point in the field of the positive ion the electrostatic energy has the density given by (2), and the same is true in the field of the distant negative ion. In transferring the proton to a distant particle, work must have been done in creating these two electrostatic fields.

Let the initial distance between the particles AH and B be denoted by r. The mutual potential energy of the two charged particles is $-e^2/r$, as in the simple ionic dissociation depicted in Fig. 8*a*. If the value of r is sufficiently great, the energy associated with the electrostatic fields will not depend appreciably on r. For the proton transfer there is thus a characteristic quantity similar to $\mathbf{D}_{vac}$.

Let us now suppose that the same two particles are situated in a certain solvent, the large distance between them being again r. When we make the transfer

$$\mathrm{AH} + \mathrm{B} \rightarrow \mathrm{A}^- + (\mathrm{BH})^+ \tag{28}$$

we set up two electrostatic fields as before; but the work required to set up these fields is much smaller, owing to the free energy lost during the process by the solvent molecules in the co-spheres of the two ions. The mutual potential energy of the ions is now $-e^2/\epsilon r$, as depicted in Fig. 8*b*; for very large values of r the curve does not differ appreciably from a straight line, and the work required to transfer the proton has a characteristic value [equal to the difference in energy between the proton levels of the particles in (28)]. Thus, corresponding to the quantities $\mathbf{D}_{vac}$ and $\mathbf{D}$, we shall use the symbols $\mathbf{J}_{vac}$ and $\mathbf{J}$, to denote the work required to transfer a proton, respectively, in a vacuum and in a solvent. The electrostatic part of $\mathbf{J}_{vac}$ in (28) is the work required to set up the ionic fields in a vacuum, when the two ions are remote from each other. The electrostatic part of $\mathbf{J}$ is the work required to set up the electrostatic fields of the two ions, when these are remote from each other in a solvent at temperature T.[1] At the same time the values of both $\mathbf{J}_{vac}$ and $\mathbf{J}$ will be partly determined by the relative binding energies of the proton in AH and $(\mathrm{BH})^+$. If these are gaseous particles in a vessel that contains only a few particles, it is clear that, when we speak of the quantity $\mathbf{J}_{vac}$, we have in mind a quantity that is independent of the volume of the

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[1] As mentioned in the footnote to Sec. 15, the discussion of equation (27) given there will apply to the electrostatic part of J.

vessel, and independent of the number of particles present in it. Similarly, if we imagine the proton transfer (28) carried out in a solvent that contains only a few solute particles, it is clear that, when we speak of the quantity **J**, we are speaking of a quantity that is independent of the volume of the solution, and independent of its composition.

18. The Quantities D, L, Y, and J. We notice a close resemblance between the quantities **D**, **L**, **Y**, and **J**. By the process (28) two ions are formed. In Chapter 1 we discussed three ways in which ions are added to a dilute solution; with these three we may now include the type (28) as a fourth process. To sum up, we may say that in a gas or vapor each of the quantities $\mathbf{D}_{vac}$, $\mathbf{L}_{vac}$, $\mathbf{Y}_{vac}$, and $\mathbf{J}_{vac}$ is independent of the size of the vessel, and independent of the number of particles in the vessel, provided that this number is small. Similarly, in very dilute solution, each of the quantities **D**, **L**, **Y**, and **J** is independent of the volume and the composition of the solution. In other processes in dilute solution that we shall discuss, we may find a unit of work, analogous to **D**, **L**, **Y**, and **J**; we may call each of these quantities the *characteristic unit* of the process, and denote it in general by **U**. In an isothermal process the work done is a change in the free energy. The *total* change in the free energy is not independent of the composition of the solution; on the contrary, it is strongly dependent on the concentration, even at very low concentrations. When ions are added to a solution, neither **D** nor **L** nor **Y** nor **J** is equal to the total change in the free energy; the latter includes a part which depends strongly on the concentration. This question will be discussed in detail in Chapter 5.

19. Two Spherical Conductors. In connection with such processes as (28), where a charge is transferred, it is of interest to discuss the following problem. In Fig. 15 let A and B be two spherical conductors immersed in the same polar dielectric. Initially, A, which has a larger radius than B, bears an electric charge; and we intend to transfer the whole of this charge to B, which is supposed to be at a great distance from A. When this charge has been transferred, the solvent dipoles near B will have lost a certain amount of free energy and a certain amount of entropy. Around B in Fig. 15 has been drawn a concentric (dotted) circle with radius equal to that of A; this circle is to represent a concentric sphere of the same size as the conductor A. Calling this A', we can say that the field outside the sphere A' is identical with that outside the distant conductor A, and that consequently the amount of entropy lost by the dipoles outside A' is exactly equal to the amount originally lost by the dipoles in the vicinity of A, when A bore the charge; we have then only to consider the dipoles that lie inside this concentric sphere. These dipoles have lost an *additional* amount of entropy.

Similarly, when we are discussing the *free energy* we can say that the amount lost by the dipoles outside A' is exactly equal to the amount originally lost by the dipoles in the vicinity of A, when A bore the charge. The dielectric lying inside A' will have lost an *additional* amount of free energy, when the charge has been transferred. It is rather easy to conclude that the transfer of the charge from A to B is accompanied by a net loss of free energy, and that, conversely, work must be done to transfer the charge from B to A. But this conclusion would, of course, be quite wrong. It is the transfer of charge from B to A that is accompanied by a loss of free energy.

Suppose, for example, that the conductor A initially bears a negative charge on its surface—that is to say, a certain number of electrons are distributed over its surface. When the whole of this charge has been transferred to the smaller sphere B, the same number of electrons are distributed over a small surface area; the average distance between the electrons is smaller than before; to bring them nearer together, work must have been done against their mutual repulsion. This process is, it is true, accompanied by a loss of free energy by the dielectric lying inside the sphere A'; but the magnitude of this loss is necessarily smaller. Hence, to transfer the charge isothermally from A to B a net amount of work is required; and the converse process is accompanied by a net loss of free energy.

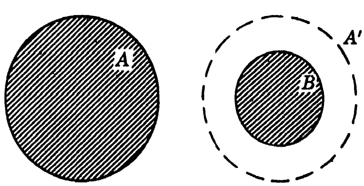

FIG. 15

Problems

1. Let the spherical conductors A and B of Fig. 15 have radii a and b; and let them be situated in a solvent whose dielectric constant obeys (14). The sphere A initially bears a charge q, while B is uncharged. Find expressions for the values of ΔF, ΔS, and ΔH for the isothermal transfer of the charge to the distant sphere B.

2. Two spherical conductors A and B both have a radius a; but A is situated in a solvent having a dielectric constant ϵ_1 while B is situated in a solvent of dielectric constant ϵ_2. Both ϵ_1 and ϵ_2 obey (14) with ϑ_1 and ϑ_2. The sphere A initially bears a charge q, while B is uncharged. Find expressions for ΔF, ΔS, and ΔH for the process of transferring the charge q from A to B.

3. Consider 1 mole of a completely dissociated uni-univalent solute in aqueous solution at extreme dilution at 25°C, each positive and each negative ion having a diameter equal to 3.0 angstroms. Find from (19), in calories per mole per degree, what *would* be the total amount of entropy lost by the solvent in the fields of all these ions, if (19) *could correctly be used* for a sphere as small as 3 angstroms.

CHAPTER 3

Complete and Incomplete Ionic Dissociation. Brownian Motion in Liquids. The Mechanism of Electrical Conduction. Electrolytic Conduction. The Structure of Ice and Water. The Mutual Potential Energy of Dipoles. Substitutional and Interstitial Solutions. Diffusion in Liquids.

20. Complete and Incomplete Ionic Dissociation. In the foregoing chapter mention has been made of electrolytes that are completely dissociated in solution, and of weak electrolytes where free ions are accompanied by a certain proportion of neutral molecules. In the nineteenth century it was thought that aqueous solutions of even the strongest electrolytes contained a small proportion of neutral molecules. Opinion as to the relation between strong and weak electrolytes has passed through certain vicissitudes; and we shall describe later how this problem has been resolved.

When an ionic solution contains neutral molecules, their presence may be inferred from the osmotic and thermodynamic properties of the solution. In addition there are two important effects that disclose the presence of neutral molecules: (1) in many cases the absorption spectrum for visible or ultraviolet light is different for a neutral molecule in solution and for the ions into which it dissociates; (2) historically, it has been mainly the electrical conductivity of solutions that has been studied to elucidate the relation between weak and strong electrolytes. For each ionic solution the conductivity problem may be stated as follows: in this solution is it true that at any moment every ion responds to the applied field as a free ion, or must we say that a certain fraction of the solute fails to respond to the field as free ions, either because it consists of neutral undissociated molecules, or for some other reason?

Two ideas introduced into physics have had a profound influence on the attitude adopted to this problem. Before 1920 it was recognized that a highly polar molecule in a vacuum, such as the NaCl molecule, may almost be regarded as a pair of ions held in contact by their mutual attraction. If this is true in a vacuum, we can ask what ought to be said about a Na^+ ion and a Cl^- ion that happen to be in contact with each other in an aqueous solution of NaCl?

Furthermore, about 1920 the idea had become prevalent that many common crystals, such as rock salt, consisted of positive and negative ions in contact. It then became natural to suppose that, when this crystal dissolves in a liquid, the positive and negative ions go into solution separately. Previously it had been thought that, in each case when the crystal of an electrolyte dissolves in a solvent, neutral molecules first go into solution, and then a certain large fraction of the molecules are dissociated into ions. This equilibrium was expressed by means of a dissociation constant. Nowadays it is taken for granted that nearly all the common salts in aqueous solution are completely dissociated into ions. In those rare cases where a solute is not completely dissociated into ions, an equilibrium is sometimes expressed by means of an *association constant;* that is to say, one may take as the starting point a completely dissociated electrolyte, and use this association constant to express the fact that a certain fraction of the ions are not free. This point of view leads directly to an emphasis on the existence of molecular ions in solution. When, for example, a solution contains Pb^{++} ions and Cl^- ions, association would lead directly to the formation of molecular ions, with the equilibrium

$$Pb^{++} + Cl^- \rightleftarrows (PbCl)^+ \tag{29}$$

Likewise for Fe^{+++}

$$Fe^{+++} + Cl^- \rightleftarrows (FeCl)^{++} \tag{30}$$

The conductivity of a solution containing such molecular ions may be small compared with the value that would result from complete dissociation into atomic ions. In this way, in the absence of neutral molecules, we can have a weak electrolyte. The association constant for (29) has a value that is, of course, the reciprocal of the dissociation constant for the molecular ion $(PbCl)^+$; the logarithms of the two equilibrium constants have the same numerical value, but opposite sign.

The discussion of molecules and molecular ions will be continued in Sec. 29. Here we shall begin the detailed examination of solutes that are completely dissociated into ions. The conductivity of aqueous solutions of such solutes has been accurately measured at concentrations as low as 0.00003 mole per liter. Even at these concentrations the motions of the positive and negative ions are not quite independent of each other. Owing to the electrostatic forces between the ions, the mobility of each ion is slightly less than it would be in a still more dilute solution. For example, an aqueous solution of KCl at 25°, at a concentration of 3.2576×10^{-5} mole per liter, was found to have an equivalent conductivity equal to 149.37 reciprocal ohms, whereas the extrapolation of a series of measurements to infinite dilution yielded the slightly higher value 149.86.[1]

This equivalent conductivity Λ for any solute is defined by

$$\Lambda = \frac{1000\kappa}{c} \tag{31}$$

where κ is the specific conductivity of the solution, and c is the concentration in equivalents per liter. The value of Λ that is obtained by extrapolation to infinite dilution is often denoted by Λ_0. The difference between Λ and Λ_0 mentioned for KCl is in agreement with the predictions of the Debye-Onsager theory; this theory does not attempt to say anything about the values of Λ_0 for different species of ions, but predicts how Λ will differ from Λ_0 in very dilute solutions. At infinite dilution Λ_0 is the sum of contributions, one characteristic of the cation, the other of the anion; in other words, the contribution of the cation is independent of the species of anion present, while that of the anion is independent of the species of cation present.

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \tag{32}$$

where λ_0^+ and λ_0^- are, respectively, the equivalent conductivities of the cation and anion at infinite dilution. Values of λ_0^+ and λ_0^- for aqueous solution at different temperatures are given in Table 2, while values for solutes in methyl and ethyl alcohol are given in Table 5 in Sec. 35.

21. Brownian Motion in Liquids. In all kinds of electrical conductivity at room temperature it is well recognized that the motion of the charges carrying the current is merely a drift superimposed on a random motion that is already present in the absence of a field. In a metal, for example, the free electrons are already executing a random motion; and, when a voltage is applied, a drift velocity is superimposed on this movement. In a dilute ionic solution each positive ion and each negative ion, in the absence of a field, executes a random movement among the solvent molecules; when a field is applied, the positive ions have a tendency to drift in one direction, while the negative ions tend to drift in the opposite direction. If we wish to compare different species of ions, and account for the observed mobility of each in an applied field, we first have to examine the nature of the random movement of any particle in a liquid.

Although the term "Brownian motion," as already mentioned in Chapter 1, was originally introduced to refer to the random motion of particles of visible size, there is no reason why we should not use the

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[1] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932); D. A. MacInnes, "Principles of Electrochemistry," Reinhold, 1939.

term for solute particles of molecular size, or even for the molecules of the solvent itself; for, of course, in any pure liquid the molecules are continually changing places; although at any moment a molecule may be completely enclosed by its neighbors, yet in course of time it will certainly describe a random path through the liquid. It is well recognized that the phenomenon of diffusion that is observed in pure liquids and gases is a direct consequence of the ordinary random motion of the particles. In a solution the diffusion of a solute involves the random motions of both solute and solvent particles.

Table 2. Equivalent Conductance in Aqueous Solution

	0°C	18°C[a]	25°C[b]
H^+		316.55	349.8
Li^+		33.28	38.69
Na^+		43.39	50.11
K^+	40.4	64.44	73.52
Rb^+		67.5	
Cs^+	44.4	67.65	78.1
Ag^+	32.9	53.77	61.92
Tl^+		65.7	74.7
NH_4^+			73.4
$(C_2H_5)_4N^+$		28.1	
OH^-		176.6	197.6
F^-		46.65	
Cl^-	41.3	65.41	76.34
Br^-	43.1	67.4	78.3
I^-	43.4	67.4	76.8
ClO_3^-		54.99	
BrO_3^-		47.9	
IO_3^-		34.02	
NO_3^-	40.4	61.74	71.44
ClO_4^-		58.4	68.0
MnO_4^-	31.0		61.7
$HCOO^-$		47.0	
CH_3COO^-		33.5	
Picrate		25.4	
$\frac{1}{2}Mg^{++}$			53.06
$\frac{1}{2}Ca^{++}$			59.50
$\frac{1}{2}Sr^{++}$			59.46
$\frac{1}{2}Ba^{++}$			63.64

[a] C. W. Davies, "Conductivity of Solutions," Chapman and Hall, 1930.

[b] H. S. Harned and B. B. Owen, "Electrochemistry of Solutions," Reinhold, 1950.

For electrically charged particles there are, in fact, three quantities that are intimately related—namely, the mobility in an electric field, the rate of diffusion in the absence of a field, and the character of their random (Brownian) motion. Einstein[1] established the quantitative relation between rate of diffusion and the character of the Brownian motion; and at the same time, for electrically charged particles, he derived the relation between the mobility u in an applied field and the Brownian motion, and hence the relation between the electrical mobility and the diffusion coefficient $\mathfrak{D}$. For a particle bearing a charge e this relation is

$$\frac{u}{\mathfrak{D}} = \frac{e}{kT}$$

where k is Boltzmann's constant and T the absolute temperature. This relation had been proposed by Nernst.

It has already been mentioned that in an aqueous solution of KCl at a concentration of 3.26×10^{-5} mole per liter, the equivalent conductivity was found to have a value, 149.37, that differed appreciably from the value obtained by the extrapolation of a series of measurements to infinite dilution. We may say that, even in this very dilute solution, each ion, in the absence of an electric field, does not execute a random motion that is independent of the presence of other ions; the random motion of any ion is somewhat influenced by the forces of attraction and repulsion of other ions that happen to be in its vicinity. At the same time, this distortion of the random motion affects not only the electrical conductivity but also the rate of diffusion of the solute, if this were measured in a solution of this concentration.

22. The Mechanism of Electrical Conduction. Let us first give some description of electrical conduction in terms of this random motion that must exist in the absence of an electric field. Since in electrolytic conduction the drift of ions of either sign is quite similar to the drift of electrons in metallic conduction, we may first briefly discuss the latter, where we have to deal with only one species of moving particle. Consider, for example, a metallic bar whose cross section is 1 cm², and along which a small steady uniform electric current is flowing, because of the presence of a weak electric field along the axis of the bar. Let the bar be vertical and in Fig. 16 let AB represent any plane perpendicular to the axis of the bar, that is to say, perpendicular to the direction of the current.

If we reduce the electric field to a value near zero, the current will fall to a negligible value. The situation will now be as follows: the number of electrons which, in their random motion, cross the plane AB in one direction does not differ appreciably from the number which cross the

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[1] A. Einstein, *Ann. Physik*, **19**, 371 (1906); J. Kirkwood, *J. Chem. Phys.*, **14**, 180 (1946).

plane AB in the opposite direction. If, however, we restore a weak electric field, this balance will be upset. The number which cross the plane AB downward from above will be either greater or less than the number which cross the plane AB upward from below in the same period of time. It is this *excess* which constitutes a flow of current.

If we say that, with a given applied field, in unit time this excess consists of N electrons, the current density will be Ne, since we are dealing with unit area. In Fig. 16 let us suppose that the excess flow of electrons is in the downward direction; we can then, to show the character of the flow, make the following construction. Parallel to the plane AB, consider a plane CD, also of unit area; and let the distance between CD and AB be chosen such that the total number of conduction electrons in the volume between CD and AB at any moment is N.

Then, fixing attention again on the number of electrons crossing the plane AB in 1 second, we can make the following statement: when the presence of the given electric field has upset the original balance, the density of the current crossing AB is the same as it would be if, in 1 second, all the electrons initially between CD and AB had crossed AB and no other electrons had crossed AB (in either direction). Actually, some electrons, in their random motion, will have crossed AB from below; besides, there is no reason why some electrons, initially above the plane CD, should not have crossed both the planes CD and AB in this period of time. All we have said is that the position of the plane CD has been chosen such that the number of electrons between CD and AB at any time is equal to the "excess" crossing AB, that is to say, equal to N.

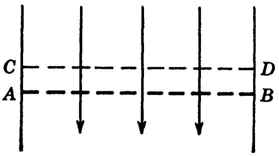

FIG. 16

In accordance with Ohm's law, if we were to double the intensity X of the electric field, the current would be doubled; that is to say, the plane CD would have to be placed at twice the distance from AB. If the number of conduction electrons per unit volume is ρ, and the distance between the planes CD and AB is denoted by v, we have $\text{N} = \rho v$, since we are discussing the unit area. Hence the net resultant charge transported in unit time across AB, that is, the current density, is given by

$$j = \text{N}e = \rho e v \tag{33}$$

As we have seen, Ohm's law requires that the distance v between the planes shall be proportional to the intensity X of the field; thus we may write $v = uX$, where u is the value which v will have when X is unity (unity in whatever units we decide to use, electrostatic units or volts per centimeter). Furthermore, the specific conductivity is given by

$$\kappa = \frac{j}{X} = \rho e u \tag{34}$$

If we were to forget that the flow of current is due to a random motion which was already present before the field was applied—if we were to disregard the random motion entirely and assume that each and every electron, in the uniform field X, moves with the *same* steady velocity, the distance traveled by each electron in unit time would be the distance v used in the construction of Fig. 16; this is the value which would lead to a current density j under these assumptions, since all electrons initially within a distance v of the plane AB on one side would cross AB in unit time, and no others would cross. Further, in a field of unit intensity, the uniform velocity ascribed to every electron would be the u of (34); this quantity is known as the "mobility of the charged particle." (If the mobility is given in centimeters per second, the value will depend on whether electrostatic units or volts per centimeter are used for expressing the field strength.)

23. Electrolytic Conduction. The same treatment is easily applied to ionic conduction, if the plane AB in Fig. 16 is taken to be a plane in an electrolytic conductor, similar to the electronic conductor discussed above. In the absence of a field the number of negative ions which cross AB in unit time in one direction will not differ appreciably from the number that cross AB in the reverse direction; and, treating the positive ions separately, we may make the same remark about the positive ions.

Let us now consider the situation when this balance has been upset by the presence of a weak electric field perpendicular to AB. The motion of the ions will no longer be completely random, but a tendency to drift will be superimposed on the random motion. If in unit time there has been an appreciable excess flow of negative ions across AB in one direction, we can be certain that there has been an appreciable excess flow of positive ions across AB in the opposite direction. These two separate contributions will together constitute the electric current.

Consider now the observed values of the equivalent conductivity for the various species of ions given in Table 2 [disregarding the ions $(OH)^-$ and H^+, which need special consideration]. If we ask, from this point of view, why such a wide variety of values is found, this must be ascribed to the wide variety in the character of the random motion executed by different species of ions in the absence of an electric field. We shall not go into the details of Einstein's theory of the Brownian motion; but the liveliness of the motion for any species of particle may be expressed by assigning a value to a certain parameter; for a charged particle in an electric field, the mobility of the particle will be proportional to this value, and so will the diffusion coefficient for the particle in the absence of a field. In Chapter 4 we shall examine the factors that influence the character of the random motion of ions. Here, in order to continue the discussion of (34), let us accept the fact that in any dilute solution we must expect that the random motion of the positive ions will be either more lively or less lively than the random motion of the negative ions. For simplicity consider the solution of a uni-univalent salt, in which the number of positive ions per unit volume is necessarily the same as the number of negative ions. When a weak electric field perpendicular to *AB* is applied, we must expect that the excess flow of positive ions across *AB* in one direction will be either greater or less than the excess flow of negative ions across *AB* in the opposite direction. This will necessarily be so if, in the absence of a field, the random motion of the positive ion is more lively or less lively than that of the negative ion. If the plane *CD* in Fig. 16 is taken for the negative ions, we shall need, for the positive ions, another plane on the opposite side of *AB*, such as *EF* in Fig. 17. In general, the distance between *EF* and *AB* will need to be different from the distance between *CD* and *AB*. If these distances are denoted by v_+ and v_-, respectively, the total current, according to (33), will be given by

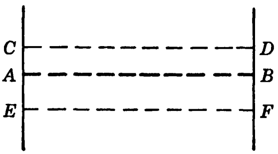

FIG. 17

$$j = \rho e(v_+ + v_-)$$

and the specific conductivity by

$$\kappa = \rho e(u_+ + u_-) \tag{35}$$

In (31) κ is related to Λ by the quantity $c/1000$, which is the number of moles per cubic centimeter. If $c/1000$ is multiplied by Avogadro's constant N, the product is equal to ρ. We may therefore write

$$\kappa = \frac{\rho\Lambda}{N} = \frac{\rho}{N}(\lambda^+ + \lambda^-) \tag{36}$$

Now Ne is equal to the faraday $\mathfrak{F}$. Comparing (36) with (35) we find

$$(u_+ + u_-) = \frac{(\lambda_+ + \lambda_-)}{Ne}$$

Hence, in view of the additivity of the conductivities,

$$u_+ = \frac{\lambda_+}{\mathfrak{F}} \qquad u_- = \frac{\lambda_-}{\mathfrak{F}} \tag{37}$$

Thus the actual mobility of an ion, in centimeters per second, is obtained by dividing the equivalent conductivity by the faraday. Some values of mobility are given in Table 3.

TABLE 3. DRIFT VELOCITIES OF IONS IN A FIELD OF 1 VOLT/CM; AQUEOUS SOLUTION AT 18°C

	Cm/Sec
Li^+	0 00034
Na^+	0.00045
K^+	0 00066
Cl^-	0 00067
NO_3^-	0 00064

Consider, for example, a dilute aqueous solution of KCl, in which a field of 1 millivolt/cm is maintained. From the mobilities given in Table 3 we calculate that, when, for example, $\frac{1}{25}$ second has elapsed, the average drift in either direction for the K^+ and the Cl^- ions will have been less than $(0.0007 \times 10^{-3})/25$ cm, that is to say, less than 3×10^{-8} cm (which is the diameter of one water molecule). Clearly, this distance is nothing but an *average* drift of the ions; for during the $\frac{1}{25}$ second, the ions in their (almost) random motion will, of course, have moved in all directions. As mentioned above, periods of molecular vibration usually lie between 10^{-12} and 10^{-13} sec; and in $\frac{1}{25}$ second each ion may have shifted its position many thousand times. Owing to the presence of the applied field the motion of the ions will not be quite random; as a result of their drift the solution will appear to carry a steady current.

In the remainder of this book, in discussing the mobility of any species of ion, we shall be concerned only with the characteristic value obtained by extrapolation to infinite dilution. In the following chapters we shall accordingly use the letter u to denote the mobility at infinite dilution.

24. The Structure of Ice and Water. It has not yet been necessary to consider in detail the properties of particular solvents. In Table 1 we gave a list of values for the dielectric constants of various solvents; but apart from this we have not yet paid attention to the observed properties of solvents or of the ions which are commonly dissolved in them. Before continuing the discussion which was in progress in Sec. 23, it will be useful to review in some detail the state of our knowledge of the liquids which are used as solvents, and of the species of ions which are most often studied in solution. Although non-aqueous solutions are of great interest for the sake of comparison, nevertheless aqueous solutions are still of paramount importance, and we shall pay most of our attention to H_2O and D_2O and to ions dissolved in these liquids.

Both the hydroxyl ion $(OH)^-$ and the water molecule H_2O contain the same number of electrons as a doubly charged oxygen negative ion $O^{=}$.

The hydroxyl ion may be regarded as an ion $O^{=}$ containing a proton embedded in the electronic cloud and neutralizing one of the negative charges. Similarly the H_2O molecule must be regarded as $O^{=}$ with two protons embedded within it.[1] The position ascribed to the two protons is shown in Fig. 18*a*; the angle between the lines joining the protons to the oxygen nulceus is about 105°, very nearly the tetrahedral angle. The structure of ice, described below, leads one to suppose that the H_2O molecule contains, in addition to the two protons, two negatively charged regions, the centers of the negative regions being such that the four charges (two positive and two negative) lie, as in Fig. 19, near the corners of a tetrahedron. Thus, in Fig. 18*a*, if the protons lie in the plane of the paper at the points *P*, *P*, the centers of the negative regions will lie, one above, and one below, the point *M*. If now the molecule were rotated through 90° about the axis *AB*, we should obtain Fig. 18*b*, where the two negative regions would be centered around the points *N*, *N* that lie in the plane of the paper, while the protons lie, one above, and one below the point *Q*.

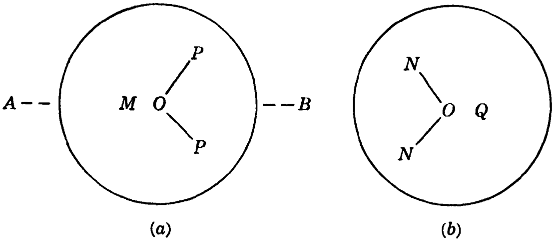

FIG. 18

Suppose now that we have a number of such tetrahedra, in each of which two corners bear positive charges, and the other two corners negative charges. Figure 19 shows how a structure can be built up, throughout which each positive corner is adjacent to the negative corner of a neighbor, each tetrahedron having four neighbors.

In ice each molecule has four neighbors, and the lattice is supposed to be held together by the electrostatic forces between adjacent charges in the manner just described. The resultant structure is shown in Fig. 20. If the centers of the lightly shaded molecules lie in the plane of the paper, the unshaded molecules lie above, and the heavily shaded molecules below the plane of the paper. It will be noticed that only two of the molecules are shown with their full complement of neighbors.

By measurements of X-ray scattering from a liquid, one can determine

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[1] The same idea must be extended to the NH_3 molecule and the $(H_3O)^+$ and $(NH_4)^+$ ions.

the number of nearest neighbors of a molecule, and the average distance apart; also the number of next-nearest neighbors and their average distance apart. Owing to the presence of partial disorder one does not expect the average number of nearest neighbors of a molecule in the liquid to be an integer. X-ray measurements on water[1] were made at five different temperatures, 1.5, 13, 30, 62, and 83°C. It was found that at 1.5° and at 13° the number of nearest neighbors was 4.4, rising to 4.6 at 30°C. The average distance apart (distance between centers) was found to be 2.9 angstroms, as compared with 2.76 angstroms in ice.

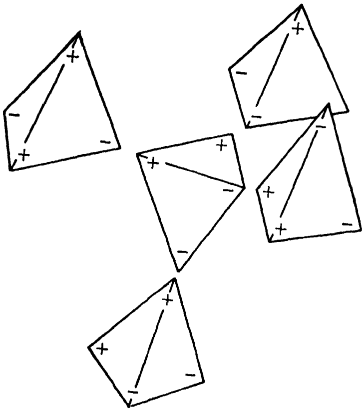

FIG. 19

In water at room temperature some molecules have more than four nearest neighbors, but at any moment the majority have four neighbors, as in ice. If the molecules tend to have a tetrahedral arrangement like that of ice, the average distance between next-nearest neighbors would be

$$2.76(\tfrac{8}{3})^{\frac{1}{2}} = 4.51 \text{ angstroms}$$

The X-ray measurements at 1.5, 13, and 30° do, in fact, show a large concentration of molecules at about 4.5 angstroms. This is strong evidence in favor of widespread local tetrahedral arrangement in water at room temperature and below.

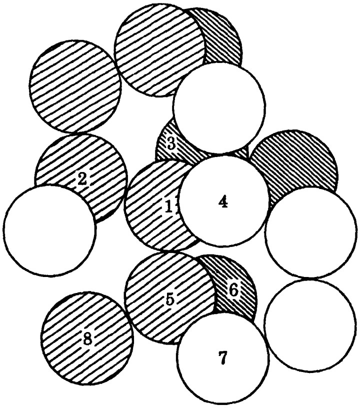

FIG. 20. The structure of ice Molecules numbered 8, 7, 6 are in contact with 5, while molecules 5, 4, 3, 2 are in contact with 1. Molecules 2, 3, 4 are among the next-nearest neighbors of 5, while molecules 6, 7, 8 are among the next-nearest neighbors of 1. [*Diagram taken from E. J. W. Verwey, Rec. trav. chim.* **60,** 893 (1941).]

Long-range order will, of course, be absent in the liquid. But any small volume of the liquid presumably contains many groups of molecules where a tetrahedral arrangement prevails.[2] The size of each such group

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[1] J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6,** 670 (1938).

[2] J. A. Pople, *Proc. Roy. Soc.*, **205A,** 163 (1951).

doubtless fluctuates all the time. The molecules that momentarily have more than four neighbors are doubtless molecules that lie momentarily in the interstices between such ordered groups. Consider, for example, the group of 16 molecules shown in Fig. 20; reference has already been made to the planes in which the centers of the molecules lie. In ice the pattern would be repeated throughout the lattice with the corresponding planes strictly parallel. In water the state of affairs in any region will be continually fluctuating. At any moment we may expect to find that the water consists largely of ordered groups of molecules, each similar to that of Fig. 20; but there is no reason why the molecular planes in one such group should bear any simple relation to the planes in an adjacent group. Suppose that we have two such adjacent groups, each with its own approximately tetrahedral structure, but the one group being tilted with respect to the other at any arbitrary angle; if we fill in the gap between the two groups with additional molecules, the position and orientation of any one of these molecules may be such that it momentarily belongs to one group or to the other or to neither.

In water we do not know what is the average size of these approximately regular groups; but we must suppose that the thermal agitation is continually breaking up the larger groups, while elsewhere, at the same time, molecules are falling into an ordered arrangement, so that a balance between order and disorder is maintained. We have seen that below room temperature the average number of nearest neighbors is 4.4. In the history of any one molecule we must suppose that the number of nearest neighbors often fluctuates between 4 and 5—or, more likely, between 4 and 6.

25. The Mutual Potential Energy of Dipoles. While the tetrahedral model of the H_2O molecule is suitable to account for the structure of ice and water, a simpler model is useful for certain purposes. The value of the dipole moment of a free H_2O molecule is given in Table 41. When a pair of equal and opposite charges are separated by a fixed distance l, they form an electrical dipole, whose moment is equal to the product of l with the magnitude of one of the charges. In treating the H_2O molecule as a dipole, we may think of an effective positive charge as situated at a point midway between the two protons, while an equal negative charge is situated on the opposite side of the molecule, beyond the oxygen nucleus. As we shall see, the magnitude of each charge is only a fraction of an electronic charge. In the accepted model of the H_2O molecule, depicted in Fig. 18*a*, the distance between each proton and the oxygen nucleus is about 0.9 angstrom. The length l of the H_2O dipole will therefore be rather more than 1 angstrom; and its dipole moment would be more than 4.8×10^{-18} e.s.u., if the magnitude of each charge were that of the electronic charge, 4.8×10^{-10} e.s.u. Since the dipole moment is observed to be only 1.8×10^{-18} e.s.u., we must conclude that the two protons combine to provide an effective positive charge of about one-third of an electronic charge, while an equal negative charge lies on the opposite half of the molecule. This simple model may be used to make a rough estimate of mutual potential energy of two molecules, when their centers are separated by a distance r.

For two permanent dipoles the mutual potential energy is a minimum when the axes of the dipoles lie along the line joining their centers, as shown in Fig. 21*b*. When their axes are perpendicular, as shown in Fig. 21*a*, their mutual potential energy is of course zero; to separate the dipoles, no work would be required. It is clear then that, when the dipoles lie as depicted in Fig. 21*b*, the work required to separate them will be equal to the work required to turn either of them though 90° in the plane of the paper, while the other remains fixed.

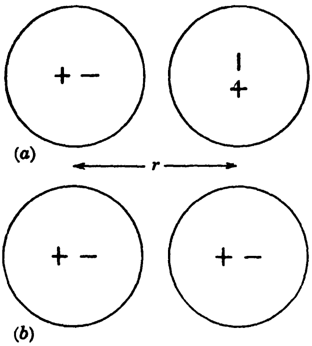

FIG. 21

When each of two small dipoles has a dipole moment μ, and the distance between their centers, r, is large compared with the length of either dipole, their mutual potential energy in the position of Fig. 21*b* is[1]

$$-\frac{2\mu^2}{r^3} \tag{38}$$

When r is not large compared with the length of either dipole the value will be somewhat greater. For two molecules in water we may substitute $r = 2.9 \times 10^{-8}$ centimeter, and for μ insert the value from Table 41. Since the observed heat of evaporation of water is in the neighborhood of 0.5 electron-volt, we expect to find a value of the order of 0.25 electron-volt, since we are discussing here a molecule that has only one neighbor. We obtain

$$\begin{aligned}\frac{2\mu^2}{r^3} &= \frac{2(1.8 \times 10^{-18})^2}{(2.9 \times 10^{-8})^3} \\ &= 0.24 \times 10^{-12} \text{ erg} \\ &= 0.15 \text{ electron-volt}\end{aligned}$$

Using a more detailed model for the H_2O molecule, Bernal and Fowler[2] obtained a value somewhat greater than this for the mutual electrostatic

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[1] See Note 2 of the Appendix.

[2] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

potential energy of two H_2O molecules in ice or water. At room temperature the value of kT is in the neighborhood of $\frac{1}{40}$ electron-volt; thus the value of kT is small compared with the work to turn a dipole through 90° or even through 45°. As a result, in water at room temperature each molecular dipole exercises some control on the orientation of adjacent molecules and is in turn controlled by its neighbors.

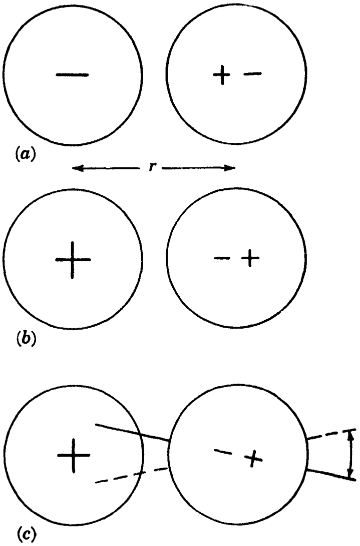

FIG. 22

Let us consider next the mutual electrostatic energy of an atomic ion and one water molecule in a vacuum. The interaction will have its greatest value when the two particles are in contact and when the axis of the dipole lies along the line joining them, as shown in Figs. 22*a* and 22*b*. When the length of the dipole is small compared with the distance apart, the electric potential energy is equal to

$$-\frac{e\mu}{r^2} \tag{39}$$

for a singly charged ion,[1] and twice this for a doubly charged ion. Some atomic ions are larger than a water molecule, while some are smaller. Let us estimate the mutual energy for an ion like K^+ whose radius is roughly equal to that of a water molecule, namely, 1.36 angstroms.

For a singly charged ion we find

$$\begin{aligned}-\frac{e\mu}{r^2} &= -\frac{4.8 \times 10^{-10} \times 1.8 \times 10^{-18}}{(2.72 \times 10^{-8})^2}\\ &= -1.1 \times 10^{-12} \text{ erg}\\ &= -0.7 \text{ electron-volt}\end{aligned}$$

This is the mutual electrostatic potential energy when the dipole lies as shown in Fig. 22. We see that the value is more than four times as large as the value obtained above for the mutual potential energy of two H_2O dipoles in their most favorable position.

We can likewise consider the amount of work required to turn the dipole through an angle about an axis perpendicular to the line passing through the center of the ion. The amount of work will clearly be

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[1] See Note 2 of the Appendix.

greater than that discussed above for the same dipole in the field of a similar dipole. When the dipole has sufficient energy, it will be able to execute angular oscillations in the field of the ion, similar to the familiar oscillations that a magnetic needle will execute in the earth's magnetic field. Such a motion is illustrated in Fig. 22*c*. When the amplitude of such an oscillation is small, the motion is often called "libration," owing to its similarity to the motion of the beam of a balance.

Similar angular oscillations can be executed by any dipole in the field of other adjacent dipoles. In both cases the kinetic energy associated with this angular oscillation corresponds to the kinetic energy of rotation that the free dipole molecule would have in a vacuum. Part of the thermal energy of ice and of water will be associated with such libration of the molecules in the fields provided by their neighbors. In water the motion will be highly irregular owing to the continual shifting of the relative position of adjacent molecules.

26. Substitutional and Interstitial Solutions. At temperatures near its freezing point the structure of water is often called *pseudo-crystalline.* This structure, as we have seen, is maintained by the strong forces between adjacent molecules By the application of high pressures it is possible to compress water at room temperature until it occupies only 80 per cent of its original volume.[1] In this process the molecules themselves are not compressed but are caused to take up a more compact arrangement. To reduce the volume to 80 per cent, pressures greater than 10^4 atmospheres are required. This enormous pressure is necessary because the molecules tenaciously resist any alteration in the relation between neighbors. It shows to what a slight degree the thermal agitation succeeds in breaking up the almost crystalline order.

Diagrams such as Fig. 20 depicting structure in three dimensions are difficult to interpret, as well as being laborious to draw. The compression of a liquid may, however, be illustrated schematically by means of diagrams depicting structure in two dimensions. Figure 23*a* shows 40 circles of the same size, which may be taken to represent the molecules of a liquid. In Fig. 23*b* the 40 circles have been crowded into an area about four-fifths as large. If we neglect the fact that three of the circles have been shaded, we may take Fig. 23*b* to represent the same liquid as Fig. 23*a*, when under an extremely high pressure. Consider now what will happen if this applied pressure is gradually reduced The intense forces between adjacent molecules will pull the molecules into the same kind of structure that they had originally. In this way we shall go back from Fig. 23*b* to Fig. 23*a*.

Our main purpose here is to ask what will happen if the compressed

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[1] "International Critical Tables," Vol. 3, p 40, McGraw-Hill, 1928.

liquid contains a few solute particles, whose size is nearly the same as the size of the solvent particles. It is for this purpose that in Fig. 23*b* three of the circles have been shaded. In the compressed liquid of Fig. 23*b* we have 37 solvent particles and 3 solute particles; and we wish to ask what will happen to the latter when the pressure is gradually removed. We shall have to take into account not only the intense forces between adjacent solvent molecules but also the strength and character of the forces of attraction between a solute particle and the solvent molecules that happen to be in contact with it. When these forces are weak, the solvent may be able to resume its original structure even in the immediate vicinity of each solute particle. When, however, these forces are very strong, the solvent near a solute particle will be able to resume its structure only insofar as this agrees with the requirements of the solute particle.

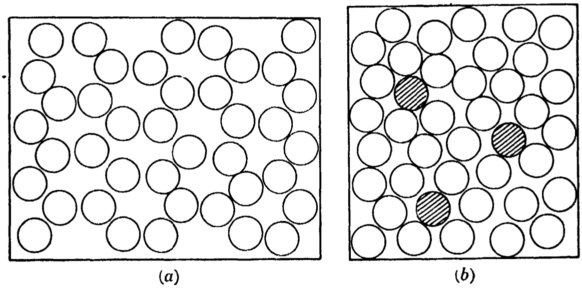
(*a*) (*b*)

Fig 23

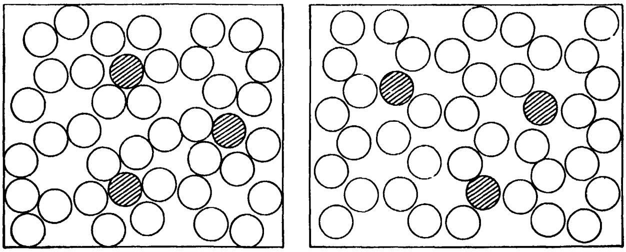
(*a*) (*b*)

Fig. 24

Figures 24*a* and 24*b* show two possibilities for the final state, when the pressure has been removed. If Fig. 24*a* is compared with Fig. 23*a*, it will be seen that the solvent has regained its original structure, in which each molecule has three molecules in contact with it (except of course at the edge of the diagram), while each of the solute particles has been pushed into a space between the solvent particles—that is to say, into an interstitial position. A solution where the solute particles occupy interstitial positions is called an "interstitial solution."[1]

On the other hand, if Fig. 24*b* is compared with Fig. 23*a*, it will be seen that here each solute particle occupies a position that in the pure solvent would be occupied by a solvent particle. Such a solution, which can be formed by one-for-one substitution, is called a "substitutional solution."[1] This kind of solution will not be formed if the forces of attraction between adjacent solute and solvent particles are weak, while the forces of attraction between adjacent solvent particles are strong. For, if we look at Fig. 24*b*, we see that each solute particle prevents three solvent particles from coming together under their mutual attraction—that is to say, it prevents them from falling to a state of much lower potential energy. We can be certain that, when neon or argon is dissolved in water, the solute particles will *not* tend to take up such positions, which are suitable only for a solute particle which attracts an adjacent solvent particle with a force at least as great as the force of attraction between two adjacent solvent particles.

In the case of a singly charged atomic ion in aqueous solution we have estimated the mutual potential energy between the ion and an adjacent water molecule when they are of nearly the same size, and have found the value to be about four times as great as the mutual potential energy of two adjacent water molecules. We conclude then that in the vicinity of an atomic ion the water structure will have to build itself round the ion, insofar as this is possible.

The theory of the structure of ice and water, proposed by Bernal and Fowler, has already been mentioned. They also discussed the solvation of atomic ions, comparing theoretical values of the heats of solvation with the observed values. As a result of these studies they came to the conclusion that at room temperature the situation of any alkali ion or any halide ion in water was very similar to that of a water molecule itself—namely, that the number of water molecules in contact with such an ion was usually four. At any rate the observed energies were consistent with this conclusion. This would mean that each atomic ion in solution occupies a position which, in pure water, would be occupied by a water molecule. In other words, each solute particle occupies a position normally occupied by a solvent particle; as already mentioned, a solution of this kind is said to be formed by the process of one-for-one substitution (see also Sec. 39).

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[1] R. W. Gurney, "Introduction to Statistical Mechanics," Chapter 7, McGraw-Hill, 1949.

27. Diffusion in Liquids. Suppose that we have two quantities of water, in one of which all the H_2O molecules contain the oxygen isotope O^{18}, and in the other of which they contain the usual isotope O^{16}; we know that, if we carefully place the two in contact, the molecules in each will, in course of time, slowly diffuse into the other; this will take place even at temperatures near the freezing point. Although, as noted, X-ray studies of water show the presence of a high degree of local order, we must suppose that each molecule, in course of time, describes a random motion through the liquid. In describing a liquid, the problem is to reconcile the random motion with the presence of a high degree of local order. Although a molecule may often belong to an ordered group, like that depicted in Fig. 20, nevertheless in course of time, it will describe a random path through the liquid.

Let us fix attention on a particular H_2O molecule A in the interior of water (if we wish to identify this molecule we can suppose that it contains a nucleus of the oxygen isotope O^{18}); and let us consider the water molecules which happen to be nearest neighbors of this molecule at the moment. These molecules have been in contact with A for different lengths of time. Since all the molecules in the liquid wander about, there was a time when none of these molecules was in contact with A. Further, if we could now begin to watch these molecules, we should find that, after the lapse of different periods of time, they become separated from A and each is replaced by another molecule. Similar remarks can be made about the molecules which come into contact with any chosen molecule. We can now raise the question—What is the rate of turnover of this process? The rate depends on the degree of local order and disorder, which in turn depends on the strength and character of the forces between adjacent molecules.

To make this problem precise, consider two molecules which at any time cease to be nearest neighbors. Let us denote by τ the length of time during which they have been in "contact"—that is, during which they have been nearest neighbors to each other. If we consider all the molecules in a definite amount of liquid at temperature T during a certain period of time, we can denote by $n(\tau)\ \delta\tau$ the total number of occasions on which two neighbors separate after a period of continuous contact lying between τ and $(\tau + \delta\tau)$. Or, more conveniently, if we consider any two molecules which at a certain moment become nearest neighbors, we can denote by $p(\tau)\ d\tau$ the probability that the time elapsing before they separate again will have a value lying between τ and $(\tau + d\tau)$.

If we compare different liquids at temperature T, there will be a characteristic function $p(\tau)$ for each liquid. With rise of temperature, as the Brownian motion becomes more lively, $p(\tau)$ will doubtless change in such a way as to favor shorter periods of contact. At any temperature T there will be a mean value of τ; the probability that two molecules remain in contact for a period many times longer than this mean value will be small. If we suppose that, for any two molecules that are nearest neighbors, the act of separation is brought about by the operation of random events, the problem is similar to some encountered in the kinetic theory of gases (where the probability that a molecule will travel a distance l, long compared with the mean free path λ, without making a collision, is proportional to $e^{-l/\lambda}$). If any two adjacent molecules in the liquid happen to have already been in contact for a period greater than the average, this fact neither diminishes nor augments the probability of their separating; thus for large values of τ, at any rate, $p(\tau)$ will be of the form

$$p(\tau) = Ae^{-\tau/\tau_0} \tag{40}$$

where τ_0 is a parameter characteristic of the liquid at this temperature.

Something quantitative is known about the time scale of $p(\tau)$ in the case of molten metals, which are rather simple liquids. From the rate of self-diffusion of radioactive Pb atoms in molten lead, for example, it has been possible to estimate the length of time during which any two atoms of the liquid are likely to be nearest neighbors. And, further, it was shown by Andrade that this value can be successfully correlated with the viscosity of the liquid metal.[1] In the course of its Brownian motion a particle of the liquid takes on the average a certain time to move a distance equal to its own diameter. It is, of course, possible that, while so moving, a particle and *all* of its z neighbors will remain in contact—that is, it is possible that occasionally a group of $(z + 1)$ or more particles moves a short distance en bloc. But in the random motion of the molecules in the liquid as a whole this is likely to be an unusual occurrence; when a particle of the liquid, in its Brownian motion, has moved a distance equal to its own diameter, at least one of its nearest neighbors is likely to have been changed—this neighbor is likely to have been replaced by another molecule.

From the rate of diffusion of radioactive Pb in molten lead, Andrade estimated that it takes an atom about 2×10^{-11} second to move a distance equal to its own diameter.[1] If the period of atomic vibration is 5×10^{-13} second, this time is equivalent to about 40 atomic vibrations. From the considerations brought forward by Andrade, it appears that the same estimates would apply to liquid mercury above its melting point—that is, near room temperature. When we ask how often the particles of such a liquid change neighbors, it is clear that the rate of turnover is extremely large. If, for example, in (37) we set τ_0 equal to 10^{-10} second, the chance that two particles remain in contact for as long as 7×10^{-10} second is less than one in a thousand.

It was mentioned in Sec. 24 that in water at room temperature the average number of nearest neighbors for any H_2O molecule is about 4.5, indicating that the number continually fluctuates between 4 and 5, or between 4 and 6. Whenever the number of neighbors of a particular molecule falls from 5 to 4, presumably any one of the five neighbors may

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[1] E. N. da C. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

be the one to leave. As the rate of turnover is great, it is improbable that two molecules spend a long time in contact with each other. If it is unlikely that they spend 10^{-7} second in contact, it will be still less likely that they spend 10^{-6} second, and still more unlikely that they spend 10^{-5} second in contact before separating. A satisfactory theory of liquid structure would tell us the form of $p(\tau)$ and would enable us to treat such problems as the diffusion of one isotope through another.

Problem

Using the method given in Note 2 of the Appendix, obtain an expression for the mutual potential energy of the two dipoles shown in Fig. 21

CHAPTER 4

The Contact between Solvent and Solute Particles Molecules and Molecular Ions in Solution. Incomplete Dissociation into Free Ions. Proton Transfers in Solution. Stokes's Law. The Variation of Electrical Conductivity with Temperature. Correlation between Mobility and Its Temperature Coefficient. Electrical Conductivity in Non-aqueous Solvents. Electrical Conduction by Proton Jumps. Mobility of Ions in D_2O.

28. The Contact between Solvent and Solute Particles. Although something has been said about the electrical conductivity of aqueous solutions, a large part of the foregoing chapter was devoted to the solvent itself. We may next apply the method of Sec. 27 to the random motion of a solute particle. Suppose that in water we have *one* solute particle, whose size is roughly the same as the size of an H_2O molecule. Let us pay attention to the water molecules that from time to time come into contact with this solute particle. We can obviously give to this problem a treatment similar to that given to contact between the solvent molecules themselves. Any water molecule that comes into contact with this solute particle will spend a time τ before separating and resuming an independent random movement. After a long time has elapsed, $n(\tau)\ \delta\tau$ may be used to denote the number of occasions on which duration of contact with this solute particle has had a value lying between τ and $(\tau + \delta\tau)$. In this way we can set up a function $p(\tau)$ such that the quantity $p(\tau)\ \delta\tau$ gives the probability that, when contact is made, its duration will have a value lying between τ and $(\tau + \delta\tau)$. For each species of solute particle in water at room temperature the function $p(\tau)$ will have a form characteristic of the species, favoring relatively short or relatively long periods of contact.

In Sec. 25 we examined the force of attraction between an atomic ion and a solvent dipole, and compared it with the attraction between two solvent dipoles. If we discuss water molecules in contact with the potassium ion K^+, for example, we may expect to find that the function

$p(\tau)$ favors longer periods of contact than occur between two H_2O molecules in pure water. Furthermore, a small ion allows in (39) a closer approach than a larger ion. If then we consider water molecules in contact with Na^+ in aqueous solution, we may expect to find that $p(\tau)$ favors longer duration of contact than in the case of K^+, Rb^+, or Cs^+.

To represent $p(\tau)$ in accordance with (40), two exponential curves have been drawn in Fig. 25, one favoring longer periods of contact than the other. These curves may be taken to refer to the same ion in a solvent at two different temperatures, or to refer to two different species of ions at the same temperature. The curves must intersect, for the following reason. The duration of a contact must certainly have *some* value; in other words the total probability is unity. Now when a curve in Fig. 25 is completed, the total area under the curve represents the probability that τ has *some* value. In every case, then, the curve must be drawn so that the total area under the curve is equal to unity. A satisfactory theory would tell us how these curves should be drawn for various species of ions. In Sec. 32 we shall again examine the factors that influence the mobility of ions.

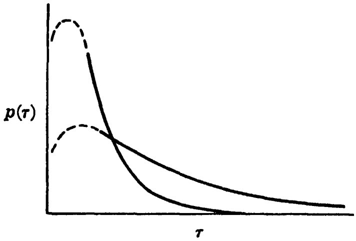

FIG 25

29. Molecules and Molecular Ions in Solution. When two alkali atoms are brought together in a vacuum, the quantum-mechanical forces of attraction between them,[1] which give rise to the diatomic molecules Li_2, Na_2, and K_2, are similar to those between two hydrogen atoms, which give rise to H_2. Now the two valence electrons of the calcium atom are two 4*s* electrons; and the singly charged calcium ion Ca^+ has one 4*s* electron, like the potassium atom. Thus, when two Ca^+ ions are brought together in a vacuum, there will be the same quantum-mechanical forces of attraction. Owing, however, to the fact that the calcium nucleus bears a greater positive charge than that of the potassium atom, the electrostatic repulsion between the nuclei prevents the formation of a stable $(Ca_2)^{++}$ ion in a vacuum.

If we had any means of reducing the electrostatic repulsion without, at the same time, affecting the quantum-mechanical attraction, we should have the possibility of forming such doubly charged molecular ions. Now a polar solvent has just the required properties; the alignment of the solvent dipoles greatly reduces the electrostatic repulsion, but the quantum-mechanical forces of attraction arise from the rapid motion of

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[1] R. W Gurney, "Elementary Quantum Mechanics," Chapter 6, Cambridge, 1934.

electrons, which is so rapid that the dipoles do not respond at all to them. The valence electrons of the mercury atom are two 6*s* electrons, and the mercury ion Hg^+ has one 6*s* electron, like the atom of gold. In aqueous solution the electrostatic repulsion between the two nuclei is greatly reduced, while the quantum-mechanical attraction is scarcely affected, with the result[1] that the well-known stable $(Hg_2)^{++}$ ion is formed [although no stable $(Ca_2)^{++}$ ion seems to exist].

In Chapter 2 the curve of Fig. 7 was introduced, to show the mutual potential energy arising from short-range forces in contrast to that arising from long-range electrostatic forces. To account for the existence of molecules and molecular ions in solution, we need the same curve with the scale of ordinates reduced so as to be comparable with those of Fig. 8*b* rather than with those of Fig. 8*a*. Such a curve is reproduced in Fig. 26*a* and again in Fig. 27*a*. But in Fig. 26*b* we have the mirror image of the curve of Fig. 8*b*, to represent the electrostatic repulsion between two ions of like sign in solution. The resultant curve obtained by adding the ordinates of Figs. 26*a* and 26*b* is shown in Fig. 26*c*. The potential energy of the $(Hg_2)^{++}$ ion, when plotted against the distance between the two Hg nuclei, must have this form.

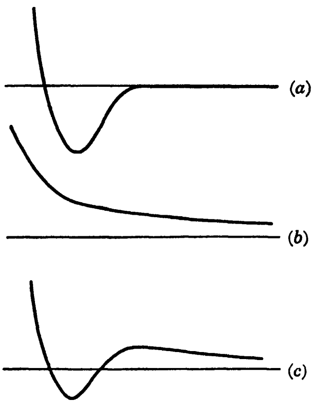

FIG 26

The negative ions O^-, S^-, Se^-, and Te^- have, respectively, the same number of electrons and the same electronic configuration as the halogen atoms F, Cl, Br, and I. When we bring together two Te^- ions in a vacuum, or in a solution, we have the same quantum-mechanical forces of attraction as between two iodine atoms. In a vacuum, however, no stable $(Te_2)^=$ ions will be formed owing to the intense electrostatic repulsion. But as long ago as 1923 it was discovered[2] that the tellurium negative ions in aqueous solution exist in the form $(Te_2)^=$. In this molecular ion the potential energy plotted against the distance between the two nuclei must again follow a curve like that depicted in Fig. 26*c*.

We discussed the function $p(\tau)$ for the duration of contact between two solvent molecules in Sec. 27, and in Sec. 28 for the contact between a solvent molecule and an ion. We can now extend the same ideas to the duration of contact between two ions in a dilute solution. Consider,

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[1] R. W. Gurney, *J Chem. Phys.*, **6**, 499 (1938).

[2] Karsanowsky, *Z. anorg. Chem.*, **128**, 17 (1923).

for example, an aqueous solution of calcium chloride at room temperature. In their random motions a Ca^{++} ion and a Cl^- ion may come into contact with each other. A time τ will elapse before they lose contact, and each resumes its separate random motion. A function $p(\tau)$ will describe the probability that the duration of such a contact will have a value τ. Since the solute $CaCl_2$ is regarded as completely dissociated into ions in aqueous solution at room temperature, $p(\tau)$ will doubtless favor very short periods of contact.

Consider next a similar solution of $PbCl_2$. The radius ascribed to the ion Pb^{++} is only a little larger than that of Ca^{++}. The question arises whether the form of the function $p(\tau)$ for contact between Pb^{++} and Cl^- will be similar to that for contact between Ca^{++} and Cl^- in the same solvent. It has been mentioned in Sec. 20 that in aqueous solution $PbCl_2$ has an abnormally low conductivity. This has been ascribed to the association of Pb^{++} and Cl^- ions to form molecular ions of the form $(PbCl)^+$. We are led to inquire whether we can draw a clear distinction between such a molecular ion, on the one hand, and a pair of ions that happen to remain in contact for a time τ.

We can make a precise statement on this question, basing our distinction on the contrast between long-range and short-range forces of attraction. Between the ions Ca^{++} and Cl^- the only short-range forces will be forces of repulsion when their electronic shells come into contact; for both the ions Ca^{++} and Cl^- contain the same number of electrons as a neutral argon atom, and the electronic structure is similar to that of argon; there will therefore be no quantum-mechanical forces of attraction between Ca^{++} and Cl^-. On the other hand, the Pb^{++} ion does not have a rare-gas structure. The low conductivity of $PbCl_2$ in aqueous solution doubtless arises from the fact that short-range quantum-mechanical forces of attraction between Pb^{++} and Cl^- are superimposed on the usual long-range electrostatic forces.

In the above case we obtained a molecular ion $(PbCl)^+$ because we started with a pair of ions whose charges differed in magnitude. If, instead, we consider a pair of singly charged ions of opposite sign, or a pair of doubly charged ions of opposite sign, we may obtain a neutral molecule in solution. And we may use the same concepts in order to draw a clear distinction between a genuine neutral molecule, and a pair of ions which happen to remain in contact for a time τ.

As an example we may mention an aqueous solution of thallous chloride, $TlCl$. The radius ascribed to the ion Tl^+ is a little larger than that of K^+, and about equal to that of the rubidium ion Rb^+. The electrical conductivity of a dilute solution of $TlCl$ is not very different from that of KCl or $RbCl$, but its variation with the concentration of $TlCl$ is abnormal. With increase of concentration the conductivity falls below the expected values. We notice that, whereas the ions Rb^+ and K^+ have the same electronic structure as krypton and argon, the ion Tl^+ does not have a rare-gas structure, and there is the possibility of short-range forces of attraction.

The curve of Fig. 27*a*, which is the same as that of Fig. 26*a*, has already been referred to above. In Fig. 27*b* we have a curve for the long-range electrostatic forces of attraction between two ions of unlike sign in solution. When both short-range and long-ranges forces of attraction are present, we have to add the ordinates. The resultant curve, obtained by adding the ordinates, is shown in Fig. 27*c*. It will be seen that the short-range forces give rise to a narrow pocket at the end of the electrostatic curve, the additional depth of this pocket being the depth of the potential minimum in Fig. 27*a*. For each solute that is completely ionized in aqueous solution we must suppose that this potential pocket is absent or else is so shallow that it has no appreciable effect.

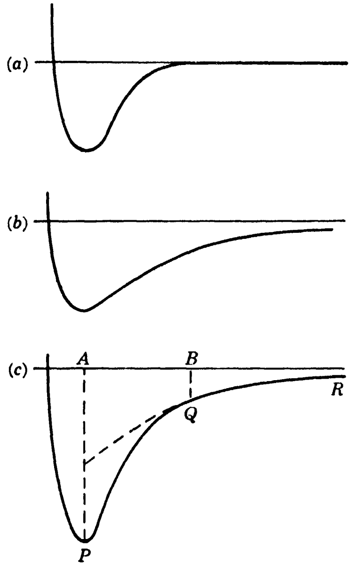

FIG. 27

We see that we can attach a definite physical meaning both to the existence of a neutral molecule in solution, and to the dissociation of this molecule into a pair of ions. Consider points near *P* and near *Q* in Fig. 27*c*. A point on the curve near *P* corresponds to the situation where the distance between the nuclei of the two ions has, say, the value *OA*, while a point on the curve near *Q* corresponds to the separation *OB*. If the separation of the nuclei is increased from *OA* to *OB*, a considerable amount of work is done against the short-range forces of attraction, in order to go from *P* to *Q*. But at *Q* the short-range forces are no longer operative; and the neutral molecule has been dissociated into a pair of ions, between which there is the usual electrostatic attraction.

A diagram similar to Fig. 27*c* enables us to attach a definite physical meaning to the dissociation of a molecular ion, such as $(PbCl)^+$ into a pair of atomic ions.

Returning to the point *Q* in Fig. 27*c*, it is evident that, if we wish further to increase the separation of the two ions, an additional amount of work is required, in order to go from Q to R in the diagram. The magnitude of this electrostatic work will depend on whether we are dealing with singly charged or doubly charged ions and will depend on the solvent in which the ions are dissolved. Since these electrostatic forces are operative for all species of ions, whether short-range forces are present or not, we may at this point return to an examination of the wide question raised in Sec. 20 as to the relation between strong and weak electrolytes in different solvents.

30. Incomplete Dissociation into Free Ions. As is well known, there are many substances which behave as a strong electrolyte when dissolved in one solvent, but as a weak electrolyte when dissolved in another solvent. In any solvent the Debye-Hückel-Onsager theory predicts how the ions of a solute should behave in an applied electric field, if the solute is completely dissociated into free ions. When we wish to survey the electrical conductivity of those solutes which (in certain solvents) behave as weak electrolytes, we have to ask, in each case, the question posed in Sec. 20: in this solution is it true that, at any moment, every ion responds to the applied electric field in the way predicted by the Debye-Hückel theory, or does a certain fraction of the solute fail to respond to the field in this way? In cases where it is true that, at any moment, a certain fraction of the solute fails to contribute to the conductivity, we have to ask the further question: is this failure due to the presence of short-range forces of attraction, or can it be due merely to the presence of strong electrostatic forces?

Even in a very dilute solution containing uncharged solute particles we may expect to find a few pairs of solute particles in contact or near contact. In an ionic solution, if we first pay attention to ions bearing charges of the same sign, we are, if anything, likely to find *fewer* pairs in such situations. Turning next to ions of opposite sign, the question is whether we shall find an appreciably larger number of pairs in contact or near contact than in a solution of uncharged particles at the same concentration. The answer to this question must be put in terms of the energy of thermal agitation. We can say definitely that if, in a certain dilute solution, we find many such close pairs, it is due to the fact that the energy of thermal agitation at the temperature considered is insufficient to ensure that these ions execute independent random motion. We can add that if, in the absence of a field, these pairs of oppositely charged ions are unable to execute independent Brownian motion, then when an external field is applied, they will not contribute to the electric current. To see that this is true, we have only to examine the energies involved. If the random motion of the two ions is not independent, this is because the magnitude of their mutual potential energy is larger than, or at least comparable with kT, which at room temperature is $\frac{1}{40}$ electron-volt. The question is whether an applied field will be able to break up the pair. If the field applied to the solution is as great as 1 volt/cm, the work required to take an electronic charge through a distance of 10^{-7} cm is only 10^{-7} electron-volt. We see that the energy available from the field is nearly a million times too small.

In 1926 the idea was put forward by Bjerrum[1] that, when discussing the solute particles of a weak electrolyte, we do not have to choose between free ions and neutral molecules but that there is a kind of intermediate state. To this third state Bjerrum gave the name *associated ion pair*. An associated ion pair is a pair of oppositely charged ions caught in each other's field, in the manner described above; one or more solvent molecules may separate the two ions, between which only the usual long-range electrostatic forces are operative. A solute will behave as a completely dissociated electrolyte only provided that associated ion pairs are not formed; in addition, short-range forces of attraction like those in $(PbCl)^+$ must be absent. The problem then is to decide under what conditions associated ion pairs will be present. In the solution of a uni-univalent or of a di-divalent substance an associated ion pair will be electrically neutral and in important respects will behave like a neutral molecule: (1) it will not contribute to the electric current, and (2) there will be a dissociative equilibrium in the solution between the free ions and the neutral ion pairs; this equilibrium can be described by means of a dissociation constant just as for neutral molecules.

A criterion for the presence of associated ion pairs was suggested by Bjerrum. This at first appeared to be somewhat arbitrary. An investigation by Fuoss,[2] however, threw light on the details of the problem and set up a criterion that was the same as that suggested by Bjerrum. According to this criterion, atomic ions and small molecular ions will not behave as strong electrolytes in any solvent that has a dielectric constant less than about 40. Furthermore, di-divalent solutes will not behave as strong electrolytes even in aqueous solution.[3] Both these predictions are borne out by the experimental data.

31. Proton Transfers in Solution. We must turn now to another aspect of the problem—the familiar fact that the most important weak electrolytes are those involving proton transfers, namely, the familiar weak acids and weak bases. In aqueous solution, as is well known, the salts of weak acids (if di-divalent and di-trivalent salts are excluded)

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[1] N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

[2] R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

[3] See, for example, B. B. Owen and R. W. Curry, *J. Am. Chem. Soc.*, **60**, 3077 (1938).

behave as strong electrolytes, while the acids themselves are weak electrolytes. In a solution of sodium acetate, for example, if we bring together a cation and an anion, bringing the Na^+ ion into contact with that part of the $(CH_3COO)^-$ ion that bears the negative charge, the maximum amount of potential energy has been lost, and now the forces of mutual repulsion between the electronic shells come into play. Consider next an aqueous solution of acetic acid, in which we bring together an $(H_3O)^+$ and an anion, until their electronic shells come into contact. The situation here is different in one respect, since a further step is possible: one of the protons in the $(H_3O)^+$ ion may be transferred to the interior of the anion. If the proton remains in the vacant level of this anion, this leaves a neutral acetic acid molecule surrounded by neutral water molecules. In this last step the electrostatic field surrounding the ions has disappeared, and the energy associated with this field has been dissipated; in fact, the amount of electrostatic energy lost in this last step is comparable with the amount lost in the previous process of bringing the two ions together. At the same time, there is the binding of the proton in the anion to be taken into account. For each species of anion the binding energy has a characteristic value.

In the same way, in an aqueous solution of HCl we can consider an $(H_3O)^+$ ion brought into contact with a Cl^- ion, and we can imagine one of the protons taken from the $(H_3O)^+$ and introduced into the electronic cloud of the Cl^- ion. This leaves a neutral HCl molecule surrounded by neutral water molecules. If we wished to transfer the proton back to any adjacent water molecule, we should have to supply the energy necessary to recreate the electrostatic field that has disappeared in this last step. Nevertheless, this last step will be reversed spontaneously. The vacant level offered to the proton by an adjacent water molecule is so much lower than the lowest level that can be occupied by a proton in the HCl molecule that the proton will quickly fall out of the latter into one of the adjacent water molecules. Evidently the energy released in this process is more than sufficient to recreate the electrostatic field appropriate to the two ions in contact. As a result, the strongest acids appear to be completely dissociated, not only at the lowest concentrations, but also in moderately dilute solutions. On the other hand, when the molecule of a weak acid is in water, we have the converse situation. The vacant proton level provided by an adjacent H_2O molecule lies higher than the level occupied by the proton in the acid molecule. In order to transfer a proton to a distant water molecule, work has to be done first against short-range forces, and then against the long-range electrostatic forces; compare Fig. 27*c*. In Sec. 29 it was pointed out that the quantum-mechanical forces arise from the motion of electrons that is so rapid that the molecular dipoles cannot respond; the forces are therefore nearly independent of the environment and are relatively insensitive to temperature, in contrast to the electrostatic forces. It is because the quantum-mechanical forces are independent of temperature that, as was stated in Sec. 15, when a contribution from quantum-mechanical forces is present, the change in entropy involves only the electrostatic contribution, which is sensitive to temperature, and the discussion of equation (27) applies to the electrostatic contribution separately.

32. Stokes's Law. In the simplest problem of laminar flow one considers the velocity gradient in a fluid near a plane wall, assuming that the fluid in contact with the wall adheres to it and, if the wall is moving, moves with it without slip. In the problem associated with the name of Stokes the boundary is a spherical surface, such as would be provided by a rigid spherical body that is pulled through the fluid with uniform velocity; in this case it is assumed that the fluid in contact with the spherical wall adheres to it and moves with it without slip. A discussion of the velocity gradients near the sphere leads to an expression for the viscous drag in terms of the known viscosity of the fluid. For a sphere of radius a the force K that is required to maintain a terminal velocity v is given by

$$K = 6\pi\eta av\left(1 + \frac{3}{8}\rho\frac{av}{\eta}\right)$$

where η is the viscosity and ρ the density of the fluid. When the second term in parentheses is small compared with unity, this reduces to

$$K = 6\pi\eta av \tag{41}$$

the solution that was given in 1845 by Stokes. In treating the problem in terms of viscosity, one is assuming that the radius a of the sphere is large compared with the inhomogeneities of the medium; that is to say, large compared with a molecular diameter in the case of motion through a liquid, and large compared with the mean free path in the case of motion through a gas.

Let us consider more closely what is meant when we say that the liquid moves with the sphere without slip. The thinnest film that can adhere to the sphere is a monomolecular film. If the radius of a molecule is a_m, the thickness of a monomolecular film will be $2a_m$. When a rigid sphere of radius a is moving through the liquid with velocity v, and a monomolecular film is moving with it without slip, the result is that a rigid sphere of radius $(a + 2a_m)$ is moving through the liquid with velocity v. When a is very large compared with $2a_m$, this is not important. On the other hand, when a and a_m are of the same order of magnitude—when, for example, a itself is not greater than $4a_m$, there is clearly a discrepancy of at least 50 per cent between the radius of the original sphere and that of the sphere with its monomolecular film. Stokes's law is not intended to apply to such a case, and we must not expect to obtain quantitative results by inserting the radius a into (41).

Returning to a sphere of large radius, we may add that, when it is moving with velocity v, its motion is opposed by the viscous drag (41), whatever the reason for its motion with velocity v. The motion may be due entirely to thermal agitation, as in the case of the diffusion of particles whose density is the same as that of the liquid. Or the motion may be partly due to thermal agitation and partly to an external field, as in the case of a small particle falling under gravity; or, in the case of a particle bearing an electric charge, the motion may be influenced by the presence of an electric field. In each case the viscous drag acting on the sphere has the same value, (41). Thus, for a sphere whose radius is large compared with the inhomogeneities of the medium, (41) may be used in three problems: (1) Brownian motion, (2) diffusion, and (3) mobility in an electric field.

In the nineteenth century a liquid was thought to be like a gas. In a gas a molecule makes a collision, travels freely, makes another collision, again travels freely, and so on. It was thought that a liquid should be described in the same way—only with much shorter free paths. In a solution each solute particle would make frequent collisions with solvent molecules. But in an aqueous solution containing atomic ions the question was asked: between collisions is the atomic ion traveling alone, or does it travel with water molecules attached to it? Electrochemists unanimously came to the conclusion that to each species of atomic ion several water molecules were attached, to form a hydrate; when they spoke of the mobility of the ion, they meant the mobility of this large rigid hydrated ion.

The internal structure of a liquid at a temperature near its freezing point has been discussed in Sec. 24. Each molecule vibrates in a little cage or cell, whose boundaries are provided by the adjacent molecules, as in Fig. 20, and likewise for each solute particle in solution in a solvent near its freezing point. It is clear that the question of the hydration of ions no longer arises in its original form. In aqueous solution an atomic ion will never be in contact with less than three or four water molecules, which in turn will be in contact with other water molecules, and so on. There is an electrostatic attraction, not only between the ion and the molecular dipoles in immediate contact with it, but also between the ion and molecular dipoles that are not in contact with it. For solvent dipoles that are in contact with a small doubly charged ion, such as Ca^{++}, the function $p(\tau)$ may favor rather long periods of attachment. But for singly charged ions it is especially difficult to attach much meaning to the idea of a rigid hydrated ion with a spherical boundary.

Since the term "hydration" refers to aqueous solutions only, the word "solvation" was introduced as a general term for the process of forming a solvate in solution. The terms "solvation" and "heat of solvation" were introduced at a time when little or nothing was known about polar molecules. We know now that, when an atomic ion is present in a solvent, the molecular dipoles are subject to the ionic field, whose intensity falls off in $1/r^2$. We cannot draw a sphere round the ion and say that molecules within this sphere react with the ion to form a solvated ion, while molecules outside do not. The only useful meaning that can now be attached to the term solvation is the *total* interaction between ion and solvent. As already mentioned, this is the sense in which the term is used in this book.

In various contexts the idea of water molecules firmly attached to ions has been so prevalent that surprise was sometimes expressed when evidence to the contrary was found; for example, "We thought it probable that in alcoholic solutions containing a little water and a lot of LiCl most of the water would be firmly attached and its activity reduced almost to zero. This, however, is not the case. The activity of water in the solution containing 0.17 moles of water per thousand grams is only reduced to 25% of its original value by 4 m LiCl."[1]

33. The Variation of Electrical Conductivity with Temperature. In making a wide survey of the various properties of ions in solution, we continually meet three types of problems: (1) comparing different species of ions in the same solvent; (2) dealing with the same species of ions in different solvents; and (3) dealing with ions in the same solvent at different temperatures. We may mention here a fact that will be met again in later chapters—that a simple theory is sometimes more successful in dealing with the third type of problem than with the other two. Whether we are discussing mobilities or some other property, a simple theory may predict fairly well the rate at which this property varies with temperature, even when the same theory is of little use in discussing aspects (1) and (2); that is to say, we can sometimes predict a temperature coefficient within a few per cent of the observed value, even when the relative values predicted for ions of different sizes, or for ions in different solvents, are nowhere near the truth.

The application of Stokes's law to mobilities is a case in point. In Sec. 35 we shall show that, if we compare mobilities of ions in methanol, ethanol, and water, a crude application of Stokes's law yields values that do not even lie in the right order. Nevertheless, when we discuss ionic

[1] R. Shaw and J. A. V Butler, *Proc. Roy. Soc.*, **129A**, 533 (1930).

mobilities in aqueous solution as a function of temperature, the results are quite interesting; the observed temperature coefficients are fairly close to the values expected from theory; and furthermore, where for certain species a deviation is found, a simple interpretation of the discrepancy seems to yield useful information about the environment of the ion.

With rise of temperature any solvent becomes less viscous. For visible particles the Brownian motion is observed to become more lively; and in the same way we should expect a solute particle to execute a more lively random motion. As a result, the mobility of each species of ion should increase with rise of temperature.

Since the expression (41) is deduced for a sphere whose radius is large compared with the molecules of the liquid, it is not known to what extent the behavior of atomic and small molecular ions should be in accordance with (41). It is clear that, if (41) were applicable, the value of the mobility should vary inversely with the viscosity. If for any ion the K on the left-hand side of (41) is set equal to the constant force acting on the ion in a field of unit intensity, the v on the right-hand side of (41) becomes equal to the mobility u. Since K is independent of temperature the product of u and η should be independent of temperature. From Table 42 it will be seen that at 25°C the viscosity of water is almost exactly half the viscosity at 0°C; thus, according to (41) the mobility u of each ion should be double.

In general, if at any two temperatures T_1 and T_2 the viscosity of a solvent has the values η_1 and η_2, and the mobility of an ion has the values u_1 and u_2, the quantity $u_2\eta_2/u_1\eta_1$ would be equal to unity for any ion whose behavior is in accordance with (41). Taking T_2 to denote a temperature greater than T_1, if we write

$$C_1^2 = \frac{u_2\eta_2}{u_1\eta_1} \tag{42}$$

C_1^2 will serve as a measure of the mean temperature coefficient of the mobility over the range between T_1 and T_2; the value of C_1^2 will be greater or less than unity according as the temperature coefficient of the mobility is unusually great or small.

Shortly after the formulation of the Debye-Hückel theory, a survey of the data on ionic mobilities from this point of view was made, extrapolating the values to infinite dilution.[1] Table 4 gives values of C_1^2 for atomic and molecular ions for T_1 = 0°C and T_2 = 18°C.

34. Correlation between Mobility and Its Temperature Coefficient. For most species of ions in Table 4 it will be seen that the value of C_0^{18} is appreciably less than unity; with rise of temperature the mobility increases

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[1] P. Walden and H. Ulich, *Z. physik. Chem.*, **106**, 89 (1923).

somewhat less rapidly than is expected from (41). The values given at the bottom of the table for the tetraethyl-ammonium positive ion and the picrate negative ion—both very large ions—are near unity, as expected from (42) for large particles. In Fig. 28 values of C_0^{18} are plotted for each ion against the equivalent conductivity at 18°C. Unlike

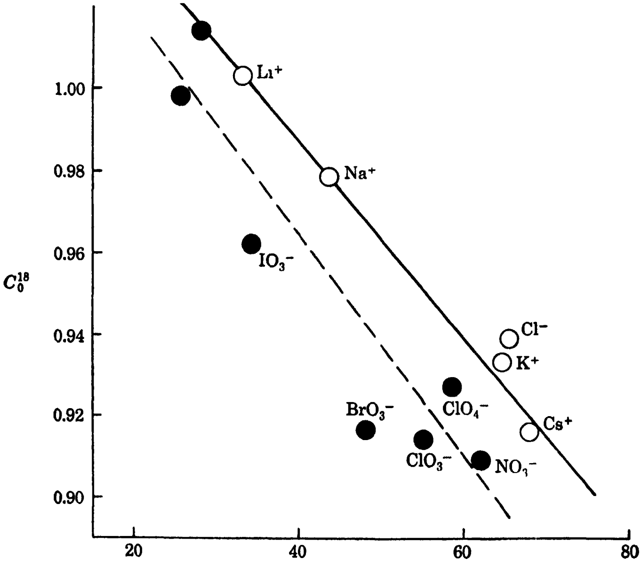

FIG. 28. Values of C_0^{18} from Table 4 plotted against the equivalent conductivity at 18°C.

most properties of solutes, which are known only for ion pairs, the quantities plotted in Fig. 28 are known for positive and negative ions separately.

TABLE 4. TEMPERATURE VARIATION OF IONIC MOBILITIES

	C_0^{18}		C_0^{18}
Li^+	1.00$_3$	NO_3^-	0.90$_9$
Na^+	0.97$_8$	ClO_3^-	0.91$_4$
K^+	0.93$_3$	BrO_3^-	0.91$_6$
Cs^+	0.91$_6$	IO_3^-	0.96$_2$
Cl^-	0.93$_9$	ClO_4^-	0.92$_7$
		$(C_2H_5)_4N^+$	1.01$_4$
		$C_6H_2(NO_2)_3O^-$	0.99$_8$

It will be seen that ions which have an unusually high mobility have, at the same time, an abnormally low temperature coefficient for the mobility. The points in the diagram make a definite pattern, the values for the atomic ions lying near to a straight line, while the points for molecular ions lie about a nearly parallel line. We may ask next whether there is any reason to expect that ions of exceptionally high mobility will have an abnormally small temperature coefficient.

Consider first how the properties of pure water vary with temperature. With rise of temperature the degree of short-range order progressively decreases, and this is reflected in the rapid decrease in the viscosity of the water. Suppose now that, in the co-sphere of an ion, at room temperature or below, there is (for some reason) a local loosening of the water structure; this will have two effects: (1) in its Brownian motion the ion will have a greater freedom of movement than it otherwise would have; its random motion will be more lively, and consequently, in an electric field, it will have a greater mobility; (2) we may suppose that, with rise of temperature, the freedom of movement of the ion will be less affected than it otherwise would be. In the water there is only a certain amount of order to be lost; and if, in the co-sphere of the ion a certain amount of this order has been lost already at a low temperature, there will remain less order to be progressively lost as the temperature rises; see Sec. 85. We may expect then that, although as the temperature rises, the random motion will become somewhat more lively, and the mobility will indeed increase, nevertheless the increment in the mobility for this species of ion will be less than normal. In this way we could account for the fact that the ions that have the highest mobilities in Fig. 28 have at the same time the smallest temperature coefficients. In Chapter 9 we shall find that there is strong independent evidence that the above line of argument is correct.

35. Electrical Conductivity in Non-aqueous Solvents. Let us now discuss the random motion of an atomic ion dissolved in methanol or ethanol. It will be seen from Table 41 that the value of the dipole moment on the OH group of these molecules differs little from that of the

TABLE 5. EQUIVALENT CONDUCTIVITIES IN METHANOL AND ETHANOL AT 25°C[a]

	Methanol	Ethanol		Methanol	Ethanol
H^+	142.2	59.5	Cl^-	51.3	24.3
Li^+	39.7	14.9	Br^-	55.5	25.8
Na^+	45.7	18.7	I^-	61.0	27.9
K^+	53.7	22.0	NO_3^-	60.8	27.9
Rb^+	57.4	23.6	CH_3O^-	51.8	....
Cs^+	57.4	23.6	$C_2H_5O^-$		23.3
Ag^+	50.3	17.5			
NH_4^+	57.9	19.2			

[a] M. Barak and H. Hartley, *Z. physik. Chem.*, **165**, 290 (1933)

H_2O molecule. Now (39) gives the magnitude of the mutual electrostatic energy of such a dipole and an ion separated by a distance r. When the OH group of a methanol or ethanol molecule is in contact with an atomic ion the value of r to be inserted in (39) presumably is roughly the same as when a water molecule is in contact with the same ion. This would lead us to expect that the force of attraction between an ion and an adjacent solvent molecule would be similar in the three liquids.

Turning now to the Brownian motion of the ion, we must ask to what extent adjacent solvent molecules will tend to accompany the ion in its random motion, as a result of the mutual attraction. It appears that the strength of this mutual attraction will be similar in the three solvents. But we notice that the size of the solvent molecules that tend to accompany the ion is considerably larger in methanol than in water and will be still larger in ethanol. This fact must be taken into account, if we attempt to predict the relative mobilities of the ion in the three solvents.

The values of the viscosities of the three liquids are given in column 4 of Table 6. It will be seen that the viscosity of ethanol is twice that of methanol, while the viscosity of water has a value lying intermediate between these. Values for the limiting conductance of NaCl are given in column 5; the value in aqueous solution is larger than in either of the alcohols, and the same is true of other solutes. In the past these results have been regarded as puzzling, since from Stokes's law a naïve application of (41) would lead us to expect that the value in aqueous solution should lie intermediate between those in methanol and ethanol, since the viscosity of water lies intermediate between the viscosities of the other liquids. From what has been said above, however, it is clear that, although every ionic mobility is influenced by the viscosity of the solvent, the value of the viscosity of the pure liquid is not a reliable guide when we want to know the degree to which a solvent molecule in contact with an

TABLE 6. ELECTRICAL CONDUCTIVITY IN VARIOUS SOLVENTS

Ion pair	Solvent	Temp., °C	Viscosity, η	Limiting conductance, Λ	$\eta\Lambda$
NaCl	Water	25	0.008949	126.45	1.132
	Methanol	25	0.00545	96.9	0.528
	Ethanol	25	0.0109	42.5	0.463
KCl.	Water	25		149.89	1.342
	Methanol	25		105.0	0.568
	Liquid NH_3	−34	0.002558	348.1[a]	0.891

[a] V. F. Hnizda and C. A. Kraus, *J. Am. Chem. Soc.*, **71**, 1565 (1949).

ion tends to accompany this ion in its random motion, and the degree to which this diminishes the mobility of the ion.

36. Electrical Conduction by Proton Jumps. As mentioned in Sec. 24, a hydroxyl ion may be regarded as a doubly charged oxygen ion $O^{=}$, containing a proton inside the electronic cloud of the ion, which has the same number of electrons as a fluoride ion. The radius of the hydroxyl ion cannot be very different from that of the fluoride ion. But it will be seen from Table 2 that the mobility of the hydroxyl ion is about four times as great. This arises from the fact that a large part of the mobility is undoubtedly due to proton transfers.[1] Consider a water molecule in contact with a hydroxyl ion. If a proton jumps from the molecule to the ion,

$$H_2O + (OH)^- \rightarrow (OH)^- + H_2O$$

the result is the same as if the molecule and the ion had changed places. Figure 29*a* is intended to depict two H_2O molecules and a hydroxyl ion, the latter containing only one proton. Figure 29*b* shows the resulting situation, if a proton has jumped as indicated by the arrow in Fig. 29*a*. The next event may be either that the same proton jumps back again or that another proton jumps, as indicated by the arrow in Fig. 29*b*. In the absence of a field we must suppose that for each hydroxyl ion such proton transfers take place many times a second, so that the effective random motion of the ion due to this effect is more important than the actual Brownian motion of the ion itself in the intervals between proton jumps. When a field is applied these proton jumps will still take place in all directions, but owing to the presence of a mechanism that will be described below, the number of proton jumps having a component parallel to the field will be slightly greater than the number having a component antiparallel to the field.

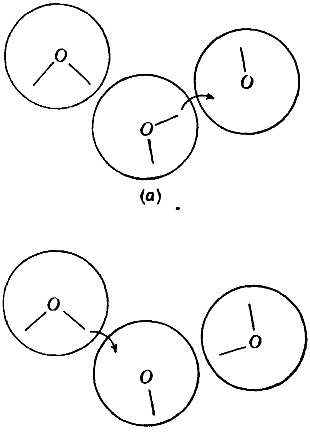

FIG. 29

As will be seen from Table 2, the mobility of the hydrogen ion is even greater than that of $(OH)^-$. This high mobility is ascribed to successive proton jumps of the kind

$$(H_3O)^+ + H_2O \rightarrow H_2O + (H_3O)^+$$

Conductivity due to similar proton jumps is present in other solvents. Consider a bisulfate ion dissolved in sulfuric acid. The relation between

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[1] E. Hückel, *Z. Elektrochem.* **34,** 546 (1928).

the $(HSO_4)^-$ ion and the H_2SO_4 is the same as between $(OH)^-$ and H_2O; the $(HSO_4)^-$ ion is a solvent molecule from which a proton has been removed. A series of solutions containing different bisulfates dissolved in sulfuric acid were found to have almost identical conductivities.[1] This fact was not explained until the transport numbers of the positive and negative ions were measured. In barium bisulfate, for example, it was found that more than 99 per cent of the current was being carried by the negative ions.[2] The difference between one species of positive ion and another could not make itself apparent when in each case the positive ions were carrying less than 1 per cent of the current.

The viscosity of pure H_2SO_4 at 25°C is 27.6 times greater than that of water; consequently the normal migration of ions is extremely slow. The comparatively high mobility of the $(HSO_4)^-$ ion undoubtedly arises from successive proton transfers to the ion from an adjacent solvent molecule:[2]

$$H_2SO_4 + (HSO_4)^- \rightarrow (HSO_4)^- + H_2SO_4$$

Owing to the enormous viscosity of the solvent, the result of these proton transfers is more striking than in other liquids.

It was pointed out in Sec. 24 that the HOH molecule may be regarded as an oxygen ion in which two protons are embedded. In the same way the OH group in an alcohol molecule may be regarded as an O^- ion containing a proton. The positive charge associated with the embedded proton, together with an equal negative charge, gives to the OH group a dipole moment; and it has been suggested[3] that in a liquid alcohol some dipoles become linked to form chains, as depicted in Fig. 30, where *O*, *O* denotes the positions of the oxygen nuclei, and *P*, *P* the positions of the protons.

When a strong acid, such as HCl, is dissolved in methanol, the proton is doubtless transferred to a CH_3OH molecule, to form a $(CH_3OH_2)^+$ ion, analogous to the $(H_3O)^+$ ion in water. It will be seen that the value given in Table 5 for the mobility of the hydrogen ion in methanol is much greater than for the other ions, indicating that proton transfers take place readily in this solvent, though the effect on the relative mobilities is not so large as in water.

When a strong acid is dissolved in ethanol the $(C_2H_5OH_2)^+$ ion is likewise formed; and it will be seen from Table 5 that the mobility of the hydrogen ion again indicates some contribution from proton jumps, though the effect is smaller than in methanol.

Returning to aqueous solutions, in view of the fact that the CH_3OH

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[1] A. Hantzch, *Z. physik. Chem.*, **61**, 257 (1907).

[2] L. P. Hammett and F. A. Lowenheim, *J. Am. Chem. Soc.*, **56**, 2620 (1934)

[3] G. Oster and J. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

molecule and the C_2H_5OH molecule have a vacancy for an additional proton, it is of interest to consider the addition of a trace of methyl or ethyl alcohol to the dilute aqueous solution of a weak acid and to ask whether there is any effect which can be attributed to the capture of protons from the $(H_3O)^+$ ions; or, alternatively, whether the addition of a trace of water to the dilute solution of an acid in either alcohol will have an effect that can be attributed to the capture of protons by H_2O molecules, to form $(H_3O)^+$. Various phenomena show that the second effect is present, but not the first. A trace of water added to a dilute solution of HCl in ethyl alcohol causes a marked drop in the electrical conductivity, which is ascribed to the partial suppression of proton jumps resulting from the capture of protons from the $(C_2H_5OH_2)^+$ ions, thus:

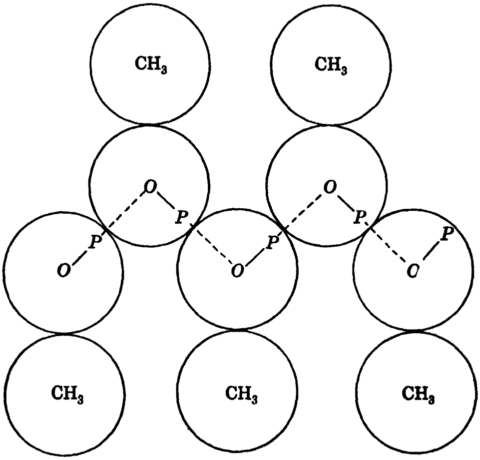

FIG. 30. Possible arrangement of molecules in liquid methanol.

$$(C_2H_5OH_2)^+ + H_2O \rightarrow C_2H_5OH + (H_3O)^+ \tag{43}$$

Since a small trace of water suffices to produce a large effect, the equilibrium of (43) evidently lies far in favor of the right-hand side (see also Sec. 115), indicating that a water molecule dissolved in ethyl alcohol provides a vacant level for an additional proton that lies lower than the level occupied by the protons in the OH_2 group of the $(C_2H_5OH_2)^+$ ion. A proton captured in this lower level of $(H_3O)^+$ will have to wait until it receives the necessary energy before it can move back to an alcohol molecule. In the meantime the $(H_3O)^+$ ion can merely contribute to the electrical conductivity by drifting slowly in the field; only when the proton has returned to an alcohol molecule can the rapid proton jumps be resumed.

A similar drop in electrical conductivity, though not so marked, is observed on adding a trace of water to a dilute solution of HCl in methanol, which is attributed to the proton transfer

$$(CH_3OH_2)^+ + H_2O \rightarrow CH_3OH + (H_3O)^+ \qquad (44)$$

In Figs. 31 and 32 the ordinates give the equivalent conductivity of HCl, each point being the result of a series of measurements extrapolated to infinite dilution.[1] For comparison with similar diagrams given in a later chapter, where the interpretation of the results will be further discussed, abscissas have been chosen with the mole fraction of the water running from right to left. In Fig. 31 the values of the ordinates run from 99.2 upward, 99.2 being the value that it was found necessary to ascribe to the conductivity of the pair of ions $(H_3O)^+$ and Cl^- in the nearly pure methanol. In Fig. 32 the ordinates run from 44.4 upward, 44.4 being the value ascribed to the conductivity of these ions in the nearly pure ethanol. In ethanol with added water the equilibrium (43) has also been studied by a spectrophotometric method. The results, which will be mentioned in

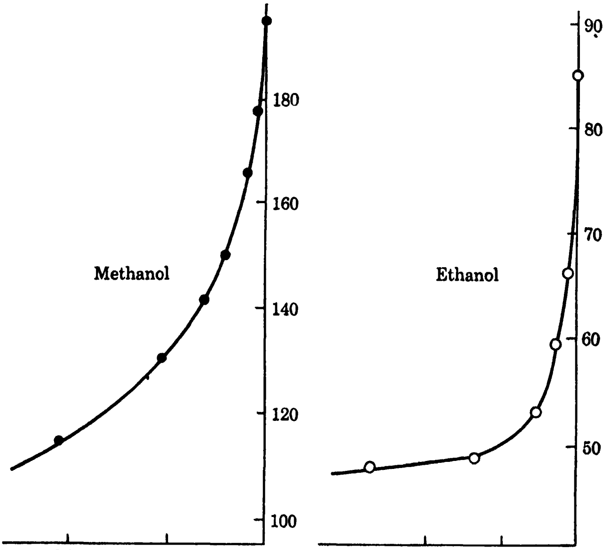

FIG. 31. FIG. 32.

FIGS. 31 and 32. Abscissas give the mole fraction of water, ordinates give the equivalent conductivity of HCl.

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[1] L. Thomas and E. Marum, *Z. physik. Chem.*, **143**, 213 (1929).

Sec. 115, confirm the value of the equilibrium constant that had been found from the conductivity.

The situation depicted in Fig. 29*a* permits a pair of successive proton jumps having a large component in the direction from left to right. By imagining a diagram which is the mirror image of Fig. 29, we can visualize the converse situation which permits proton jumps from right to left. In the absence of a field such converse situations will occur equally often. We can now raise the question whether a uniform external field, say from left to right, can somehow bring it about that situations permitting proton transfers in one direction will occur more frequently than their converse. Such a mechanism was proposed by Hückel,[1] and revived by Wannier.[2] Consider, for example, the hydroxyl ion in Fig. 29. The proton embedded in the $(OH)^-$ ion gives to the ion a dipole moment; it is assumed that the value of this dipole moment is greater than in the H_2O molecule. A uniform external field will exert a couple on each dipole Consequently, each hydroxyl ion will spend more time with its proton facing the anode than with it facing the cathode. A glance at Fig. 29 shows that this implies that each $(OH)^-$ is more often in a position to receive a proton from one direction than from the other. In this theory of Hückel the function of the field is to provide a greater number of opportunities for the protons to jump in the direction of the field than in the reverse direction. The same remark must be made for such ions as $(H_3O)^+$ and $(CH_3OH_2)^+$, etc. In such ions it is again the protons which give to the ion its dipole moment, and it is this dipole moment that promotes proton jumps in the right direction. We can say then that the proton jumps contribute to the electrical conductivity through the presence of a self-regulating mechanism.

We should now consider the possibility that in some cases proton jumps take place readily but do so in random directions owing to the absence of the requisite dipole moment. Returning to Fig. 30, suppose that the proton is removed from the OH group of a methanol molecule; we obtain thereby a negative metholate ion, $(CH_3O)^-$, which bears the same relation to CH_3OH as the hydroxyl ion bears to H_2O. Suppose, for example, that the proton is removed from the molecule on the extreme right of Fig. 30. The negative ion so formed is at once in a position to receive a proton from its neighbor, which thereby is converted into a negative ion and is, in turn, ready to receive a proton from the molecule on its left. Successive proton transfers can thus run down the chain, and will undoubtedly do so. The question is whether such proton jumps

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[1] Hückel, *loc. cit.*

[2] G. Wannier, *Ann. Physik*, **24**, 545 (1935).

take place much more readily in the direction of the field than against the field.

The proton in the OH group of CH_3OH gives to the OH group a dipole moment. But, in removing the proton to form the $(CH_3O)^-$ ion, we have removed the dipole moment. The same remark applies to the etholate ion $(C_2H_5O)^-$ in ethanol, and to the other alcoholate ions. In each of these cases the ion does not possess the self-regulating mechanism.

Let us next consider liquid ammonia as solvent, in which the positive ion $(NH_4)^+$ corresponds to $(H_3O)^+$ in water. From this ion a proton can jump to an adjacent solvent molecule.

$$(NH_4)^+ + NH_3 \rightarrow NH_3 + (NH_4)^+$$

The question arises whether an external electric field will have any large influence on the direction of these proton transfers. In the NH_3 molecule all three protons are situated in one hemisphere of the electronic cloud, and so give to the molecule a dipole moment. In the $(NH_4)^+$ ion, on the other hand, it is generally accepted that the four protons are placed symmetrically at the corners of a tetrahedron. Accordingly, the $(NH_4)^+$ ion will have no dipole moment.

Turning now to the experimental data, we find that the mobility of the $(NH_4)^+$ ion in liquid ammonia does not have any high value that would indicate a contribution from proton jumps.[1] Nor does the $(CH_3O)^-$ ion in methanol or the $(C_2H_5O)^-$ ion in ethanol solution.[2] These experimental data do not *force* us to accept the Hückel mechanism; but if we do not accept the mechanism, we shall have to make some *ad hoc* assumptions to explain these experimental results.

It should be noted that in a solution containing these ions the solute should show an abnormally high rate of diffusion, in spite of the normal electrical mobility. If the above explanation is correct, the truth is that proton jumps take place freely, leading to a high rate of diffusion; only when an electric field is applied, the proton jumps continue to be almost randomly directed. This could be tested experimentally. If the diffusion of NH_4Cl were compared with that of KCl in liquid ammonia solution, its rate of diffusion should be somewhat higher than that expected from the observed values of the relative conductivity in this solvent. The same comparison could be made between the diffusion rate of CH_3OK and KCl in methanol solution. If $\mathfrak{D}^0_+$ and $\mathfrak{D}^0_-$ are, respectively, the diffusion coefficients of the positive and the negative ions at infinite dilution, the diffusion coefficient of the solute is given by

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[1] C. A. Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., 1922.

[2] See values in Table 5.

$$\frac{1}{\mathfrak{D}^0} = \frac{1}{\mathfrak{D}^0_+} + \frac{1}{\mathfrak{D}^0_-}$$

37. Mobility of Ions in D_2O. The viscosity of liquid D_2O at room temperature has a value 1.232 times the viscosity of H_2O. Since the D_2O and H_2O molecules are so similar in other respects, we should expect the mobility of ions dissolved in D_2O to be smaller than in H_2O. The conductivity of potassium chloride and potassium acetate was measured in mixtures of D_2O and H_2O up to a composition containing 97 per cent of D_2O.[1] The values for ions in D_2O, given in Table 7, were obtained by extrapolation from values obtained in the mixed solvent containing a few per cent of H_2O. As was expected, the conductivity in D_2O was found to be smaller than in H_2O. But the change was not quite so great as the change in the viscosity, as is shown by the ratios in the last column of Table 7. We must conclude that, for some or all of the ions, the random motion in D_2O is about 2 per cent more lively than would be required by the relative viscosities of the two liquids.

TABLE 7. EQUIVALENT CONDUCTIVITY IN H_2O AND D_2O AT 25°

	H_2O	D_2O	Ratio
KCl.	141.4	117.0	1.209
NaCl	125.6	104.5	1.202
CH_3COOK	114.4	94.8	1.205
CH_3COONa	91.36	75.3	1.210
HCl or DCl	411.9	302.1	

The conductivity of DCl in D_2O solution depends to a large extent on the ease with which a deuteron can jump from a $(D_3O)^+$ ion to an adjacent D_2O molecule. From the value given for DCl in Table 7 it is clear that such deuteron transfers take place with greater difficulty than the corresponding proton transfers in H_2O; see Sec. 79.

Problem

Taking from Table 43 the value for the viscosity of water at 25°C, calculate what *would* be the velocity of a sphere of diameter 3.0 angstroms, bearing an electronic charge, in a field of 1 volt/cm, if equation (41) *could correctly be used* for a sphere as small as 3 angstroms, moving through water; and find what would be the equivalent conductivity of a uni-univalent solute in water at 25°C, if both the cation and the anion could be treated as spheres having this radius. Compare the result with the experimental values given in Table 2.

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[1] W. N. Baker and V. K. La Mer, *J. Chem. Phys.*, **3**, 408 (1935).

CHAPTER 5

Ideal and Non-ideal Solutions. Treatment of Solutions by Statistical Mechanics. A Solution Containing Diatomic Solute Particles. A Solution Containing Polyatomic Solute Particles. An Interstitial Solution. Review of Solutions in General. Quantities Dependent on, and Quantities Independent of, the Composition of the Solution. Unitary Quantities and Cratic Quantities. Molality and Activities on the Molality Scale.

38. Ideal and Non-ideal Solutions.

The concluding sentences of Chapter 2 summarized certain aspects of the processes associated with the quantities **D**, **L**, **Y**, and **J**. It was pointed out that in each of these processes the *total* change in the free energy consists of two parts, one of which is independent of the volume and composition of the solution, while the other is strongly dependent on the concentration, even in extremely dilute solution. Each of the quantities **D**, **Y**, **L**, and **J** is independent of the concentration, while the total change in the free energy is not. The situation is quite similar to the corresponding processes in a gas or vapor, where the quantities $\mathbf{D}_{vac}$, $\mathbf{L}_{vac}$, $\mathbf{Y}_{vac}$, and $\mathbf{J}_{vac}$ are independent of the volume of the vessel, while the total change in the free energy depends strongly on the number of particles (of the relevant species) per unit volume.

In dilute solution the problem may be approached from two directions: (1) from the point of view of traditional thermodynamics, and (2) from the point of view of modern statistical mechanics. We shall begin by examining briefly the former approach.

The traditional treatment of a liquid non-ideal solution is to compare its behavior with that of an ideal solution, which obeys Raoult's law over the whole range of composition, and for which the free energy of mixing is known. Consider the mixing of two liquids, of which one contains n_A particles of species A, while the other contains n_B particles of species B; and consider the change in the free energy that accompanies the mixing of these particles. It is recognized[1] that, if the mixture obeys

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[1] See, for example, L. E. Steiner, "Introduction to Chemical Thermodynamics," p. 299, McGraw-Hill, 1948.

Raoult's law over the whole range of composition, this is because the total change in the free energy, on mixing the particles, is given by $n_AkT \ln x_A + n_BkT \ln x_B$, where x_A is the mole fraction of A in the solution and x_B is the mole fraction of B. For a solution that contains in addition n_c particles of species C, and so on, terms must be added, thus

$$n_AkT \ln x_A + n_BkT \ln x_B + n_CkT \ln x_C + \cdots \tag{45}$$

where $x_A = n_A/(n_A + n_B + n_C + \cdots)$ is the mole fraction of A and so on. This gives the change in the free energy, irrespective of whether the mixture is a liquid or a solid.

At the same time it is recognized that the pairs of substances which, on mixing, are most likely to obey Raoult's law are those whose particles are most nearly alike and therefore interchangeable. Obviously no species of particles is likely to fulfill this condition better than the isotopes of an element. Among the isotopes of any element the only difference between the various particles is, of course, a *nuclear* difference; among the isotopes of a heavy element the mass difference is trivial; and the various species of particles are interchangeable. Whether the element is in its liquid or solid form, the isotopes of a heavy element form an ideal solution. Before discussing this problem we shall first consider the solution of a solid solute in a liquid solvent.

If we wish to discuss the solution of a solid in a liquid at room temperature, the traditional procedure is as follows: We first consider the solute at a temperature above its melting point; that is, we consider the solid in molten form. We then imagine that we carefully supercool this liquid until it reaches the required temperature T. We then take a suitable quantity of this liquid and mix it with the liquid solvent at temperature T. The final result is, of course, the same as if the same quantity of *solid* solute had been dissolved in this solvent. By this imaginary procedure for any solid, the free energy of solution is divided into two parts—the free energy of melting to form the supercooled liquid, and the free energy of mixing of this liquid with the liquid solvent. The question now arises, whether the change in the free energy on mixing is given by the simple expression (45). If so, the resultant solution will be an ideal (or perfect) solution; if not, the solution will be a non-ideal solution.

39. Treatment of Solutions by Statistical Mechanics. Since the vapor pressure is directly connected with the free energy, in the thermodynamic treatment the free energy is discussed first, and the entropy is derived from it. In the treatment by statistical mechanics, however, the entropy is discussed first, and the free energy is derived from it. Let us first consider an element that consists of a single isotope. When the particles share a certain total energy E, we are interested in the number of recognizably different ways in which this energy may be shared by the particles; let us denote this thermal quantity by W_{th}. Let us next consider a heavy element that consists of two or more isotopes, the various species being denoted by $A, B, C, \ldots$. Here we have to take into account the fact that, if an A-particle and a B-particle are exchanged, we obtain a recognizably different configuration; and this is true whether the substance is in the liquid or crystalline form. In addition to the thermal quantity W_{th}, we have to compute the total number of permutations of the particles that give rise to recognizably different configurations. Let us denote this configurational number of W_{cf}. For any number of isotopes its value is given by[1]

$$W_{cf} = \frac{(n_A + n_B + n_C + \cdots)!}{n_A!\, n_B!\, n_C! \cdots} \tag{46}$$

This gives the number of possible permutations, irrespective of whether the solution is a solid or a liquid. Using Stirling's approximation, we may obtain from (46)

$$-\ln W_{cf} = n_A \ln x_A + n_B \ln x_B + n_C \ln x_C + \cdots \tag{47}$$

The contribution that (46) makes to the free energy of mixing is $-kT \ln W_{cf}$; and it will be noticed that, if the right-hand side of (47) is multiplied by kT, it becomes identical with (45), which is the *total* change in the free energy, when an ideal solution is formed from its components.

Leaving isotopic mixtures, let us consider the mixing of any two liquids A and B, where the molecules of A and B are of nearly the same size. In deriving (46) it is assumed that the mixing of the particles takes place by a simple process of one-for-one substitution. In any mixture for which we may correctly use (46) the question arises whether the quantity $-kT \ln W_{cf}$ provides the *total* change in the free energy. If not, the solution is not an ideal solution. Starting with the pure liquids A and B, at the same temperature T, suppose that we take one particle from the interior of A, and one particle from the interior of B, and interchange them, placing the A-particle in the interior of B, and the B-particle in the interior of A. In this process Fowler and Guggenheim[2] denote the total increment in potential energy by $2w_{AB}$, and point out[3] that, in general, w_{AB} will vary with temperature. If from a distant site in the liquid A we take another A-particle, and from a distant site in the liquid B we take another B-particle, and interchange them, we again have to do work

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[1] See, for example, R. W. Gurney, "Introduction to Statistical Mechanics," McGraw-Hill, 1949.

[2] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," p. 352, Cambridge, 1939.

[3] *Ibid.*, p. 356.

equal to $2w_{AB}$, and so on. In each interchange the quantity w_{AB} makes a contribution to the change in the free energy; and thus (47) will not give the total change in the free energy, unless w_{AB} is zero; if w_{AB} is not zero the solution will not be an ideal (or perfect) solution.

In an ideal solution the components A, B, and C . . . are on an equal footing, and there is no distinction between solvent and solute. In this book we are mainly interested in very dilute ionic solutions, where the mole fraction of one component, known as the solvent, is very near unity, and where (at least) two solute species are present, the positive and the negative ions; we shall use n_A and x_A to refer to the solvent particles and shall denote the solute species by B and C. Let us write

$$\frac{n_B}{n_A} = y_B \qquad \frac{n_C}{n_A} = y_C \tag{48}$$

and by analogy with the mole fractions, let us call y_B and y_C the *mole ratios* of the solutes B and C in the solution. Consider now the mole fraction $x_B = n_B/(n_A + n_B + n_C)$; in an extremely dilute solution where $n_B + n_C$ is small compared with n_A the mole ratio y_B will differ from x_B by an amount which is small compared with the experimental error in the most accurate measurements of the various quantities.

If a small additional number of particles of any species is added to the solution to which (47) applies, the mole fraction of every species will thereby be changed. Taking this into account, we find from (47) that if, for example, dn_B particles of species B are added, the increment in $\ln W_{cf}$ per particle is given by

$$\begin{aligned} \frac{\partial}{\partial n_B} \ln W_{cf} &= -\ln x_B - 1 + (x_A + x_B + \cdot\cdot\cdot) \\ &= -\ln x_B \end{aligned} \tag{49}$$

Since x_B is less than unity, this represents a positive increment in W_{cf}. The expression (49) is correct at any concentration. In an extremely dilute solution, instead of $-\ln x_B$ we may, with sufficient accuracy, write $-\ln y_B$.

We mentioned above one case of a non-ideal solution. In Secs. 40 to 42 we shall discuss three more examples, and in Sec. 43 we shall review the results obtained.

40. A Solution Containing Diatomic Solute Particles. We have begun in Sec. 39 to sketch the application of statistical mechanics to solutions; this is a rather new branch of physics, and relatively few problems have been solved. Since the author has elsewhere[1] devoted 40 pages to a

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[1] Gurney, *op. cit.*, Chapter 7.

simple discussion of the subject, only certain aspects will be considered briefly here.

In studying the most familiar electrolytes, we have to deal with various molecular ions as well as atomic ions. The simplest molecular solute particle is a diatomic molecule that has roughly the same size and shape as *two* solvent particles in contact, and which goes into solution by occupying any two adjacent places that, in the pure solvent, are occupied by two adjacent solvent particles. This solution is formed by a process of substitution, but not by simple one-for-one substitution. There are two cases to discuss; either the solute molecule is homonuclear, of the type B_2, or it is heteronuclear, of the type BC. In either case let the number of solute molecules be denoted by n_B, the number of solvent particles being n_A. In the substitution process, each position occupied by a solvent particle is a possible position for one half of a solute molecule, and it is convenient to speak of each such position as a *site*, although in a liquid this site is, of course, not located at a fixed point in space.

In the pure solvent let each particle have z nearest neighbors in contact with it. Let us ask how, removing two adjacent solvent particles from the interior, we may insert a solvent molecule. When a particular site is to be occupied by the B-half of the molecule BC, there are clearly z choices for the position of its C-half. This is true for each of the n_B solute particles, provided that the solution is so dilute that they do not compete for the available sites to an appreciable extent. From the independent orientations of n_B solute particles, the quantity W_{cf} receives the factor z^{n_B} if the molecules are heteronuclear and receives the factor $(z/2)^{n_B}$ if the molecules are homonuclear.

In this way we can obtain[1] an expression for W_{cf} in a solution containing a few solute molecules; a symmetry factor can be included, to make the expression applicable to either heteronuclear or homonuclear particles:

$$W_{cf} = \left(\frac{2z}{\sigma}\right)^{n_B} \frac{(\frac{1}{2}n_A + n_B)!}{(\frac{1}{2}n_A)!\,n_B!} \tag{50}$$

where σ has the value 2 for a homonuclear and unity for a heteronuclear molecule. Now, when additional solute particles are added to the solution, we wish to know the increment in $\ln W_{cf}$ per particle added. From (50) we obtain

$$\frac{\partial}{\partial n_B} \ln W_{cf} = \ln \frac{2z}{\sigma} - \ln \frac{n_B}{\frac{1}{2}n_A + n_B} \tag{51}$$

For comparison with (49) the right-hand side of (51) may be written in the form

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[1] Gurney, *op. cit.*, p. 164.

$$\ln \frac{2z}{\sigma} - \ln x_B - \ln \frac{n_A + n_B}{\frac{1}{2}n_A + n_B} \tag{52}$$

As has already been mentioned, (50) is a good approximation only when n_B is very small compared with n_A. In this case the value of the last term in (52) does not vary appreciably with the concentration and in fact does not differ appreciably from the constant value $-\ln 2$.

Alternatively, the right-hand side of (51) may be written in the form

$$\ln \frac{2z}{\sigma} - \ln y_B - \ln \frac{n_A}{\frac{1}{2}n_A + n_B} \tag{53}$$

where y_B is the mole ratio from (48); and the same remarks will apply to the last term in this expression. Hence we reach the conclusion that at extreme dilution (51) takes the form

$$\frac{\partial}{\partial n_B} \ln W_{cf} = \text{constant} - \ln x_B \tag{54}$$

or alternatively

$$\frac{\partial}{\partial n_B} \ln W_{cf} = \text{constant} - \ln y_B \tag{55}$$

These expressions differ from (49), the form characteristic of the ideal (or perfect) solution.

41. A Solution Containing Polyatomic Solute Particles. In the same way one can discuss a molecular solute particle that has roughly the same size and shape as three, or more, solvent particles. The author has considered[1] the case of $(z + 1)$ particles; that is, where the size and shape of the solute particle are roughly the same as those of a solvent particle together with the z particles in contact with it. Suppose, for example, that in Fig. 16, where $z = 4$, the molecules 1, 2, 3, 4, and 5 are removed, and a solute molecule of the form BC_4 (like the carbon tetrafluoride molecule) is inserted, so that the central atom occupies the site 1, while the other four atoms occupy the adjacent sites, 2, 3, 4, and 5. If one of the four peripheral solute molecules was different from the other three (if one of the fluorine atoms in CF_4 was recognizably different from the other three), this atom could occupy any one of the sites 2, 3, 4, and 5; each of these orientations of the molecule would be recognizably different, and there would be four choices after the position of the central atom had been chosen. In an extremely dilute solution this would be so for each of the n_B solute molecules; W_{cf} would contain the factor 4^{n_B}, leading to expressions of the forms (54) and (55), which contain a constant term independent of the concentration. On the other hand, for a

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[1] *Ibid.*, p. 162.

solute molecule where the z peripheral atoms are identical (as in CF_4), we do not obtain recognizably different orientations in this way. Thus, although the fact that the solution is not formed by a process of one-for-one substitution is, by itself, sufficient to make the solution a nonideal solution,[1] the expression, in place of (54) or (55), tends at extreme dilution to the value $-\ln x_B$ or $-\ln y_B$ without the constant term.

42. An Interstitial Solution. For comparison let us next discuss a solution of another kind. In certain crystalline solid solutions, where the size of each solute particle is small, it is known that the solute particles take up positions in the interstices between the particles of the crystal which is acting as solvent. Such a solution is called an interstitial solution. Consider a crystal consisting of n_A particles of species A, in which n_B particles of species B have been dissolved. The crystal consisting of n_A particles provides for the B particles a number of interstitial sites equal to, or proportional to, n_A. Let this number of sites be denoted by bn_A, where b is either unity or a number somewhat greater or less than unity. We wish to compute the number of different ways in which the n_B solute particles can be arranged on the bn_A available sites. The number of recognizably different configurations W_{cf} is given by

$$W_{cf} = \frac{(bn_A)!}{n_B!(bn_A - n_B)!}$$

If a few additional B particles are added to this solution, the increment in $\ln W_{cf}$ per particle added will be

$$\frac{\partial}{\partial n_B}(\ln W_{cf}) = -\ln \frac{n_B}{(bn_A - n_B)}$$

For comparison with (54) this may be written in the form

$$-\ln x_B + \ln\left(\frac{bn_A - n_B}{n_A + n_B}\right) \tag{56}$$

In very dilute solution, where n_B is very small compared with n_A, the second term does not vary appreciably with concentration and scarcely differs from the constant value $\ln b$.

Alternatively, the right-hand side of (56) may be written

$$-\ln y_B + \ln\left(\frac{bn_A - n_B}{n_A}\right)$$

Here again in extremely dilute solution the second term will not differ appreciably from $\ln b$, and we have

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[1] *Ibid.*, p. 163.

$$\begin{aligned}\frac{\partial}{\partial n_B} \ln W_{cf} &= \ln b - \ln y_B \\ &= \text{constant} - \ln y_B\end{aligned}$$

43. Review of Solutions in General. In the discussion of these various examples we have noticed at extreme dilution the prevalence of the term $-\ln x_B$, or alternatively $-\ln y_B$. The origin of this common factor in many different types of solutions can be shown, as we might suspect, to be of a fundamental nature. For this purpose let us make the familiar comparison between a dilute solution and a gas. Since the nineteenth century it has been recognized that the behavior of any solute in extremely dilute solution is, in some ways, similar to that of a gas at low pressure. Now when a vessel of volume v contains n particles of a perfect gas at a fixed temperature, the value of the entropy depends on the number of particles per unit volume, n/v. In fact, when an additional number of particles is introduced into the vessel, the increment in the entropy, per particle added, is of the form

$$\frac{dS}{dn} = \text{constant} - k \ln \frac{n}{v} \tag{57}$$

where k is Boltzmann's constant. In discussing dilute solutions, we do not usually mention the volume v of the solution, but we make use of the fact that the volume of the solution is proportional to the number of particles; if we double the number of particles, we double the volume of the solution; and we usually mention the number of particles rather than the volume itself. In an extremely dilute solution the solute particles make a negligible contribution to the volume; the volume of the solution is proportional to n_A, the number of solvent particles, and the quantity $y_B = n_B/n_A$ is a measure of the number of solute particles per unit volume. If we are right to expect an expression analogous to (57), this would be

$$\frac{1}{k}\frac{\partial S}{\partial n_B} = \text{constant} - \ln y_B \tag{58}$$

That is to say, however many different factors contribute to the constant term that is independent of the concentration, the other term that depends on the concentration should, at extreme dilution, be of the form $-\ln y_B$. Since we identify[1] the entropy with $k(\ln W_{th} + \ln W_{cf})$, (58) is the form that we have obtained in each of the examples examined above.

To obtain an insight into the significance of (55) we have compared the solute in a very dilute solution with a perfect gas at low pressure.

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[1] *Ibid.*, p. 135.

We obtain a still better comparison, if we consider a mixture of perfect gases, A, B, C . . . in which one species A (corresponding to the solvent) is predominant, while the species B, C . . . corresponds to solutes at very low concentration. A direct link between the solution and the mixture of perfect gases is obtained in an imaginary experiment proposed many years ago by Planck.[1] We suppose that the entire solution is vaporized until it forms a mixture of gases; then the volume is increased until the behavior of this mixture of gases differs by a negligible amount from the behavior of a mixture of perfect gases. In the case of a solution formed by one-for-one substitution, where particles of all species present have roughly the same size, the form

$$\frac{1}{k}\frac{dS}{dn_B} = -\ln x_B$$

remains applicable, during the vaporization of the solution, for each of the solutes. For a perfect solution of this particular type this statement is true even when the solution is not very dilute. We are interested here in various types of solution at extreme dilution, for which we can in each case, with sufficient accuracy, use (58).

At infinite dilution the values of the quantities $-\ln x_B$ and $-\ln y_B$ become infinite. In this book, instead of "infinite dilution," we shall often prefer to use the expression "extreme dilution" (see Sec. 56).

44. Quantities Dependent on, and Quantities Independent of, the Composition of the Solution. In Chapter 1 we began by considering various processes by which additional ions may be introduced into a solvent or into a very dilute solution. Initially in such a solution we have a certain value of W_{cf}; if additional solute particles are introduced, there will be an increase in the value of W_{cf}; this means there will be an increase in the entropy and a decrease in the free energy of the solution. At the same time we recall that, in discussing polar dielectrics in Chapter 1, we saw that, when an electrostatic field is applied to a polar dielectric, there is a change of free energy and a change of entropy in the dielectric. When a few ions are added to a solvent, there is a local change in the entropy of the solvent in the immediate neighborhood of each added ion. This purely local change is, of course, independent of the amount of solvent into which the ions have been introduced, and *independent of the composition of the solution as a whole;* it is quite separate from the change in entropy and free energy associated with the change in W_{cf}. In analyzing experimental data, we cannot interpret the observed change in entropy until we understand how to distinguish between the two parts —the part that depends on the amount of solvent and on the composi-

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[1] M. Planck, "Treatise on Thermodynamics," Longmans, 1903.

tion of the solution, and the part that is independent of the composition of the solution.

In order to be in a position to discuss these two parts more easily, it will be convenient to introduce names for them. Seeing that thirty years have elapsed since the Debye-Hückel theory was first put forward, it is perhaps a little surprising that greater efforts have not been made to isolate quantities that are characteristic of the solute species and independent of the composition of the solution. In fact, there does not even appear to be any recognized terminology for making the distinction to which we have just called attention. Before we can continue the discussion of entropy or free energy, we must introduce some provisional names for the two parts. In grammar the word *crasis* is used to denote the mixing or blending of two syllables; the word is derived from the Greek κρᾶσις, a word meaning *mixing* and used chiefly for the mixing of wines. The crater, or bowl, of a volcano gets its name directly from the Greek word for a mixing bowl. For our purpose we may coin the adjective *cratic* (to be pronounced with long *a* as in crater); then, when we are discussing the entropy of a non-ideal solution, we may speak of the cratic part, when we wish to refer to the part that arises from the mixing of *a certain number of solute particles with a certain number of solvent particles,* regardless of the species of particles that have been mixed. In the same way, when we are discussing a change in the entropy of a solution due to the addition or removal of particles, and have written down an expression for this change, we may speak of the *cratic term* in this expression. Similarly when we are discussing the free energy, we may speak of the cratic part; this part depends only on the numbers of particles of different kinds that have been mixed and does not depend on the particular species involved.

In Sec. 39 we introduced the notation W_{th} and W_{cf}. When we write for the free energy

$$F = E - TS = E - kT \ln W$$

the part W_{cf} in W makes to F the contribution $-kT \ln W_{cf}$; and when we consider $\partial F/\partial n_B$ at extreme dilution, the term $-\ln x_B$ is the only quantity that depends on the composition of the solution. Hence at any temperature T, at extreme dilution, we obtain

$$\frac{\partial F}{\partial n_B} = \text{constant} + kT \ln x_B \tag{59}$$

or alternatively

$$\frac{\partial F}{\partial n_B} = \text{constant} + kT \ln y_B$$

In our study of solutions our aim is to discover quantities that are characteristic of the various solutes. We have coined a name for the cratic terms, not because we wish to focus attention on them, but because we wish to eliminate them.

When we are dealing with electrolytes, two species of particles (positive and negative ions) are added to or removed from a solution at the same time. In the case of a uni-divalent solute, three particles are added or removed at the same time. Since the cratic term depends only on the numbers of particles of various species that have been mixed, electrolytes that are completely dissociated in solution must be classified according to their valence types—uni-univalent, di-divalent, and so on. Then in any very dilute solution the correct assertion to make is that the cratic term will have the same value for all electrolytes of the same valence type.

45. Unitary Quantities and Cratic Quantities. More than once we have drawn attention to the fact that the quantities denoted by **D**, **L**, **Y**, and **J** are independent of the composition of the solution. Let us examine again the ionic dissociation of molecules in a very dilute solution, represented in Fig. 8*b*, and consider the change of free energy in the dissociation process. If in the given solution we dissociate a few more molecules into ions, we have to do, for each additional molecule dissociated, an amount of work equal to the dissociation energy **D**. If, for example, we break up q additional molecules, there will be a change in the cratic term for the solution, and at the same time the change in the free energy will receive the contribution $q\mathbf{D}$.

Consider next the process depicted in Fig. 10. If an ionic crystal is in contact with a dilute solution, and we take q additional ion pairs into the solution, there will be a change in the cratic term, and at the same time the change in the free energy ΔF will receive the contribution $q\mathbf{L}$, that is to say, a contribution consisting of q units each equal to **L**.

If in a dilute solution we carry out q proton transfers according to (28), there will be a change in the cratic term, and at the same time the free energy will receive the contribution $q\mathbf{J}$, that is to say, q units each equal to **J** Since each of the quantities $q\mathbf{D}$, $q\mathbf{L}$, $q\mathbf{Y}$, and $q\mathbf{J}$ consists of q equal units, we may call them *unitary* quantities, in contrast to the cratic term, which is a communal quantity, depending as it does on the amount of solvent as well as the amount of solute present.

We may say then that in each of those processes the change ΔF in the free energy consists of two parts, *a unitary part and a communal part.* When an ionic solution is not extremely dilute, the free energy of the solution receives a contribution from the interionic forces; this quantity depends on the concentration of the solute and is a communal quantity. When, however, the solution is extremely dilute, the interionic contribution[1] becomes negligible (smaller than the error in extrapolation from the most accurate series of measurements), while the cratic term remains large. Since we are interested here only in processes at extreme dilution, we may assert that the change ΔF in the free energy consists of two parts, a unitary term and the cratic term. We may write

$$\Delta F = \Delta F_{unitary} + \Delta F_{cratic} \tag{60}$$

The division of ΔF into two parts is true for other processes than those mentioned above. Consider, for example, the quantity $2w_{AB}$ in the mixing of two liquids by successive interchange of particles, as discussed in Sec. 39. When two very dilute solutions have already been formed by the interchange of a few particles taken from the interiors of the two liquids, the work required to interchange q additional pairs of particles will be $2qw_{AB}$, provided that each particle is taken from a place distant from any particle that has already been substituted. Now the quantity $2qw_{AB}$ is independent of the composition of the solutions and provides or contributes a unitary term; thus ΔF will be of the form (60).

We have already pointed out that, in general, w_{AB} will vary with temperature. In this respect w_{AB} resembles the quantities **D**, **L**, **Y**, and **J**, all of which are sensitive to temperature. When, for any process, we differentiate (60) with respect to the temperature, we obtain the change in entropy ΔS for the process. Now at all temperatures the unitary term in (60) is independent of the composition of the solution; and obviously, if we differentiate it with respect to the temperature, the quantity so obtained will necessarily be independent of the composition of the solution, and so will provide a unitary term in ΔS. We must write then

$$\Delta S = \Delta S_{unitary} + \Delta S_{cratic} \tag{61}$$

As pointed out in Sec. 44, the cratic term does not depend on the species of particles but only on the number of particles that have been mixed. If for any process we have obtained an experimental value of ΔS in extremely dilute solution, we may at once calculate the cratic term for the solution, and subtract it, and so obtain the value of the unitary term, which is characteristic of the particles taking part in the process.

46. Molality and Activities on the Molality Scale. In order to give a numerical value to the concentration of a solution, it is customary to

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[1] In Sec. 41 it was pointed out that, when we are dealing with a solution that is not formed by a process of one-for-one substitution, this is, by itself, sufficient to make the solution a non-ideal solution—that is to say, is sufficient, by itself, to introduce a communal term that is different from the simple cratic term. Nevertheless, in an ionic solution at any concentration this deviation is small compared with the deviation caused by the electrostatic forces between the ions. In this book it will therefore be sufficient to mention only the interionic forces when speaking of the difference between a communal term and a cratic term.

mention the number of moles of solute which are dissolved in an arbitrary amount of solvent. Thus a "0.1-molal solution," for example, is a solution in which 0.1 mole of solute has been dissolved in that amount of solvent which has been arbitrarily chosen as standard. Although this method is in current use, there is no recognized name for the basic quantity of solvent. In this book we shall use the abbreviation b.q.s. for *basic quantity of solvent.* If, for example, we were to decide to choose 10^6 grams of solvent as the b.q.s., then a "1-molal solution" would be a solution whose composition corresponds to the dissolving of 1 mole of solute in 10^6 grams of solvent. In electrochemistry it is customary to choose 1000 grams of solvent as the b.q.s., and in this book we shall always follow this custom. In calculating mole fractions and mole ratios, an important quantity is the *number of moles of solvent in the b.q.s.;* this number, which will be denoted by M, is obviously equal to 1000 divided by the molecular weight of the solvent. In H_2O, for example, M is equal to 1000 divided by 18.016, that is 55.51. Likewise in CH_3OH we have M equal to 1000 divided by 32.03, that is, 31.22. When dealing with a mixed solvent, such as a methanol-water mixture, the molality of a solute is the number of moles of this solute in 1000 grams of the mixed solvent.

Since an ionic solution contains two species of solute particles, the positive and negative ions, it is often useful to mention the molality of each species. If barium chloride, for example, dissolved in a solvent, is completely dissociated into Ba^{++} ions and Cl^- ions, the molality of the Ba^{++} will be equal to the molality of the solute $BaCl_2$, while the molality of the Cl^- will be twice as great.

There are several different scales on which the activity of a solute may be defined.[1] In thermodynamic expressions for a solute in a non-ideal solution the activity on the molality scale plays the same part that is played by the molality of a solute in an ideal solution. Since the activity is expressed in the same units as the molality, the ratio of the activity to the molality—the activity coefficient—is a pure number whose value is independent of these units; it is also independent of the particular b.q.s. that has been adopted. Thus the numerical values of all activities and molalities would change in the same ratio, if at any time a new choice were made for the b.q.s.

Problems

1. Using Stirling's approximation in the form

$$\ln n! = n \ln n - n$$

derive equation (49) and (46).

2. Derive equation (51) from (50); and in the case of an interstitial solution derive (56) from the appropriate expression for W_{cf}.

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[1] Steiner, *op. cit.*, p. 409.

CHAPTER 6

Heat of Precipitation. Entropy of Solution and Partial Molal Entropy. The Unitary Part of the Entropy. Equilibrium in Proton Transfers. Equilibrium in Any Process. The Unitary Part of a Free Energy Change. The Conventional Standard Free Energy Change. Proton Transfers Involving a Solvent Molecule. The Conventional Standard Free Energy of Solution. The Disparity of a Solution. The E.M.F. of Galvanic Cells.

47. Heat of Precipitation. Although the heat of solution of a sparingly soluble crystal may be too small to be measured calorimetrically, an experimental value may be obtained by measuring its converse, namely, the heat of precipitation. For example, the heat of precipitation of AgCl in aqueous solution was determined[1] by adding a dilute solution of $AgNO_3$ to a solution of KCl in a calorimeter at 22.5°C. In Table 8 columns 1 and 2 give the concentrations of the solutions used. In the last series of measurements a 0.0493-molal solution of $AgNO_3$ was added to a 0.535-molal solution of KCl, and a value 15,864 cal/mole was obtained for the heat of precipitation of AgCl. The value in column 3

TABLE 8

Concentration		Heat of precipitation, cal/mole	Estimated correction	Heat of solution	
$AgNO_3$	KCl			cal/mole	electron-volts
1	2	3	4	5	6
0.1482	1.607	15,722	−125	−15,847	−0.6874
0.0988	1.072	15,769	−50	−15,819	−0.6862
0.0493	0.535	15,864	40	−15,824	−0.6864
		At 22.5°C		−15,830	−0.6867
		At 25.0°C		−15,740	−0.6828

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[1] E. Lange and R. M. Fuoss, *Z. physik. Chem.*, **125**, 431 (1927).

needs to be corrected for the heat of dilution of the KNO_3 that remains in solution; column 4 gives the estimates made by Pitzer and Smith[1] for these corrections. To obtain the heat of solution, column 3 must be subtracted from column 4; the result is given in column 5 in calories per mole, while Column 6 gives the same quantity in electron-volts per ion pair. For the heat of solution at 22.5°C the value −15,830 was adopted, and for the heat of solution at 25.0°C the value −15,740 cal/mole, or −0.6828 electron-volt per ion pair.

Similar measurements were made for the heat of precipitation of silver iodide,[2] which is even less soluble in water than silver chloride. As shown in Table 33 in Sec. 102, a saturated solution of AgI at 25°C contains only 9.08×10^{-9} moles/liter, as compared with 1.34×10^{-5} for AgCl. By calorimetric measurement the heat of precipitation of AgI at 25°C was found to be 1.16 electron-volts per ion pair, or 26,710 cal/mole.

48. Entropy of Solution and Partial Molal Entropy. If the heat of solution of a solute is known, and the free energy of solution is known at some low concentration, then the entropy of solution ΔS at the same concentration can at once be found from the relation

$$\Delta F = \Delta H - T\,\Delta S$$

Consider, for example, the saturated solution of a sparingly soluble crystal. Let ΔH_{sat} and ΔS_{sat} denote the heat of solution and the entropy of solution when a few additional pairs are taken into the saturated solution. The condition for equilibrium between the solid and the solution is, of course, that there shall be no change in the free energy in this process; a saturated solution is one for which ΔF is zero. Hence we may write at once

$$\Delta S_{sat} = \frac{\Delta H_{sat}}{T} \tag{62}$$

To obtain the entropy of solution we have only to divide the heat of solution by the temperature.

Let us apply this to the values for silver chloride at 25° given above. Dividing 15,740 by the temperature, we obtain for the entropy of solution of crystalline AgCl in its saturated solution the value

$$\Delta S_{sat} = \frac{15{,}740}{298.1} = 52.8 \text{ cal/deg/mole}$$

When a certain amount of crystalline AgCl is in contact with its saturated solution, consider the process of taking an additional pair of

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[1] K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc*, **59**, 2638 (1937).

[2] E. Lange and Z. Shibata, *Z. physik. Chem.*, **A149**, 465 (1930).

ions from the crystal into the solution. Initially the pair of ions makes its proper contribution to the entropy of the crystal; finally the pair of ions makes its proper contribution to the entropy of the solution. The change of entropy per ion pair dissolved, ΔS_{sat}, is equal to the difference between these two contributions; hence, if we add ΔS_{sat} to the former, we clearly obtain the value of the latter.

In electrochemistry it is customary to multiply each of these quantities by Avogadro's constant and, when a few additional ions enter the already saturated solution, to speak of the entropy of solution per mole. Let the entropy of one mole of the crystalline solid be denoted by S_{cr}; and let S_1 and S_2 denote, respectively, the entropy of the solution before, and after, the entry of the additional solute, both expressed in calories per mole. The total initial entropy is obviously $(S_{cr} + S_1)$; and the final entropy is S_2. The difference between the final and the initial entropy is by definition ΔS_{sat}:

$$S_2 - (S_{cr} + S_1) = \Delta S_{sat} \tag{63}$$

Hence

$$S_2 - S_1 = S_{cr} + \Delta S_{sat} \tag{64}$$

In the case of a sparingly soluble substance, if each of the quantities in (64) is divided by Avogadro's constant, we confirm the statement made above— namely, that, if ΔS_{sat} per ion pair is added to the contribution made to the entropy of the crystal by each ion pair, in this way we evaluate the contribution made by one additional ion pair to the entropy of the saturated solution; and it is important to grasp that this contribution depends only on the presence of the additional pair of ions in the solution and does not depend on where they have come from. They might have been introduced into the solution from a vacuum, instead of from the surface of a solid. In (64) the quantities on the right-hand side refer to the solution of a crystal, but the quantity $(S_2 - S_1)$ does not; it denotes merely a change in the entropy of a solution due to the presence of additional ions, which may have come from anywhere. When S_1 denotes the entropy of a sufficiently large amount of solution, $(S_2 - S_1)$ is the partial molal entropy of the solute in this solution.

Returning now to silver chloride, let us apply these ideas to its saturated aqueous solution at 25°. From the value given in Table 42, we see that in solid AgCl the entropy per ion pair is almost exactly 1 millielectron-volt per degree, which is equivalent to 23.0 cal/deg/mole. It makes no difference whether we express the entropies per ion pair in electron-volts per degree or in the equivalent calories per degree per mole. In the electrochemical literature the calorie per degree per mole is used and is called "one entropy unit." (This is abbreviated e.u.)·

When solid AgCl is in contact with its saturated aqueous solution, we have found that, if additional ion pairs are transferred from the surface of the crystal to the solution, the total change of entropy is equivalent to 52.8 e.u Since the entropy of the solid is 23.0 e.u., we find that the partial molal entropy of AgCl in its saturated aqueous solution at 25°C is

$$S_{sat} = (23.0 + 52.8) = 75.8 \text{ e.u.}$$

After discussing in Chapter 1 a charged sphere in a dielectric, we saw in Sec. 14 that, when any pair of ions is added to a solvent, there will be a change of entropy in the co-sphere of each ion. If, for example, we knew the value of this change for the ion pair ($Ag^+ + Cl^-$) and likewise for the ion pair ($Ag^+ + I^-$), any difference between the two quantities could at once be ascribed to the difference between the co-spheres of the chloride ion Cl^- and the iodode ion I^-, since the contribution from the Ag^+ ion and its co-sphere would be the same in the two cases.

Since the saturated solutions of AgI and AgCl are both very dilute, it is of interest to examine their partial molal entropies, to see whether we can make a comparison between the values of the unitary terms. As mentioned above, the heat of precipitation of silver iodide was found by calorimetric measurement to be 1.16 electron-volts per ion pair, or 26,710 cal/mole. Dividing this by the temperature, we find for the entropy of solution of the crystal in the saturated solution the value

$$\Delta S_{sat} = \frac{26,710}{298.1} = 89.6 \text{ e.u.}$$

The entropy of solid AgI is a little larger than that of AgCl, namely, 27.1 e.u., as compared with 23.0 e.u. Using (64) we find for the partial molal entropy of AgI in its saturated solution the value

$$S_{sat} = 89.7 + 27.1 = 116.8 \text{ e.u.}$$

We notice that this is considerably larger than the value 75.8 obtained above for AgCl.

49. The Unitary Part of the Entropy. Let us return now to the question of the entropy associated with each ion and its co-sphere. The values 75.8 and 116.8 which we have just obtained cannot, as they stand, throw any light on this question for Cl^- and I^-, since they refer to very different concentrations of solute. The partial molal entropy of any solute contains a cratic term, which depends strongly on the concentration. If we compare the two saturated solutions, the amount of solvent that contains a given quantity of AgI is much larger than the amount of solvent that contains the same quantity of AgCl; that is to say, a given quantity of AgI is mixed with a greater number of solvent molecules than an equal quantity of AgCl. Hence the value of W_{cf} is much greater in the saturated solution of AgI than in the saturated solution that contains an equal amount of AgCl, and the cratic term will have a larger positive value.

Before we can decide whether there is a large or a small difference between the unitary terms of the Cl^- ions and the I^- ion, the difference in the cratic term must be calculated. The question is whether the difference of 41.0 e.u. between 116.8 and 75.8 merely represents the difference between the cratic terms, or whether it includes as well a difference between the unitary terms of the I^- ion and the Cl^- ion. For ions provided by any two such sparingly soluble substances this question can be settled at once by a simple calculation.

Let x and x' denote the mole fractions of the two sparingly soluble solids in their respective saturated solutions; let y and y' denote their mole ratios, m and m' their molalities, and a and a' their activities on the molality scale. If the saturated solutions are sufficiently dilute, we may, with sufficient accuracy, neglect the differences between the four ratios x/x', y/y', m/m', and a/a'. We can express the difference between the cratic terms by means of any of these quantities, thus,

$$\begin{aligned} R \ln x'^2 - R \ln x^2 = 2R \ln \frac{x'}{x} &= 2R \ln \frac{y'}{y} \\ &= 2R \ln \frac{m'}{m} \qquad (65) \end{aligned}$$

Attention was already drawn in Sec. 47 to the concentrations of the saturated solutions of AgCl and AgI, given in Table 33 as, respectively, 1.34×10^{-5} and 9.08×10^{-9}. Inserting these values we obtain

$$\begin{aligned} 2R \ln \frac{m'}{m} &= 2 \times 1.987 \times \ln \left(\frac{1.34 \times 10^{-5}}{90.8 \times 10^{-9}} \right) \\ &= 29.1 \text{ e.u.} \end{aligned}$$

We can now answer the question under discussion. Since 29.1 e.u. is considerably smaller than the total difference $(116.8 - 75.8) = 41.0$ e.u., mentioned above, we conclude that the unitary term for the ion pair $(Ag^+ + I^-)$ is greater than for $(Ag^+ + Cl^-)$. The contribution from the Ag^+ ion and its co-sphere must be, within the experimental error, the same in the two cases. Finally then, we reach the conclusion that in water at 25°C the entropy associated with the iodide ion I^- and its co-sphere is greater than that associated with the ion Cl^- and its co-sphere; in fact, the excess lies in the neighborhood of $(41 - 29) = 12$ e.u.

The numerical calculations for AgCl and AgI were given here as an example of the way in which one may obtain unitary quantities, by eliminating the cratic terms. We shall now consider the same procedure in analyzing proton transfers. The examination of ionic entropies will be resumed in Sec. 87.

50. Equilibrium in Proton Transfers. In each of the two examples that have been discussed in Sec. 49 the data were derived from a study of the equilibrium between a salt and its saturated solution. Let us next consider the conditions for equilibrium in the transfer of a proton, like that introduced in Sec. 17. In the process (28) four species are involved—two neutral particles and two ions. We may next recognize the fact that in

$$AH + B \rightarrow A^- + (BH)^+ \tag{66}$$

the two neutral species are not necessarily both solute particles, but either AH or B may denote a solvent molecule. If, for example, in aqueous solution, B denotes a water molecule, $(BH)^+$ will denote a $(H_3O)^+$ ion, thus,

$$AH + H_2O \rightarrow A \quad + (H_3O)^+ \tag{67}$$

Similarly in methanol solution

$$AH + CH_3OH \rightarrow A^- + (CH_3OH_2)^+$$

Turning next to the case where AH denotes a water molecule, A^- will clearly denote a hydroxyl ion; thus

$$H_2O + B \rightarrow (OH)^- + (BH)^+ \tag{68}$$

The expressions that we shall derive will be applicable irrespective of whether a solvent molecule is involved, or whether all four species are solute particles. In either case, numbering the species in (66) from left to right, let the numbers of particles present in the dilute solution be n_1, n_2, n_3, and n_4, their mole fractions x_1, x_2, x_3, x_4, their molalities m_1 m_2, m_3, m_4, and their activities a_1, a_2, a_3, a_4. When one additional proton is transferred from left to right in (66), the value of n_3 is increased by unity, and likewise n_4, while the values of n_1 and n_2 are diminished by unity. These changes are accompanied by an alteration in the cratic term in the free energy. In a solution where equilibrium for the process (66) prevails, the work required to transfer a few additional protons is zero; that is to say, $dF/dn = 0$; or using the usual chemical notation $\Delta F = 0$. Recalling that ΔF consists of a unitary part and a communal part, it is clear that a zero value of ΔF can come about only if the values of the *unitary and the communal terms in* ΔF *happen to be exactly equal and opposite.* At any temperature the unitary term for the proton transfer is just a given constant, and we can express the state of equilibrium for (66) in the following way: the concentrations of the various species of particles adopt values which give to the communal term a value equal and opposite to that of the unitary term.

If we go on to consider the reaction (66) in a solution so dilute that the interionic forces make a negligible contribution to the communal term in ΔF, we may refer to the cratic term, instead of the communal term; we may describe the equilibrium by saying that the concentrations of the four species adopt values which give to the cratic term in (60) a value equal and opposite to that of the unitary term:

$$\Delta F_{cratic} = -\Delta F_{unitary}$$

A solution that is so dilute that the difference between the cratic term and the total communal term may be neglected will be said to have a concentration "lying in the extremely dilute range."

At the same time, in this extremely dilute solution, the difference between the mole fraction x and the mole ratio y becomes negligible for each of the four species. Consider now the cratic terms that arise from the changes in (47), the quantity $(-\ln W_{cf})$. From (55), when in (66) one additional proton is transferred, the change from n_3 to $(n_3 + 1)$ makes a contribution that may be written either $+\ln x_3$ or $+\ln y_3$, while the change from n_4 to $(n_4 + 1)$ makes a contribution that may be written either $+\ln x_4$ or $+\ln y_4$. At the same time the changes from n_1 to $(n_1 - 1)$ and from n_2 to $(n_2 - 1)$ make contributions that may be written $-\ln x_1$ and $-\ln x_2$, or else $-\ln y_1$ and $-\ln y_2$. Adding together these four quantities, we obtain

$$\ln x_3 + \ln x_4 - \ln x_1 - \ln x_2 = \ln \frac{x_3x_4}{x_1x_2} = \ln \frac{y_3y_4}{y_1y_2} \tag{69}$$

We conclude then that in the proton transfer the cratic part of ΔF, according to (59), will be

$$kT \ln \frac{x_3x_4}{x_1x_2} \tag{70}$$

This is the quantity that must be equal to the unitary part taken with negative sign.

In electrochemistry the symbol ΔF is used to denote the value per mole, not the value per particle. To avoid confusion, we shall use dF/dn to denote the change in the free energy per proton transferred; then we shall call (70) the cratic part of dF/dn for the proton transfer.

Consider now a series of extremely dilute solutions, all at the same temperature T, containing these four species at widely different concentrations. At equilibrium the values adopted by x_1, x_2, x_3, and x_4 must be such that the ratio x_3x_4/x_1x_2 has the same value in each solution, since the unitary term is independent of the concentrations, and the quantity $\ln (x_3x_4/x_1x_2)$ must in each case be equal to this unitary term multiplied by $-1/kT$.

51. Equilibrium in Any Process. We have discussed a reaction involving either four solute species or three solute and one solvent species. The method can be used to describe the equilibrium in any type of reaction or process, involving any number of solute species in extremely dilute solution. The method could be applied, for example, to the ionic dissociation of a molecule, or to the dissociation of a molecular ion. In general, when the expression for the reaction has been written down, we suppose that the reaction takes place from left to right; then each particle (of species i) on the right-hand side makes to the cratic term the contribution $+kT \ln x_i$ while each particle on the left-hand side makes the contribution $-kT \ln x_i$. The sum of these quantities, which may be denoted by $kT\ \Sigma \pm \ln x_i$, will contain as many terms as there are particles in the reaction as written down.

Since at equilibrium $dF/dn = 0$, that part of dF/dn which depends on the amount of solvent must have a value that is equal and opposite to the part that is independent of the amount of solvent. In other words, the cratic part must be equal and opposite to the total unitary term. If the latter is denoted by U, we shall have, for equilibrium at extreme dilution

$$U + kT \sum \pm \ln x_i = \frac{dF}{dn} = 0 \tag{71}$$

Hence

$$U = -kT\ \Sigma \pm \ln x_i = -kT\ \Sigma \pm \ln y_i \tag{72}$$

The quantity U is the only part of dF/dn that is characteristic of the species that are taking part in the reaction; and if the concentrations of all the species can be measured in sufficiently dilute solution, an accurate value of U can be obtained by inserting the values of $x_1, x_2 \ldots$ in (72). In this way, a value of U correct to less than one part in 1000 can often be obtained directly. If higher accuracy is desired, or if for some reason measurements cannot be made in sufficiently dilute solution, measurements are made in a series of dilute solutions, and the value of $\Sigma \ln x_i$ at infinite dilution is obtained by extrapolation (see the example of an extrapolation in Fig. 33, in Sec. 63).

52. The Unitary Part of a Free Energy Change. In this way we can obtain values for the unitary terms characteristic of processes of each of the four types discussed in Chapters 1 and 2. At this point it will be convenient to review what was said in those chapters and to relate that discussion to (71) and (72). In Sec. 11 the dissociation energy **D** was introduced by analogy with the dissociation energy $\mathbf{D}_{vac}$, defined for the same molecule in a vacuum. In solution (as in a gas or vapor) the parts of a molecule remain united because a certain amount of work is required to separate them. In a vacuum, molecules of a species for which $\mathbf{D}_{vac}$ is large will be less dissociated than molecules of a species for which $\mathbf{D}_{vac}$ is small. Similarly in solution it must be possible to say that molecules of a species for which **D** is large will be less dissociated than those of a species for which **D** is small.

Turning next to (72), we could define, for the dissociation of any molecule or molecular ion, a characteristic unit D, by writing

$$D + kT \sum \ln x_i = \frac{dF}{dn} = 0 \tag{73}$$

In Sec. 18 we noticed that the work done in the isothermal dissociation process was a change in the free energy—but not the total change in the free energy; and we did not proceed to give a precise definition to **D**. If we were to define **D** as the total change in the free energy at extreme dilution, exclusive of the cratic part, there would be no difference between the **D** in bold-faced type and the D in ordinary type; for this is the definition that, by (73), has been given to D.

If, in the same way, we use (72) to define for the other processes the characteristic units J, L, and Y, similar remarks can be made with regard to **J** and J, with regard to **L** and L, and likewise with regard to **Y** and Y. By equation (72) a precise definition has been given to the characteristic unit of any process; and we must hope that in the future the study of ionic solutions will eventually provide a complete interpretation of these quantities. At the present time we are very far from this goal. At any rate the total unitary quantity for each process must be isolated and evaluated before it can be interpreted. In the remaining chapters of this book we shall have occasion to mention only the quantities D, L, Y, J, and U, defined in accordance with (72) and (73). If, however, anyone should wish to give a precise definition to a quantity that includes *less* than the whole of the unitary term, the symbols in bold-faced type remain available for this purpose.

In any process the change in entropy is, of course, equal to the temperature coefficient of the change in free energy, taken with opposite sign:

$$\Delta S = -\frac{d}{dT}\Delta F$$

and this expression may be written down for the cratic part and the unitary part separately:

$$\Delta S_{cratic} = -\frac{d}{dT}\Delta F_{cratic} \tag{74}$$

and likewise

$$\Delta S_{unitary} = -\frac{d}{dT}\Delta F_{unitary} \tag{75}$$

Since in the various processes considered the quantities L, D, Y, and J form the unitary part of ΔF, we see that, in these various processes, $\Delta S_{unitary}$ is either equal to $-(dL/dT)$ or $-(dD/dT)$ or $-(dY/dT)$ or $-(dJ/dT)$ (multiplied in each case by Avogadro's constant to give the value per mole).

We must now draw attention to the fact that, for any kind of process in any solution of given composition, the quantity ΔF_{cratic} is simply a constant depending on the numbers of particles involved, multiplied by the absolute temperature [as was the case in (70) for example]. As a result, differentiating ΔF_{cratic} with respect to T is equivalent to dividing by T. In other words, in any process in any solution whatever, we have

$$\Delta F_{cratic} - T\frac{d}{dT}\Delta F_{cratic} = 0 \tag{76}$$

It is a result of this relation that in any process whatever the heat of reaction per mole at extreme dilution, usually denoted by ΔH^0, is a unitary quantity, not depending on the amount of solvent present. According to the Gibbs-Helmholtz relation[1] we have

$$\Delta H^0 = \Delta F^0 - \frac{d}{dT}\Delta F^0$$

Now according to (76) the cratic part of ΔF^0 makes no contribution at all. We are left then with

$$\Delta H^0 = \Delta F_{unitary} - T\frac{d}{dT}(\Delta F_{unitary}) \tag{77}$$

Thus, in the various processes, we see that ΔH^0 is equal to $[L - T(dL/dT)]$, or $[J - T(dJ/dT)]$, and so on, multiplied in each case by Avogadro's constant.

In discussing the experimental data, we shall wish to make use of the equilibrium constants that are to be found in the literature. We must therefore inquire into the relation that the thermodynamic treatment bears to the treatment that has been given above. When the expression for any reaction, such as (66) for example, has been written down, the species that have been written on the left-hand side are called the *reactants*, and those on the right-hand side are called the *products*. The

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[1] L. E. Steiner, "Introduction to Chemical Thermodynamics," p. 232, McGraw-Hill, 1948.

usual practice is to express any equilibrium in solution in terms of the activities of the reactants and products, these being activities on the molality scale (see Sec. 46). The equilibrium constant K is defined by

$$\ln K = \sum \ln \frac{a_i}{a_i^0} \tag{78}$$

where a_i denotes the activity of the ith species when equilibrium prevails, and a_i^0 denotes the activity of the same species in the state that has arbitrarily been chosen as the standard state; in (78) Σ denotes the algebraic sum in which the term for each reactant species occurs with negative sign and the term for each product occurs with positive sign [compare the left-hand side of (71)]. In very dilute solution the value of a_i for each species approaches the molality m_i; and at extreme dilution the difference between a_i and m_i becomes negligible. If for each species the condition $a_i^0 = 1$ is adopted as defining the arbitrary standard state, (78) can obviously be written in the form

$$\ln K = \Sigma \ln a_i \tag{79}$$

In the case of the proton transfer (66), for example, we should have

$$\ln K = \ln \frac{a_3 a_4}{a_1 a_2} \tag{80}$$

an expression which has a structure similar to that of (70).

53. The Conventional Standard Free Energy Change. For any of these reactions let us now discuss the standard free energy change, usually denoted by ΔF^0; this is defined as the value of ΔF per mole when the initial state of each of the reactants is a state that has been chosen as standard, and the final state of each of the products is likewise a state that has been chosen as standard. That is to say, ΔF^0 is the over-all change in the free energy for three steps: the transfer of each of the reactants from its standard state; the reaction itself; and the transfer of each of the products to its standard state. Since at equilibrium the reaction itself makes zero contribution, ΔF^0 consists entirely of the changes in the first and third steps. These contributions are $-RT \ln (a_i/a_i^0)$ from each of the reactants and $+RT \ln (a/a_i^0)$ from each of the products. Hence the familiar expression

$$\Delta F^0 = -RT\, \Sigma \pm \ln \frac{a_i}{a_i^0} = -RT\, \Sigma \pm \ln a_i = -RT \ln K \tag{81}$$

In any solvent it is customary to use activities based on the usual choice of 10^3 grams as the b.q.s. In most reactions in solution, but not in all, the numerical value of ΔF^0 depends on the amount of solvent that has been adopted as the b.q.s. We may say that this is connected with the fact that, for most types of reaction in solution, but not in all, the value of the equilibrium constant K depends on the amount of solvent that has been adopted as the b.q.s. From what has been said above, it will be clear that one of the aims of this book is to deal, as far as possible, with quantities that are really characteristic of the various ionic species—quantities that are free from the arbitrary conventions of thermodynamics. The problem here is to disentangle such quantities. Since the quantities x and y that occur in (72) depend only on ratios of concentrations, their values do not even depend on the units in which these concentrations are expressed. To facilitate comparison between (81) and (72) it will be convenient to write

$$K_x = \Sigma \ln x, \qquad K_y = \Sigma \ln y, \qquad K_m = \Sigma \ln m,$$

At extreme dilution the difference between K_x and K_y becomes negligibly small; and so does the difference between K_m and K.

The relation between K_m and K_y depends on the number of particles taking part in the reaction—or rather upon the change in this number. As an example, let us consider the dissociation (29)

$$(\mathrm{PbCl})^+ \rightleftarrows \mathrm{Pb}^{++} + \mathrm{Cl}^-$$

Numbering the particles from left to right, we have at infinite dilution from (73) and (81)

$$D = -kT \ln \frac{x_2x_3}{x_1} = -kT \ln \frac{y_2y_3}{y_1} \tag{82}$$

and at the same time

$$\Delta F^0 = -RT \ln \frac{a_2a_3}{a_1} = -RT \ln \frac{m_2m_3}{m_1} \tag{83}$$

It was mentioned in Sec. 46 that 1000 grams of H_2O contains 55.5 moles. For any solute species in aqueous solution

$$m = 55.5y$$

Hence in (83)

$$\frac{m_2m_3}{m_1} = 55.5 \frac{y_2y_3}{y_1}$$

Since R/k is equal to Avogadro's number N, we obtain for this dissociation

$$D = \frac{\Delta F^0}{N} + kT \ln 55.5 \tag{84}$$

The term $+kT \ln 55.5$ is characteristic of a reaction in aqueous solution in which the number of solute particles is increased by unity.

In general, when the equation for any reaction or process has been written down, let there be q solute particles on the left-hand side, and let there be $(q + \Delta q)$ solute particles on the right-hand side. In any solvent let M denote the number of moles of solvent that are contained in the mass that has been adopted as the b.q.s.; then for each solute species $m = My$. At extreme dilution the ratio of K to K_x takes the value[1]

$$\frac{K}{K_x} = M^{\Delta q} \tag{85}$$

and the relation between ΔF^0 and the characteristic unit U is given by

$$U - \frac{\Delta F^0}{N} = kT \ln \frac{K}{K_x} = \Delta q(kT \ln M) \tag{86}$$

In the example (82) the value of Δq was $+1$, thus leading to the term $+kT \ln 55.5$ in (84).

In discussing the proton transfer (66), we saw that one of the neutral species could be a solvent molecule. We shall discuss that case below. Here we may notice that, when all four species are solute particles, the number of solute particles is unchanged by the reaction, or $\Delta q = 0$. In such a case ΔF^0 happens to be equal to the characteristic unit U multiplied by Avogadro's constant.

54. Proton Transfers Involving a Solvent Molecule. In electrochemistry it is still often customary to treat the dissociation of a weak acid as a simple splitting of the molecule into ions. In the case of acetic acid, for example, the equilibrium is written

$$\mathrm{CH_3COOH} \rightleftarrows \mathrm{(CH_3COO)^-} + \mathrm{H^+} \tag{87}$$

although it is generally recognized that the process would be more accurately written as the transfer of a proton to a solvent molecule; for example, in aqueous solution

$$\mathrm{CH_3COOH} + \mathrm{H_2O} \rightleftarrows \mathrm{(CH_3COO)^-} + \mathrm{(H_3O)^+} \tag{88}$$

Numbering the particles in (87) from left to right, the conventional "acid dissociation constant" is defined at infinite dilution by

$$K_A = \frac{a_2a_3}{a_1} = \frac{m_2m_3}{m_1} \tag{89}$$

and the ΔF_A^0 is taken equal to $-RT \ln K_A$. On the other hand, if the equilibrium constant for the proton transfer (88) at infinite dilution is

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[1] See Steiner, *op. cit.*, p. 260.

written down, four species are involved, and we have to introduce in the denominator $a = m = M$ for the molality of the solvent particle, where M is the number of moles in the b.q.s. For (88) we thus obtain

$$K = \frac{K_A}{M} \tag{90}$$

Now in (88) the number of particles is unchanged; and from (85) we know that in this case $K_x = K$. We thus reach the result

$$\begin{aligned} J &= -kT \ln K_x = -kT \ln K_A + kT \ln M \\ &= \frac{\Delta F_A^0}{N} + kT \ln M \end{aligned} \tag{91}$$

But this is the relation that was found in (86) to be appropriate to a process in which the number of particles is increased by unity.

We thus verify that if the proton transfer

$$\mathrm{AH} + \mathrm{H_2O} \rightarrow \mathrm{A^-} + (\mathrm{H_3O})^+ \tag{92}$$

is written in the form

$$\mathrm{AH} \rightarrow \mathrm{A^-} + \mathrm{H^+} \tag{93}$$

use of the conventional K_A for (87) leads to the same results as the use of the equilibrium constant for the proton transfer (88).

Alternatively, we can reach the same result by writing down the expressions for K_x for (87) and (88) and noticing that at extreme dilution their values will not differ appreciably, since the mole fraction or the activity of the solvent will not differ appreciably from unity.

55. The Conventional Standard Free Energy of Solution. Returning now to the solution of a crystalline solid, let us consider the free energy of solution. Taking a uni-univalent substance let ΔF denote the change in free energy per mole when additional ions are added to a solution at temperature T where the solute has the mole fraction x; and let us fix attention on the quantity

$$(\Delta F - 2RT \ln x) \tag{94}$$

We shall ask two questions: (1) how does the value of this quantity vary with the concentration of the solution into which the additional ions are being introduced, and (2) how would the value vary with concentration, if the solution were an ideal solution? We may take question (2) first and may answer at once that the value would not vary with concentration at all. For ΔF will vary with concentration, only because it contains the cratic part $+2RT \ln x$; and since this is canceled by the second term in (94), we conclude that (94) has a fixed value characteristic of the solute dissolving in the given solvent.

Turning now to the non-ideal ionic solution, we may answer question (1) by saying that the value of (94) will vary with concentration, only insofar as the solution differs from an ideal solution—in other words, only insofar as the communal term differs from the cratic term. Now in the extremely dilute range this difference is negligible, and we must conclude that in this range the value of (94) will be a *constant* within the experimental error; it is in fact N times the unitary quantity L, characteristic of the uni-univalent solute dissolving in the given solute at the given temperature. This constant value adopted by (94) in extremely dilute solutions may conveniently be written as the limiting value as x tends to zero, thus

$$\lim_{x \to 0} (\Delta F - 2RT \ln x) \tag{95}$$

Since in these extremely dilute solutions the mole ratio y does not differ appreciably from x, (95) may equally well be written

$$\lim_{y \to 0} (\Delta F - 2RT \ln y) = NL \tag{96}$$

Finally, since $y = m/M$, we may add the constant quantity $2RT \ln M$ to both sides of (96), and obtain

$$\lim_{m \to 0} (\Delta F - 2RT \ln m) = NL + 2RT \ln M \tag{97}$$

The left-hand side of (97) is just the usual standard free energy of solution ΔF^0. We see that

$$L - \frac{\Delta F^0}{N} = 2kT \ln M \tag{98}$$

in agreement with (86).

Dividing (94) by Avogadro's constant, let us proceed to ask how the quantity

$$\frac{\Delta F}{N} - 2kT \ln x \tag{99}$$

varies with concentration in less dilute solutions. As soon as we go to progressively higher concentrations lying outside the extremely dilute range, (99) is no longer constant and equal to L but differs from L by progressively greater amounts. Let us write

$$\frac{\Delta F}{N} - 2kT \ln x = L + \mathbf{d}_x \tag{100}$$

Here $\mathbf{d}_x$ is the disparity between the free energy per ion pair added to the non-ideal solution and the free energy per ion pair added to the corresponding ideal solution. It is the disparity between the communal term in the free energy and the cratic term in the free energy. In the solution of this uni-univalent solute the total communal term is equal to

$$2kT \ln x + \mathbf{d}_x \tag{101}$$

56. The Disparity of a Solution. We may begin to use the word *disparity* in a technical sense, for the quantity defined above, and to speak of $\mathbf{d}_x$ as the disparity of the solution when the mole fraction of the solute is x. In dilute ionic solutions the sign of $\mathbf{d}_x$ is always negative. The effect of the interionic forces is that ions added to a dilute solution always lose more free energy than they would when added to the corresponding ideal solution; hence the total communal term is *less* than the cratic term.

We shall be interested in the magnitude of $\mathbf{d}_x$ in comparison with kT. We may say that, when $-\mathbf{d}_x$ is less than one quarter of kT, the solution is dilute; and, when $-\mathbf{d}_x$ is less than $0.002kT$, we may say that the concentration lies in the extremely dilute range. For a uni-univalent solute let us define a number f, a function of the concentration, by writing

$$\frac{\mathbf{d}_x}{kT} = 2 \ln f \tag{102}$$

Substituting in (100) we have

$$\frac{\Delta F}{N} - 2kT \ln fx = L \tag{103}$$

At every concentration f must be given that value which makes the left-hand side of (103) constant and equal to L; here f is the usual activity coefficient for use with mole fractions. When, for example $-\mathbf{d}_x$ is equal to $0.23kT$, we have

$$\log f = -0.05 = \bar{1}.95 = \log\,(0.89) \tag{104}$$

Hence, when $-\mathbf{d}_x$ is less than $0.23kT$, the value of f lies between 0.89 and 1.00. Similarly when $-\mathbf{d}_x$ is equal to $0.002kT$, we have $\ln f = -0.001$, whence f is approximately equal to 0.999. In the whole range of solutions, where $-\mathbf{d}_x$ is less than $0.002kT$, the value[1] of the activity coefficient f varies only in the narrow range between 0.999 and 1.000. We call this the range of extremely dilute solutions.

Turning next to the quantity

$$\frac{\Delta F}{N} - 2kT \ln y$$

we recall that in the extremely dilute range this is independent of the concentration. But, as soon as we leave the extremely dilute range, this is likewise no longer constant but differs from L by progressively

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[1] In an aqueous solution at 25°C containing c moles/liter of a uni-univalent solute the value of $\mathbf{d}_x$ according to Debye-Hückel theory is given by $\mathbf{d}_x/kT = -1.02\sqrt{c}$.

larger amounts. Let us write

$$\frac{\Delta F}{N} - 2kT \ln y = L + \mathbf{d}_y \tag{105}$$

In all dilute solutions the disparity $\mathbf{d}_y$ will be negative and will have a value nearly equal to that of $\mathbf{d}_x$. Since, however, at any concentration the value of y is slightly larger than that of x, it follows that $\mathbf{d}_y$ in (105) must have a slightly larger negative value than $\mathbf{d}_x$. We are again interested in the magnitude of $\mathbf{d}_y$ in comparison with kT. Let us define a function γ such that at every concentration

$$\frac{\mathbf{d}_y}{kT} = 2 \ln \gamma \tag{106}$$

Substituting in (105), we have

$$\frac{\Delta F}{N} - 2kT \ln \gamma y = L \tag{107}$$

Finally, multiplying by Avogadro's constant, and subtracting from both sides the constant quantity $2RT \ln M$, we obtain, since $y = m/M$

$$\Delta F - 2RT \ln \gamma m = NL - 2RT \ln M = \Delta F^0 \tag{108}$$

In agreement with (98), the left-hand side is just the standard free energy of solution ΔF^0. Here γ, as defined by (106), is the usual activity coefficient on the molality scale. In particular, when the solid is in contact with its saturated solution, there is no change in the free energy when additional ions are taken into solution. In this case, if in (108) we write m_{sat} and γ_{sat}, the values of m and γ in the saturated solution, we may set ΔF equal to zero. This will be discussed in Sec. 100.

57. The E.M.F. of Galvanic Cells. In Fig. 9*b* of Chapter 2 we considered the removal of an ion from a metal surface into a solvent or very dilute solution—a process that is very important in the working of galvanic cells. Now it has long been recognized that the e.m.f. of a cell is determined by changes in the free energy that would accompany the flow of a current, if a current were allowed to flow. If we regard the cell as consisting of two half-cells, the total change in the free energy is equal to the sum of the contributions from each half-cell.

In this connection it is important to consider the ΔF of the process depicted in Fig. 9*b*. For each successive ion taken from the metal into a very dilute solution, work equal to Y must be done. Thus Y provides a unitary term and, at the same time, there will be in ΔF a cratic term depending on the concentration of the solution. At the electrode in the other half-cell, either positive ions are being removed from solution, when a current flows, or an equivalent number of negative ions are entering the solution. Let us consider a cell of the latter type containing a completely dissociated uni-univalent solute. Each half-cell provides a unitary term and a cratic term. Several cells of this type will be discussed in Chapter 13.

Referring to Fig. 9, it will be recalled that the curve of Fig. 9*b* differs from the curve of Fig. 9*a* because, when the ion is introduced into the solvent, the molecular dipoles in the co-sphere of the ion lose a certain amount of free energy. The co-sphere of each ion thereby makes a contribution (positive or negative) to the e.m.f. of the cell. For each ion added or removed, the cratic term likewise makes a contribution to the e.m.f. $\mathcal{E}$ of the cell.

Suppose now that we build a series of cells, alike in all respects save that the (very dilute and completely dissociated) solute has a different concentration in each cell. If the cells are alike in all other respects, the unitary terms must be the same in each cell; the values of the e.m.f. for the various cells will differ owing to the difference in the communal terms. In very dilute solutions the contribution made to each communal term by the interionic forces will be small, and the dependence of the e.m.f. on the concentration will arise almost entirely from the cratic term which, for each solute species, may be written $-kT \ln y$ or $-kT \ln x$. Since we are considering a uni-univalent solute, the numerical values of y_+ and y_- for the positive and negative ions will both be the same as the mole ratio of the solute.

From (59) we can then make the following prediction: if the e.m.f. of each cell in this series is measured, it will be possible to represent the values for those cells containing the most dilute solutions very nearly by an expression of the form

$$e\mathcal{E} = \text{constant} - 2kT \ln y \tag{109}$$

where the constant term contains the unitary quantities from the ionic co-spheres, and where the last term is the sum of the cratic terms $-kT \ln y_+$ and $-kT \ln y_-$ for the positive and the negative ions. If we introduce a quantity $\mathcal{E}^0$, writing $e\mathcal{E}^0$ for the constant term, (109) takes the form

$$e\mathcal{E} = e\mathcal{E}^0 - 2kT \ln y \tag{110}$$

Since in practice we cannot use extremely dilute solutions, the e.m.f.'s will be given by

$$e\mathcal{E} = e\mathcal{E}^0 - \mathbf{d}_y - 2kT \ln y \tag{111}$$

where the magnitude of the disparity $\mathbf{d}_y$ progressively increases as we go to progressively higher concentrations. Hence from (106) we obtain

$$\mathcal{E} = \mathcal{E}^0 - \frac{2kT}{e} \ln \gamma y \tag{112}$$

$$= \mathcal{E}^0 - \frac{2RT}{\mathfrak{F}} \ln \gamma y \tag{113}$$

since the faraday $\mathfrak{F}$ is equal to the electronic charge e multiplied by Avogadro's constant. The expression for the e.m.f. begins to have a familiar appearance, except that usually the molality m is introduced rather than the mole fraction y. In order to make this adjustment, we may introduce a different expression for the constant term, writing

$$e\mathcal{E}^0 = e\mathcal{E}_0 - 2kT \ln M \tag{114}$$

Then (112) and (113) take the form

$$\mathcal{E} = \mathcal{E}_0 - \frac{2kT}{e} \ln (\gamma M y) \tag{115}$$

$$= \mathcal{E}_0 - \frac{2RT}{\mathfrak{F}} \ln \gamma m \tag{116}$$

Here, as usual, the activity coefficient γ takes into account two things: (1) that the solution differs from the corresponding ideal solution, and (2) that, even if the solution were ideal, ln x in the cratic term has been replaced by ln y, which is justified only in very dilute solutions.

In this series of cells the e.m.f.'s will be given by (116). Suppose now that, from this series of cells, we take any two, and put them back to back, connecting together their positive terminals, and then closing the circuit by connecting together the negative terminals through a high resistance. A small current will flow. Since the e.m.f.'s of the cells are different, one must be the greater; and the cell which has this greater e.m.f. will force a current to flow through the other cell. In the two cells, equivalent processes will take place in opposite directions. In fact, we can say that the processes taking place in opposite directions are identical, except that the solutions mentioned above do not have the same concentration. During the flow of current, while ions are entering one solution, an equal number of ions of the same species are being deposited from the other solution; in other words, solute is gradually removed from one solution and, at the same time, an equal amount of the same solute is gradually added to the other solution. The net result is that, during the flow of current, solute is continually transferred from one solution to the other. There is no difficulty in deciding in which direction the transfer takes place. Obviously the solute will be transferred from the less dilute to the more dilute solution since, according to (59), this results in a loss of free energy by the system.

As a numerical example, let us suppose that the loss of free energy, per ion pair transferred, amounts to 10^{-13} erg—that is to say, 62.4×10^{-3} electron-volt. In this case, if we were to measure net e.m.f., driving the current, we should find the e.m.f. to be 62.4 millivolts This must be so, since the change of free energy of one electron-volt per ion pair necessarily gives rise to an e.m.f. of 1 volt, the electron-volt being defined as the work required to take an electronic charge through a potential difference of 1 volt. Conversely, an e.m.f. of 1 millivolt signifies a free energy change amounting to 1 milli-electron-volt per ion pair.

The same remarks can be made about each part of the e.m.f., separately. The unitary part of the e.m.f., expressed in volts, is numerically equal to the unitary change in the free energy, expressed in electron-volts per ion pair. At the same time, the cratic term in the e.m.f., expressed in volts, is numerically equal to the cratic change in the free energy, expressed in electron-volts per ion pair. A similar statement can be made about the interionic part; but we are usually interested in the value of the e.m.f., extrapolated to extreme dilution, where this part is negligibly small.

Problem

The heat of solution of silver bromide in water at 25°C is 20,150 cal/mole. Taking the value of the entropy and the solubility of the crystalline solid from Tables 44 and 33, find by the method of Secs. 48 and 49 the difference between the unitary part of the partial molal entropy of the bromide ion Br^- and that of the iodide ion I^-.

CHAPTER 7

Different Types of Proton Transfers. Molecular Ions. The Electrostatic Energy. The Zwitterions of Amino Acids. Autoprotolysis of the Solvent. The Dissociation Constant of a Weak Acid. Variation of the Equilibrium Constant with Temperature. Proton Transfers of Class I. Proton Transfers of Classes II, III, and IV. The Temperature at Which ln K_r Passes through Its Maximum. Comparison between Theory and Experiment. A Chart of Occupied and Vacant Proton Levels.

58. Different Types of Proton Transfers. In Sec. 51 we introduced U, the characteristic unit in any process—the unitary part of the free energy change. In the various processes U stands for D, L, J, or Y. In Sec. 80, in treating molecular ions, we shall say something about D, the work to dissociate a molecular ion in aqueous solution. In Chapter 12 we shall give a fuller treatment of the quantity L, the work required to take ions from a crystal surface into a solvent. In Chapter 13 we shall likewise consider the process of transferring ions from one solvent to another. But the present chapter will be devoted to a thorough discussion of the unitary quantity J, the work required to carry out a proton transfer in a solvent.

In this discussion we shall need to go right back to Chapter 1 and shall need to put together various aspects of ionic processes that have been considered separately in the preceding six chapters. In Sec. 15 we noticed that the relation between equations (26) and (25) was precisely the same as the relation between the equations (19) and (18) that had been obtained in Chapter 1. In Sec. 17 we discussed one type of proton transfer, which involved the formation of two ions at a great distance apart; and in the footnote to Sec. 17 it was pointed out that the discussion of equation (27) given in Sec. 15 will apply to the electrostatic part of J. Proton transfers were also considered in Sec. 31; but hitherto we have examined only the type

$$AH + B \rightleftarrows A^- + (BH)^+ \tag{117}$$

where two neutral particles are converted into a pair of singly charged ions of opposite sign. We must now make a list of other possible types. In each case we shall suppose that the particles are in extremely dilute solution.

1*a*. The proton may be transferred from a neutral particle to a distant negative ion, thus

$$AH + B^- \rightleftarrows A^- + BH \tag{118}$$

Hereby the negative ion becomes a neutral molecule, and the original neutral molecule becomes a negative ion. The original dilute solution must, of course, contain, in addition to the ions B^-, sufficient positive ions to neutralize their negative charges; these positive ions take no part in the reaction. As far as the ionic fields are concerned, the net result is that the field of one negative ion disappears and is replaced by the field of a different species of negative ion.

1*b*. In (118) either AH or BH may denote a solvent molecule. If AH denotes a water molecule and B^- denotes a (H_2PO_4) ion, we should have

$$H_2O + (H_2PO_4) \rightleftarrows (OH)^- + H_3PO_4 \tag{119}$$

In (118) if BH denotes a solvent molecule and AH denotes a H_3PO_4 molecule, the reaction is merely (119) written down from right to left. We shall need some convention for deciding in which way the reaction should be written.

2*a*. The proton may be transferred from a positive molecular ion to a distant neutral particle, thus

$$(AH)^+ + B \rightleftarrows A + (BH)^+ \tag{120}$$

Hereby the initial positive ion becomes a neutral particle and the initial neutral particle becomes a new species of positive ion. The initial dilute solution must have contained sufficient negative ions to neutralize the positive charges; these negative ions take no part in the reaction. As far as the ionic fields are concerned, the field of one species of positive molecular ion is replaced by that of another.

2*b*. In (120) either B or A may denote a solvent molecule. In an aqueous solution of NH_4Cl, for example, B in (120) may denote H_2O, and $(AH)^+$ may denote $(NH_4)^+$. In this case the process is

$$(NH_4)^+ + H_2O \rightleftarrows NH_3 + (H_3O)^+ \tag{121}$$

3*a*. The proton may be transferred from a negative molecular ion (containing a proton) to a distant neutral particle; thus

$$(AH)^- + B \rightleftarrows A^= + (BH)^+ \tag{122}$$

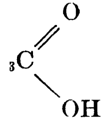
eby a doubly charged negative ion is created. The initial solution ıt again have contained positive ions that take no part in the reaction.

). In (122) B may denote a solvent molecule. In an aqueous solu- of $NaHSO_4$, for example, if B denotes H_2O and $(AH)^-$ denotes the $O_4)^-$ ion, we have

$$(HSO_4)^- + H_2O \rightleftarrows (SO_4)^= + (H_3O)^+ \tag{123}$$

ton transfers in aqueous solution were first divided into these three ɜs by Wynne Jones.[1]

). Molecular Ions. Before adding other variants to this list, it will ɔonvenient to pause here and study various aspects of the types ch have already been listed. First, something should be said about molecular ions that occur in these reactions. Although in earlier ɔters some molecular ions have been mentioned, we have not yet to consider any in detail. In discussing ionic fields we have merely ɔosed that each ion was roughly spherical with a radius *a*. When ı an ion is in a solvent, the important question is how close the adja- solvent dipoles can approach to the ionic charge. In Sec. 32 we that, if a_m is the radius of a water molecule, the centers of the H_2O)les that are in contact with the ion will lie on a sphere of radius $\vdash a_m)$.

n the other hand, we must recognize that, in many large molecular tive and negative ions, the ionic charge is confined to an atom ;roup of atoms in the molecular ion. In the acetic acid molecule  the proton vibrates within the electronic structure of one of oxygen atoms, the other oxygen atom being attached to the carbon n by a double bond.[2] When the proton has been removed and we sider the ionic field in the co-sphere of the $(CH_3COO)^-$ ion, the size he whole molecular ion is unimportant. The question is again how e the adjacent solvent dipoles can approach to the ionic charge. center of a solvent dipole cannot approach closer than $(a + a_m)$, re *a* is the radius of the atom or group of atoms that actually bears ionic charge. In the acetate ion this *a* is small compared with the of the whole molecular ion; see Sec. 84.

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[1] W. F. K. Wynne Jones, *Proc. Roy. Soc.*, **140A**, 448 (1933).

[2] [n sodium formate, and in various COOH groups, the distance between the carbon oxygen nuclei is found to be about 1.27 angstroms, the O—C—O angle being in neighborhood of 125°. L. Pauling, "The Nature of the Chemical Bond," 2d ed.,)2, Cornell University Press, 1940.

60. The Electrostatic Energy. In Chapter 2 we drew attention to the fact that, when a proton transfer (117) has been carried out in a solvent, the electrostatic fields of two ions have been created; and work must have been done to supply the amount of energy associated with these ionic fields. Let us now compare (117) with the process (123), both in aqueous solution at the same temperature. In both cases an $(H_3O)^+$ ion will be formed; but in (123), when the proton is removed from the $(HSO_4)^-$ ion, we have to separate the particles against the mutual attraction of the proton and the doubly charged ion $(SO_4)^{=}$. Consequently, more work must be done against the electrostatic forces of attraction than in the removal of a proton from a neutral particle.

Let us express this result in terms of the energy associated with the ionic fields. As far as the positive ion is concerned the amount of energy is the same in each case. Turning next to the negative ions, we recall that in a vacuum the amount of energy in the field of a charged sphere varies with the square of the charge. To estimate the amount of energy associated with a $(SO_4)^{=}$ ion in a vacuum we should first have to know the effective radius to be used. In solution we cannot say more than that we expect the amount of energy to be considerably larger than that associated with the co-sphere of a singly charged ion in the same solvent at the same temperature. The total work to transfer a proton from a $(HSO_4)^-$ ion to a distant water molecule will depend also on the relative binding energy of the proton in these two particles. But, as far as the electrostatic part of the work is concerned, we expect this part to be larger for the type (123) than for the type (117) in the same solvent at the same temperature.

In contrast to this result, consider the types (120) and (118). In (118) we have initially a certain amount of energy associated with the ionic field of the negative ion B^-; and after the proton transfer we have instead a certain amount of energy associated with the field of the ion, A^-. The latter amount may be greater than or less than the former, depending on the effective radii of the atoms or groups of atoms that bear the ionic charges. If the energy associated with the ion A^- is somewhat the greater, at least a small amount of electrostatic work must be done to transfer the proton from AH to B^-. We reach, however, the important conclusion that in such a proton transfer it is very unlikely that the amount of electrostatic work will be as large as in the type (117), where we have to set up the ionic fields of two new ions.

In a particular case of (118) it may happen that the amounts of energy associated with the two ionic fields are nearly equal; such a proton transfer may be called *nearly isoelectric.* If in (118) the energy associated with the field of A^- is less than that associated with B^-, electrostatic work would have to be done to transfer the proton in the reverse direction from BH to A^-.

Turning next to the processes of the type (120), it is clear that the relevant discussion will be quite similar to the above. Initially in (120) we have a certain amount of energy in the co-sphere of the ion $(AH)^+$, and afterward we have instead an amount of energy in the co-sphere of the distant ion $(BH)^+$; and the question is whether one of these is greater than the other. When one amount is greater than the other, the excess is, in any case, likely to be small compared with the work required to carry out a proton transfer of type (117) which involves setting up two new ionic fields. The difference between the fields of $(AH)^+$ and $(BH)^+$ is most likely to be small when these ions are of roughly the same size. Now, in the ion $(NH_4)^+$, 10 electrons move round the nuclei, and likewise 10 electrons in the ion $(H_3O)^+$; these ions should therefore be of nearly the same size, and in (121) we expect only a small amount of electrostatic work in carrying out the proton transfer (either from left to right or from right to left).

We have said nothing about the total amount of work required in these processes. Even in an isoelectric transfer there may, of course, be any amount of work to be done against the quantum-mechanical forces. The question may be reasonably asked, why we have gone to so much trouble to draw attention to the electrostatic energy, when the observed equilibrium is determined by the value of the total energy. The answer is that in discussing any ionic field the electrostatic energy is sensitive to the environment of the ion. On the other hand, as mentioned in Sec. 31, the binding energy of a proton in a molecule depends on internal factors, and the quantization of the molecule is not sensitive to the environment.

When an ion is in a solvent, the energy associated with its ionic field, being sensitive to the environment, is sensitive to the temperature of the solvent, as we saw in (19). On the other hand, quantum-mechanical forces will be relatively insensitive to the temperature of the solvent. The electrical analogue of magnetic heating and cooling arises entirely, or almost entirely, from the interaction between the ion and the solvent in its co-sphere.

When accurate measurements of the dissociation of weak acids were first made over a wide range of temperature, so many different types of behavior were found that the results could not easily be explained. It was only when the proposal was made to separate the quantum-mechanical part of the energy from the part that is sensitive to temperature, that the mechanism underlying the wide variety of behavior could to a large extent be understood.

61. The Zwitterions of Amino Acids. Now that we have decided what aspects are important, we may mention some other types of proton transfers. Consider, for example, the positive ion $NH_3^+CH_2COOH$ of glycine. If we transfer the proton from the carboxyl group to a distant water molecule, we have

$$NH_3^+CH_2COOH + H_2O \rightarrow NH_3^+CH_2COO^- + (H_3O)^+ \qquad (124)$$

As in (121) a proton has been removed from a positive molecular ion, leaving behind a particle which is, as a whole, electrically neutral, though, in this case, it bears charges to opposite sign on its two ends. The initial positive ion is replaced by a new species of positive ion, the distant $(H_3O)^+$. When the proton has been removed to a great distance, the lines of force around the $NH_3^+CH_2COO^-$ particle will have a pattern similar to the familiar magnetic lines of force of a bar magnet. At any distant point in this field the density of energy will be given by the usual expression. The total energy in this field will not be so large as that associated with the fields of two small separate ions; we may expect the value to be perhaps half as great. This will be the amount of electrostatic work done in transferring the proton, if the field of the $(H_3O)^+$ ion roughly cancels that of the initial positive ion.

We can reach the same conclusion by another argument. The proton transfer (124) may be described by saying that, while the proton is being removed from the COOH group, it is meanwhile subject to repulsion from the permanent positive charge on the NH_3^+ group. This repulsion assists the removal of the proton; hence we reach the same conclusion as before—the work that has to be done against the electrostatic forces is somewhat smaller than in the type (117).

Similar remarks apply to the proton transfer

$$H_2O + NH_2CH_2COO^- \rightarrow (OH)^- + NH_3^+CH_2COO^- \qquad (125)$$

which is similar to the type (118), in that an initial negative ion is replaced by another species of negative ion, leaving a particle which is, as a whole, neutral. During the transfer of the proton it is subject to attraction from both negative ions, but in opposite directions. A certain amount of work must be done to set up the field of the $NH_3^+CH_2COO^-$ particle, as before.

The equilibrium constant of the proton transfer (125), omitting the activity of the H_2O, is known as the base dissociation constant and is denoted by K_B, to distinguish it from the K_A of (124).

The removal of the proton in (124) may be followed by the transfer of a second proton, again to form a $(H_3O)^+$ ion, thus

$$H_2O + NH_3^+CH_2COO^- \rightarrow (H_3O)^+ + NH_2CH_2COO^- \qquad (126)$$

In this process we obtain two ions of opposite sign, as in (117). But the electrostatic work is not so large as in (117) because there is initially the energy in the field surrounding the $NH_3^+CH_2COO^-$ particle, and only the additional amount of energy has to be supplied.

To sum up the discussion of electrostatic energy in these processes, we can say that we have noticed four different types. The work done against electrostatic forces is likely to be the largest in the type (123) and the smallest in (118) and (120); while in (117) it should be larger than in (124), (125), or (126). We may label these four classes as I, II, III, and IV, where the value of the electrostatic contribution is near zero in class I and is greatest in class IV. The first dissociation of a weak acid will normally fall in class III, and the second dissociation in class IV, though we must not forget that the amount of energy in the field of a molecular ion depends on the size of the atom or group of atoms in the ion over which the charge is distributed. When this group of atoms is unusually large, as in the picrate ion, the electrostatic energy will be unusually small.

62. Autoprotolysis of the Solvent. While studying these proton transfers, there is another type that may be discussed at the same time, namely, the self-dissociation of the solvent itself. As is well known, highly purified solvents show at least a small electrical conductivity. In methanol, for example, it is generally recognized that this conductivity arises from the fact that a certain number of protons have been transferred according to the process

$$CH_3OH + CH_3OH \rightleftarrows (CH_3O)^- + (CH_3OH)^+ \tag{127}$$

In water it arises from the equilibrium

$$H_2O + H_2O \rightleftarrows (OH)^- + (H_3O)^+ \tag{128}$$

In any pure liquid, the transfer of a proton from one molecule to another (distant) molecule has been named *autoprotolysis.* In any solvent this process creates a positive and a negative ion and must clearly belong to class II; it will not differ from other proton transfers of class II except for the fact that the relation between K_x and K will be different. On the left-hand side of (127) and (128) there is no solute particle; hence the increase in the cratic term is greater than in (119) or (121). In (128) we have $\Delta q = +2$, and

$$\ln K_x = \ln K - 2 \ln M \tag{129}$$

63. The Dissociation Constant of a Weak Acid. In Sec. 36 two experimental methods by which proton transfers may be studied were mentioned—the spectrophotometric method, and the measurement of electrical conductivity. Both these methods are capable of yielding equilibrium constants of high accuracy. But most of the investigations that have been made over a wide range of temperature have been through measurements of the e.m.f. of cells, using a hydrogen electrode. Some details of this method will be given in Chapter 13, where the e.m.f. of other cells will also be discussed. Here we may merely say that a measurement with the hydrogen electrode in an aqueous solution containing $(H_3O)^+$ ions yields a result that may be interpreted as a measure of the activity of the hydrogen ions in the solution. In a very dilute solution the activity on the molality scale differs little from the molality itself; if therefore the source of these hydrogen ions is a known amount of a certain weak acid, a provisional value for the activity of the undissociated portion of the acid can be estimated, and hence a provisional value in (89) for the dissociation constant $K = a_2a_3/a_1$.

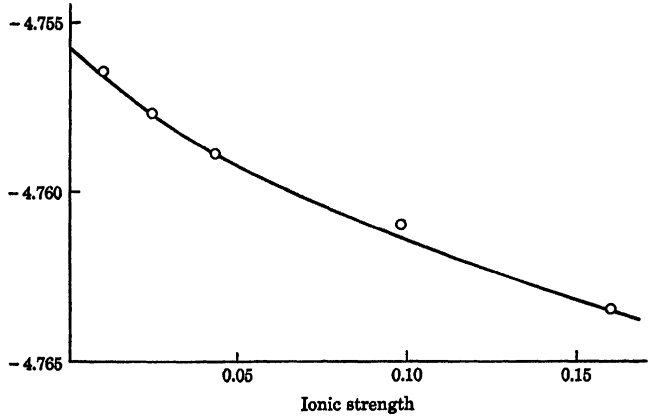

FIG. 33. Extrapolation to zero ionic strength of the equilibrium constant of acetic acid in aqueous solution at 25°C.

When the measurements have been made in dilute solutions, only a small extrapolation is required, to obtain the value of K at extreme dilution. Figure 33 shows this extrapolation for the dissociation of acetic acid in aqueous solution at 25°, the values of $\log K$ being plotted against the ionic strength. The point at which the curve meets the axis gives the value $K = 1.754 \times 10^{-5}$, while the last two experimental points correspond to the values 1.752×10^{-5} and 1.747×10^{-5}.

Values obtained in this way for various proton transfers, over a wide range of temperature, are given in Table 9. In some cases equilibrium constants have been accurately determined by measurements of the elec-

TABLE 9

		0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	Reference
Formic	$K \times 10^4$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650	1.607	1.551	a
Acetic	$K \times 10^5$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633	1.589	1.542	b
Propionic	$K \times 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229	1.195	1.160	c
n-Butyric	$K \times 10^5$	1.563	1.574	1.576	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302	1.252	1.199	d
Chloracetic	$K \times 10^3$	1.528	...	1.488	...	...	1.379	...	...	1.230	...	...	...		e
Boric	$K \times 10^{10}$	...	3.63	4.17	4.72	5.26	5.79	6.34	6.86	7.38		8.32	...		f
Phosphoric	$K_1 \times 10^3$	8.968	...	...	...	...	7.516	...	...	...	...	5.495	...		g
	$K_2 \times 10^8$	...	...	...	...	6.056	6.226	6.349	6.430	6.471	6.475	6.439	...	...	
Carbonic	$K_2 \times 10^{11}$	2.36	2.77	3.24	3.71	4.20	4.69	5.13	5.62	6.03	6.38	6.73	...		h
Sulfuric	$K_2 \times 10^2$	...	1.80	...	1.36	...	1.01	...	0.75	...	0.56	...	0.41	...	i
Oxalic	$K_2 \times 10^5$	5.91	5.82	5.70	5.55	5.40	5.18	4.92	4.67	4.41	4.09	3.83	...		j
Malonic	$K_2 \times 10^6$	2.140	2.165	2.152	2.124	2.076	2.014	1.948	1.863	1.768	1.670	1.575	1.469	1.362	k
Water	$K \times 10^{14}$	0.1139	0.1846	0.2920	0.4505	0.6809	1.008	1.469	2.089	2.919	4.018	5.474			
Glycine	$K_A \times 10^3$	...	...	3.94	...	4.31	4.47	4.50	...	4.81	...				l
	$K_B \times 10^5$	...	...	4.68	5.12	5.57	6.04	6.52	6.98	7.43	7.87				m
d-Alanine	$K_A \times 10^3$				...	4.47	4.57	4.66	4.71	4.74	4.76				n
	$K_B \times 10^5$				...	6.90	7.47	8.08	8.61	9.10	9.60			...	o

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[a] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934).
[b] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 652 (1933).
[c] *Ibid.*, p. 2379.
[d] H. S. Harned and R. O. Sutherland, *J. Am. Chem. Soc.*, **56**, 2039 (1934).
[e] D. D. Wright, *J. Am. Chem. Soc.*, **56**, 314 (1934).
[f] B. B. Owen, *J. Am. Chem. Soc.*, **57**, 1526 (1935).
[g] L. F. Nims, *J. Am. Chem. Soc.*, **56**, 1110 (1934).
[h] *Ibid.*, **55**, 1946 (1933).
[i] H. S. Harned and S. R. Scholes, *J. Am. Chem. Soc.*, **63**, 1706 (1939).
[j] I. M. Klotz and C. R. Singleterry, Thesis, Chicago, 1940; T. F. Young and L. A. Blatz, *Chem. Rev.*, **44**, 102 (1949).
[k] H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 3111 (1939).
[l] W. J. Hamer, J. O. Burton, and S. Acree, *Bur. Standards J. Research*, **24**, 292 (1940).
[m] H. S. Harned and W. L. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
[n] B. B. Owen, *J. Am. Chem. Soc.*, **56**, 24 (1934).
[o] L. F. Nims and P. K. Smith, *J. Biol. Chem.*, **101**, 401 (1933).

trical conductivity of the solutions. Values of K_c, the equilibrium constant expressed in terms of concentration, at 25°C are given in Table 10, together with the corresponding values of K_c determined by e.m.f. measurements.

64. Variation of the Equilibrium Constant with Temperature. We know that with rise of temperature the vapor pressure of any solid or liquid increases rapidly. In the same way, when we have a diatomic or a polyatomic gas, partially dissociated into atoms or into ions, the degree of dissociation increases rapidly with rise of temperature. Both these are examples of the tendency for any aggregate to be broken up by the thermal agitation. We may also say that, according to the law of van't Hoff and Le Chatelier, this increase in the dissociation constant with rise of temperature is associated with the fact that, at any temperature, the dissociation of molecules is accompanied by an absorption of heat; or conversely, that recombination to form molecules is accompanied by an evolution of heat. In such a case the degree of dissociation must increase with rise of temperature, as is observed.

TABLE 10. EQUILIBRIUM CONSTANTS FOR PROTON TRANSFERS IN AQUEOUS SOLUTION AT 25°C

Acid	$K_c \times 10^5$	
	From conductance measurements[a]	From e.m.f. measurements
Carbonic K_1. . .	0.0431	0.0452[b]
Acetic	1.753	1.749
Chloracetic	139.6	137.4
Propionic	1.343	1.332
n-Butyric	1.506	1.510

Let us turn next to molecules in solution. As already pointed out more than once, when a solute molecule exists, this is because a certain amount of work is required to split the molecule into two or more atoms or ions. The situation here is the same as in a gas; and at first sight, we should expect that with rise of temperature any increment in the thermal energy would in every case tend to break up the molecules, leading in every case to a steady increase in the dissociation constant with rise of temperature, just as we find in a gas or vapor. A glance at Table 9

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[a] D. A. MacInnes, "Principles of Electrochemistry," Chapter 18, Reinhold, 1939

[b] D. A. MacInnes and D. Belcher, *J. Am. Chem. Soc.*, **55**, 2630 (1933); the other values in this column have been taken from Table 9, using the relation $K_c = \rho K$, where ρ is the density of the solvent.

shows that, although some weak acids behave in this normal way, in several cases the behavior is quite different. Although the values given in the Table 9 for metaboric acid and for carbonic acid show a steady increase, it will be seen that the values for chloracetic acid fall from 1.528×10^{-3} at 0°C to 1.229×10^{-3} at 40°C, while the values for phosphoric acid fall from 8.983×10^{-3} to 6.439×10^{-3} at 50°C. The values for chloracetic acid are plotted as curve *a* in Fig. 34. On the other hand, it will be seen from Table 9 that the values given for formic acid, acetic

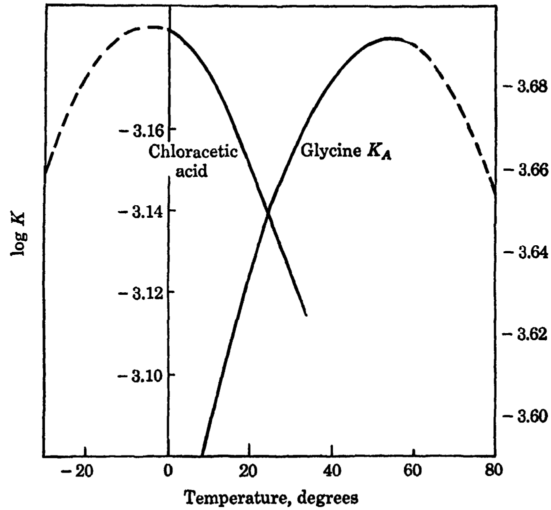

FIG. 34. The logarithm of the equilibrium constants plotted against the temperature centigrade

acid, and propionic acid first increase, pass through a maximum, and then decrease, as the temperature rises. The temperature at which the value of K passes through a maximum is usually denoted by Θ. The small circles in Fig. 41 show the experimental results for acetic acid. When a parabola is fitted to the results, the maximum is found to lie at $\Theta = 22.6$°C.

In the two sets of results plotted in Fig. 34 no maximum is observed in either case within the range of temperature covered by the experiments; nevertheless, in both cases the values appear to be tending toward a maximum lying just outside the experimental range, namely, at −5.4°C for chloracetic acid, and at 53.9 for glycine. In 1934, Harned and Embree, surveying all the data (in Table 9) that had been obtained up to that time in aqueous solution, found a remarkable uniformity in all the proton transfers: when a parabola of the form

$$\log K - \log K_{\max} = p(T - \Theta)^2 \tag{130}$$

was fitted to a set of results, for all the proton transfers investigated a single value of p, namely,

$$p = 5 \times 10^{-5} \tag{131}$$

was found to fit the experimental values very well.[1] Since then this has been extended to include all the substances in Table 13, with one exception. Only in the case of boric acid did the results appear to be anomalous; in this case it was necessary to use $p = 8 \times 10^{-5}$ instead of (131).

It will be seen that most of the dissociation constants in Table 9 lie between 10^{-3} and 10^{-11}. It is of interest to know how much work is required to dissociate any of these molecules or molecular ions, transferring a proton to a distant water molecule. Using (91) in the form

$$J = -kT \ln K_x \tag{132}$$

let us evaluate J in some typical cases. The value $K = 8.983 \times 10^{-3}$ mentioned above for H_3PO_4 at 0°C is one of the largest in Table 9. Using (86) we find $-kT \ln K_x$ from $\log K$ by means of the formula

$$-kT \ln K_x = -2.303\, kT\, [\log K - \log (55.51)] \tag{133}$$

For phosphoric acid at 0°C we find the value $J = 0.2056$ electron-volt.

The smallest value of K for any acid in Table 9 is 2.36×10^{-11} for carbonic acid at 0°C. From (132) in this case we find the value $J = 0.6708$ electron-volt. The values of K for the self-dissociation of water, given in Table 9, are still smaller. To calculate J we use (129) instead of (91), and at 60°C obtain the value $J = 1.092$ electron-volts.

The discussion of Sec. 60 led to the suggestion that it might be very useful to divide the characteristic unit J into two parts—a part sensitive to the environment, which may be denoted by J_{env}, and a part insensitive to the environment and independent of temperature, which may be denoted by J_{non}. We shall accordingly write (132) in the form

$$-kT \ln \frac{x_3 x_4}{x_1 x_2} = J_{non} + J_{env} \tag{134}$$

The factors that determine the magnitudes of J_{non} and J_{env} are quite separate and independent; and there is no reason why a small J_{env} should not be accompanied by a large J_{non}, or a large J_{env} accompanied by a small J_{non}. In surveying different species we may therefore expect a wide variety of behavior.

In Sec. 61 we provisionally arranged proton transfers into four classes,

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[1] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1050 (1934).

named I, II, III, and IV, according to the size of the electrostatic contribution. This classification should be very useful to us in applying (134), since the electrostatic contribution belongs entirely to J_{env}, and not at all to J_{non}.

Table 9 includes data on the first dissociation constants of seven weak acids; it will be recalled that we expect these to fall into class III. The table includes the second dissociation constants of five acids, phosphoric, sulfuric, oxalic, malonic, and carbonic, which fall into class IV, while the amino acids glycine and alanine provide four examples that should fall into class II.

Since at equilibrium each of the above reactions may be regarded as taking place in both directions at the same time, we need, as already pointed out, some convention as to the direction in which the reaction shall be written down. Since we wish to fix attention on the electrostatic energy, it is convenient to aim at writing down every process in such a way that, when the reaction takes place from left to right, there is an increase in electrostatic energy, so that a positive amount of work has to be done against electrostatic forces. When this is the case it does not necessarily imply that the total work J is positive. In the process (117), for example, the binding energy of the proton in $(BH)^+$ may be considerably larger than the binding energy of the proton in AH. In this case the energy liberated by quantum-mechanical forces may be more than sufficient to supply the energy required to set up the electrostatic fields of the two ions—that is to say, more than sufficient to separate the electrostatic charges against their mutual attraction. In this case there will be a net liberation of energy instead of work to be done.

We see that, in (134), depending on the relative binding energies, the value of J may be positive or negative. In a particular case we may find J equal to zero. This condition could be satisfied only at a particular temperature, since the electrostatic energy in the ionic field is sensitive to temperature.

65. Proton Transfers of Class I. Writing (132) in the form

$$-kT \ln K_x = J_{non} + J_{env} \tag{135}$$

let us ask, for what type of proton transfer are we likely to find the simplest behavior. Since J_{non} is independent of temperature, clearly the behavior should be simple when J_{env} is zero or near zero. Now, as far as the electrostatic energy is concerned, we have seen that for proton transfers of type (118) and type (120) the contribution to J_{env} may be zero, or near zero.

Experiments are available only over the small range of T between 273 and 333°; let us then ask what behavior will be expected if, over this range of temperature, J may be written in the form

$$J = J_{non} + \alpha T \tag{136}$$

where the value of the parameter α is small. We see that (135) is now

$$-\ln K_x = \frac{J_{non}}{kT} + \frac{\alpha}{k} \tag{137}$$

which is of the form

$$-\ln K_x = \frac{A}{T} + B \tag{138}$$

where A and B are constants. Thus, if J is of the form (136), experimental values of $-\ln K_x$, plotted against $1/T$, will lie on a straight line, in contrast to the curvature shown by all the proton transfers listed in Table 9.

TABLE 11

Anilinium ion[a]

$$(C_6H_5NH_3)^+ + H_2O \rightarrow C_6H_5NH_2 + (H_3O)^+$$

$$-\log K = \frac{1.553 \times 10^3}{T} - 0.614$$

Ortho-chlor-anilinium ion[a] $(C_6H_4ClNH_3)^+$

$$-\log K = \frac{1.33 \times 10^3}{T} - 1.77$$

Ammonium ion[b] $(NH_4)^+$

$$-\log K = \frac{2.706 \times 10^3}{T} + 0.139$$

[a] K. J. Pedersen, *Kgl. Danske Videnskab. Selskab* , **14** (1937); *ibid.*, **15** (1937).

[b] D. H. Everett and W. F. K. Wynne Jones, *Proc. Roy. Soc.* **169A**, 204 (1938).

If any equilibrium constants show this linearity, this behavior is most likely to be found among proton transfers of type (118) and type (120). The expressions for log K given in Table 11 show this linearity; they represent, within the experimental error, the accurate data obtained by measurements on three proton transfers in aqueous solution. All three are of the type (120).

66. Proton Transfers of Classes II, III, and IV. Although, as Table 9 shows, the value of K may decrease with rise of temperature, or may increase, or may pass through a maximum, the tentative theory proposed in Sec. 64 leads to the conclusion that for proton transfers of classes II, III, and IV the value of $-kT \ln K_x$ should in no case decrease or pass through a maximum or a minimum but in every case should increase steadily with rise of temperature. According to (132) the quantity $-kT \ln K_x$ is equal to J, which consists of a part J_{env} increasing with temperature, and a part J_{non} independent of temperature.

This prediction is fulfilled by all the values in Table 9; in every case the value of $-kT \ln K_x$ *increases throughout the range covered by experiment.* Having established this fact, the next step is to look at the rate at which the values of J increase with rise of temperature. For most of the substances in Table 9 values of K are available at 20 and at 40°C. Let us then calculate the values of J at these two temperatures[1] and by subtraction find in each case the increment in J over this range of temperature. From what has been said above we know that we expect the increment in J to depend on whether the proton transfer belongs to class I, II, III, or IV. Though it is true that the electrostatic energy depends to some extent on the radii of the ions involved, we expect to find the largest increments in class IV, the next largest in class III, and so on. On the other hand, the increment in J should not depend on the value of J itself. A large value of J may show a smaller increment than a smaller value of J, if the latter contains a larger J_{env} than the former.

TABLE 12. VALUES OF J IN ELECTRON-VOLTS AT 20 AND AT 40°C

Substance		20°C	40°C	Difference
Class I:	Ammonium	0.6301	0.6364	0.0063
	Anilinium	0.3737	0.3782	0.0045
	Chloranilinium	0.2623	0.2638	0.0015
Class II:	Alanine K_A	0.2380	0.2527	0.0147
	K_B	0.3434	0.3593	0.0159
	Glycine K_A	0.2389	0.2523	0.0134
	K_B	0.3488	0.3648	0.0160
Class III:	Acetic	0.3780	0.4045	0.0265
	Boric	0.6409	0.6755	0.0346
	Butyric	0.3813	0.4100	0.0287
	Formic	0.3196	0.3422	0.0226
	Propionic	0.3848	0.4122	0.0274
	Water	1.0275	1.0584	0.0309
Class IV:	Carbonic K_2	0.7048	0.7431	0.0383
	Malonic K_2	0.4319	0.4656	0.0337
	Oxalic K_2	0.3496	0.3789	0.0293
	Phosphoric K_2	0.5217	0.5548	0.0331

The results are shown in Table 12. Column 2 gives the value of $J = -kT \ln K_x$ at 20°C, while column 3 gives the value at 40°C. The

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[1] The formula for finding the value of J in electron-volts at 20°C in aqueous solution: to the value of $-\log K$ add 1.744 and multiply the result by 0.5827. To find J at 40°C: after adding 1.744, multiply by 0.6213.

last column gives the difference between these two. It will be seen that, with one exception, the values in column 4 fall very clearly into four groups, as expected. The one exception is boric acid, for which, as already mentioned in Sec. 64, the experimental data are anomalous, since the value $p = 8 \times 10^{-5}$ in equation (130) is required to fit the data, instead of the usual value 5×10^{-5}.

The satisfactory result shown in Table 12 suggests that one might give a more detailed and quantitative discussion of the variation with temperature. If we are to do this, we need some standard of comparison with which to compare the experimental results. Just as we compare an imperfect gas with a perfect gas, and compare a non-ideal solution with an ideal solution, so we need a simple standard behavior with which to compare the observed behavior. We obtain this standard behavior if, supposing that J_{env} is almost entirely electrostatic in origin, we take J_{env} to vary with temperature as demanded by the macroscopic dielectric constant ϵ of the medium;[1] that is to say, we assume that J_{env} as a function of temperature is inversely proportional to ϵ. For this standard electrostatic term we may use the notation J_{el} instead of J_{env}.

Now in the neighborhood of room temperature, we have seen in Sec. 8 that for H_2O, D_2O, and for several common solvents, $1/\epsilon$ can be expressed in the form

$$\frac{1}{\epsilon} = \frac{e^{T/\vartheta}}{\epsilon_0} \tag{139}$$

where the ϑ is a temperature characteristic of the solvent. Values of ϑ were given in Table 1, together with those of ϵ_0. If in the standard behavior J_{el} is proportional to $1/\epsilon$, it is clear that (135) will take the form

$$\ln K_x = -C\frac{a + e^{T/\vartheta}}{T} \tag{140}$$

where $Ca = J_{non}/k$ and $Ce^{T/\vartheta} = J_{el}/k$.

67. The Temperature at Which ln K_x Passes through Its Maximum. Consider now the case where $a = 0$, that is to say, where we have pure electrostatic forces, with $J_{non} = 0$. The function $-(e^{T/\vartheta})/T$ passes through a maximum at $T = \vartheta$; for if we differentiate with respect to T, and set the result equal to zero, we have

$$\frac{e^{T/\vartheta}}{T^2} - \frac{e^{T/\vartheta}}{\vartheta T} = 0 \tag{141}$$

that is to say, for pure electrostatic forces, with J_{non} equal to zero, values of ln K would be found to lie on a curve passing through a maximum at

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[1] L. P. Hammett, *J. Chem. Phys.*, **4**, 613 (1936); "Physical Organic Chemistry," p. 83, McGraw-Hill, 1940.

$T = \vartheta$. Curve I in Fig. 35 is a plot of $-(e^{T/\vartheta})/T$ for $\vartheta = 219$. It will be seen that the curve passes through a maximum at 219°K. In Table 1 we saw that the value of ϑ for each of the common solvents lies well below the range of temperature covered by experiment. Addition of a nonelectrostatic contribution J_{non} shifts the position of this maximum. With a positive value of a in (140), the maximum is shifted to a higher temperature, that is to say, toward room temperature. In this way, one accounts for the maximum in log K that has been observed for so many weak acids in aqueous solution. An example is shown in Fig. 35, where curve II is a plot of $-(a/T)$ with $a = +1.5$. On adding the ordinates of curves I and II, we obtain curve III. The effect of adding a small J_{non} has been to shift the position of the maximum downward and to the right. In this case fewer protons will be transferred owing to the increment in J, and the value of log K will pass through a maximum at a temperature near 300°K. It is clear from Fig. 35 that the addition of a larger J_{non} to the given J_{el} would shift the maximum still farther to the right; and by examining (140), we may next decide in what way the position of the maximum should depend on the magnitudes of J_{non} and J_{el}. If we differentiate the right-hand side of (140) with respect to T, and set the result equal to zero, we have

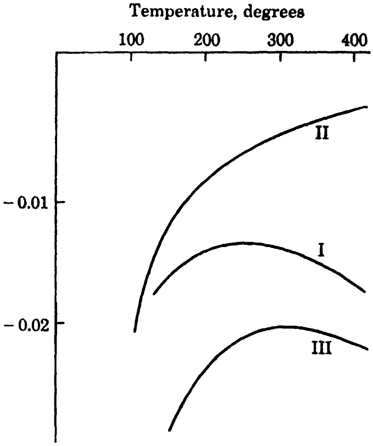

FIG. 35. Curve I is a plot of $-e^{T/\vartheta}/T$ with $\vartheta = 219$; curve II is a plot of $-1.5/T$; and curve III is obtained by adding the ordinates of I and II.

$$\frac{a}{T^2} + \left(1 - \frac{T}{\vartheta}\right)\frac{e^{T/\vartheta}}{T^2} = 0$$

We see that the value of (140) will pass through a maximum at a temperature T^* given by

$$T^* = \vartheta\left(1 + \frac{a}{e^{T^*/\vartheta}}\right) \tag{142}$$

Now according to (140) the quantity $a/e^{T/\vartheta}$ is equal to J_{non} divided by J_{el}. Hence

$$T^* = \vartheta\left(1 + \frac{J_{non}}{J^*_{el}}\right) \tag{143}$$

where J_{el}^{*} is the value of J_{el} at the temperature T^{*}. Thus the position of the maximum depends, not on the value of J, which is $(J_{non} + J_{el})$, or of J_{non} or of J_{el}, but only on their ratio. This is an important result; for if we compare various weak acids, choosing them at random from Table 13, we should find that K passes through a maximum at a temperature that is not correlated at all with the degree of dissociation of the acid; for the latter is, of course, determined by $(J_{non} + J_{el})$.

68. Comparison between Theory and Experiment. The last column of Table 12 gave the difference between the value of J at 313°K and the value of J at 293°K. Since J_{non} is independent of temperature, this difference is the increment in J_{env} between these two temperatures—or if we use (140) it is the increment in J_{el} between these two temperatures. We see then that in class II the value of J_{el} increases by about 0.016 electron-volt in the 20° interval, while in class IV it increases by more than 0.03 electron-volt. In each case, according to (140), the increment in J_{el} is proportional to J_{el} itself; for the increment is

$$C(e^{313/\vartheta} - e^{293/\vartheta})$$

Now the quantity in parentheses is just a number that has the same value in each case; hence the increment is proportional to C and hence proportional to J_{el} itself. Accordingly, the values in the last column of Table 12 imply that for proton transfers in class IV the value of J_{el} is rather more than twice as great as for proton transfers in class II.

We may next ask whether the maxima of K occur at temperatures that are roughly in agreement with those expected from (143). This question may be put in three different forms.

1. Let us first discuss the four proton transfers in class II. We see that in the last column all four values lie near 0.016 electron-volt, indicating that the value of J_{el} is nearly the same in all four cases. On the other hand, we notice from Table 9 that, for both glycine and alanine, the value of K_B is a hundred times smaller than K_A. We must ascribe this to the presence of a larger J_{non} in the basic proton transfer. According to (143) this implies in (130) a greater value of Θ. The observed values of Θ for K_B are near 90°C, while for K_A the values of Θ are smaller, namely 53.9° for glycine and 44.8° for alanine.

2. Table 9 contains six values of K lying between 10^{-5} and 10^{-4}. One of these (oxalic acid) belongs to class IV, three belong to class III, and the remaining two are the values of K_B just discussed. The fact that these six values of K lie between 10^{-5} and 10^{-4} means that the values of J do not differ by more than 20 per cent. Since $J = (J_{non} + J_{el})$, a given value of J may arise from moderate values of J_{non} and J_{el}, or from a larger value of J_{non} combined with a smaller J_{el}, or from a smaller J_{non}

combined with a larger J_{el}. As a result, according to (143) the maximum of K would occur either at a moderate temperature or at a higher temperature or at a lower temperature. We have already seen that the values of Θ for the K_B lie near 90°, while Table 13 shows that the value of Θ for oxalic acid lies at −6.8°, and for the three proton transfers in class III the value of Θ falls near room temperature. In the three classes the maxima occur in the positions that we expect from (143).

3. As another test, we may compare two proton transfers for which Θ happens to fall at almost the same temperature. For phosphoric acid K_2 passes through a maximum at 43.1°, as shown in Table 13, while K_A for alanine falls at 44.8°, as mentioned above. According to (143) this implies that the ratio J_{non}/J_{el} has roughly the same value in these two proton transfers, and therefore that the ratio J/J_{el} has likewise roughly the same value. From the last column of Table 12 we infer that the value of J_{el} for the K_A of alanine is just less than half of the J_{el} for phosphoric acid; in fact, this is true for both the K_A and the K_B of alanine. On looking at the values of J at 20 and 40°, we see that in both cases the value for K_A is indeed rather less than half the value for phosphoric acid, as predicted. (On the other hand, the values of J for K_B betray the presence of a larger J_{non}.) For a qualitative discussion at any rate, we find that (143) has stood up to the three tests rather well.

TABLE 13. CONSTANTS FOR ACIDS IN AQUEOUS SOLUTION[a]

Acid	Θ, °C	$-\log K_\Theta$	Acid	Θ, °C	$-\log K_\Theta$
Phosphoric K_1.	−18.0	2.030	Alanine K_B	88.0	3.933
Glycine K_A .	+53.9	2.309	Glycine K_B .. .	93	3.988
Alanine K_A . .	+44.8	2.330	Oxalic K_2 .	−6.8	4.226
Chloracetic........	−5.4	2.815	Acetic.	22.6	4.756
Formic...........	24.7	3.572	Butyric..... .	8.0	4.803
Glycolic.	30.2	3.830	Propionic . .	20.9	4.873
Lactic... ...	23.5	3.862	Phosphoric K_2 .	43.1	7.189
			Boric	77.0	9.021

[a] H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 50 (1939).

It was pointed out above that, if we choose any two acids at random from Table 9, we are not likely to find any correlation between the position of the maximum of K and the value of K itself. But this would not be true, if we compare two acids, paying due regard to the probable value of J_{non}. Three dissociation constants in Table 9 have values smaller than 10^{-7}; and in all three cases the value of Θ falls above 40°. This is doubtless because, in aqueous solution, such a low degree of dissociation cannot occur without an unusually large value of J_{non}; and the latter has the effect of giving to Θ an unusually large value.

69. A Chart of Occupied and Vacant Proton Levels. With two exceptions, each of the values of J given in Tables 9, 10, and 11 refers to the process where a proton is raised to the vacant proton level of an H_2O molecule from a lower occupied proton level of a species of molecule or molecular ion; in each case the value of J gives the amount by which this initially occupied level lies *below* the vacant level of H_2O. Obviously, using these values, it is at once possible to map out a chart of the proton levels of these various particles in aqueous solution, as has been done in Fig. 36. The two exceptions in Table 9 are the values derived from the K_B of glycine and alanine. In these cases, as shown in (125), a proton is transferred to a vacant level from the ordinary occupied proton level in a water molecule; the value of J gives the amount by which the vacant level lies above this occupied proton level of H_2O.

In the ionic dissociation of water itself, discussed in Sec. 62, the proton is raised to the vacant level of one H_2O molecule from the occupied level of another (distant) H_2O molecule; the value of J at 25°C is very nearly 1 electron-volt, as shown in Table 12. Since both these proton levels of the H_2O molecule are important, two energy scales have been provided in Fig. 36. The scale on the left counts downward from the vacant level of H_2O, while the scale on the right counts upward from the occupied level of H_2O.

In preparing to construct a diagram for these energy levels, the first thing to notice is that each level has two aspects, according as we are thinking of it as an occupied or as a vacant level. When, for example, a proton has been added to an H_2O molecule, an $(H_3O)^+$ ion has been formed; and when we speak of the energy of the occupied proton level of the $(H_3O)^+$ ion, this is merely another name for the energy of the vacant proton level of the neutral H_2O molecule. Moreover, although the hydroxyl ion contains a proton, it has a vacancy for another proton; and if we speak of the energy of the vacant level of the $(OH)^-$ ion, this is the same as the energy of the ordinary occupied proton level of H_2O. In the same way, when we speak of the occupied proton level of the bicarbonate ion $(HCO_3)^-$, the energy of this proton level is the same as the energy of the vacant proton level of the $(CO_3)^=$ ion.

In constructing a diagram to display quantitatively the relationships between the proton levels of various species of particles in the same solvent, it is desirable to label each level with both its names. This has been done for each level in Figs. 36 and 37, the name of the occupied level being given on the left, and the name of the corresponding vacant level being given on the right.

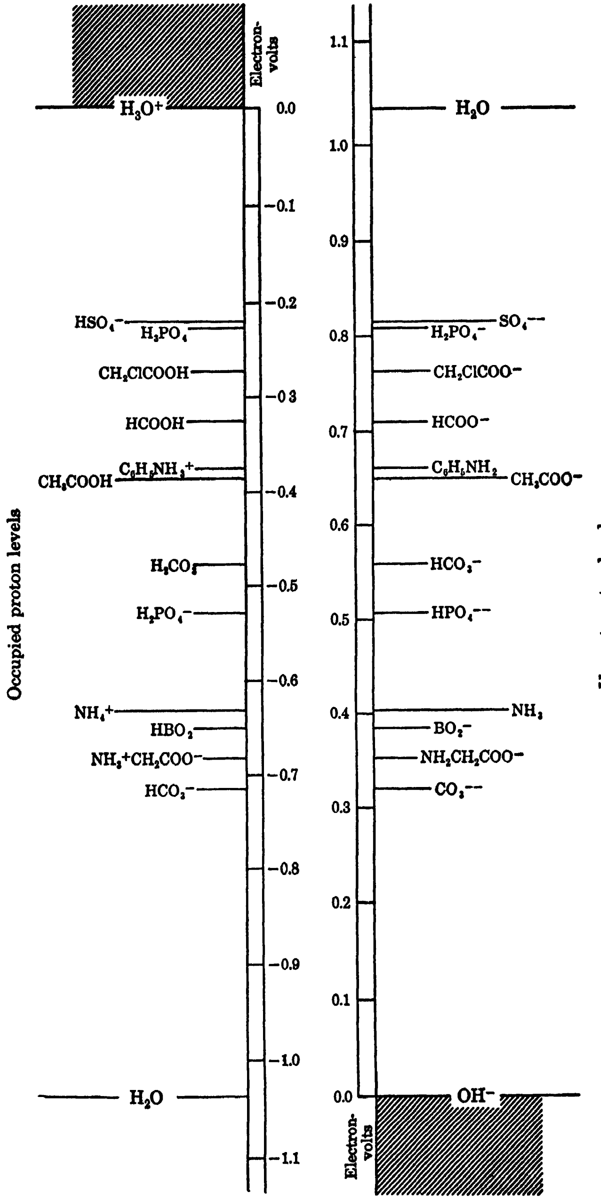

FIG. 36. Values of J in water at 25°C.

In discussing the ionic dissociation of acids in aqueous solution, it was mentioned in Sec. 31 that for the strongest acids the dissociation appears to be complete, not only at the lowest concentrations, but also in moderately dilute solutions. We must suppose that for each of these solute molecules the occupied proton level lies above the vacant proton level offered by a water molecule. In other words, when a distant $(H_3O)^+$ ion has been formed by proton transfer, a certain amount of work would be required to raise the proton from the $(H_3O)^+$ ion to the vacant proton level in the distant anion. In Fig. 36 the occupied proton levels of the HCl, $HClO_4$, and H_2SO_4 molecules in aqueous solution must lie somewhere above the level of $(H_3O)^+$, while in each case the vacant proton level of Cl^-, $(ClO_4)^-$, or $(HSO_4)^-$ lies an equal distance above the vacant level of H_2O. We should like to know, for each acid, the energy of this level, for inclusion in Fig. 36; for there may be wide intervals between the levels of HCl, H_2SO_4, and $HClO_4$. But no method of obtaining direct information on this question has been widely accepted as reliable. In Fig. 36 the correct position of the occupied level of the $(HSO_4)^-$ ion has been shown, but the position of the vacant proton level of the same ion is unknown.

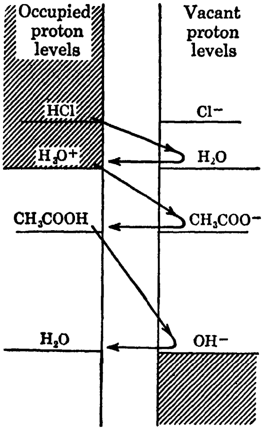

FIG. 37

For the sake of illustration, the proton levels of HCl and Cl^- have been drawn in Fig. 37 a little above the level of $(H_3O)^+$. Starting with the protons in HCl, we can imagine an experiment, in which we cause these protons to fall, by a series of steps, toward the bottom of the diagram. When a little HCl is dissolved in water, the protons from nearly all the HCl molecules will immediately fall to vacant levels in H_2O molecules, to form $(H_3O)^+$ ions, as indicated by the arrows at the top of Fig. 37.

Suppose next that we mix this solution with an aqueous solution containing lower vacant proton levels—say, with an aqueous solution containing an equal quantity of sodium acetate; that is, a solution containing Na^+ ions and $(CH_3COO)^-$ ions. The Na^+ ions do not have an affinity for a proton; but, as shown in Fig. 37, the vacant level of the $(CH_3COO)^-$ ion in aqueous solution lies well below the occupied level of the $(H_3O)^+$ ion. Consequently a proton from nearly every $(H_3O)^+$ ion will very quickly fall, as shown by the next arrows in the diagram, into the vacant level of a $(CH_3COO)^-$ ion, to form a neutral CH_3COOH molecule. From here we can make the protons fall again, if we mix this solution with a solution containing a solute with a lower vacant proton level. Take, for example, an aqueous solution of sodium hydroxide, containing Na^+ ions and $(OH)^-$ ions. The vacant proton level of each $(OH)^-$ ion lies well below the occupied level of neutral CH_3COOH. Hence the protons fall once more, leaving the CH_3COOH molecules to revert to $(CH_3COO)^-$, while at the same time each hydroxyl ion is converted to a neutral H_2O molecule.

In Fig. 37 two areas have been shaded. The area in the upper left corner, where protons in occupied levels are unstable, we have already discussed. In the lower right-hand corner the shaded area is one where vacant proton levels cannot remain vacant to any great extent. In aqueous solution any solute particle that has a vacant proton level lower than that of the hydroxyl ion will capture a proton from the solvent molecule, since the occupied level of the latter has the same energy as the vacant level of a hydroxyl ion. Consequently any proton level that would lie in this shaded area will be vacant only on the rare occasions when the thermal agitation has raised the proton to the vacant level of a hydroxyl ion. On the other hand, there are plenty of occupied proton levels that lie below the occupied level of the H_2O molecule. For example, the occupied level of the NH_3 molecule in aqueous solution lies a long way below that of H_2O.

There are, of course, many substances, soluble in water, whose molecules contain one or more protons, but which, like the NH_3 molecule, show no spontaneous tendency to lose a proton when hydroxyl ions are present. In each of these molecules the energy level occupied by the proton must, as in NH_3, lie below the occupied level of H_2O. If methanol is an example of this class, the vacant proton level of the metholate ion $(CH_3O)^-$ in aqueous solution must lie below the vacant level of $(OH)^-$.

Although we have used Fig. 37 to illustrate the spontaneous falling of protons to lower vacant levels, the values of J given in Table 12 were all obtained from solutions where a small number of protons were thrown up to, and maintained in, higher levels by the thermal agitation. Some more examples of such proton transfers arising from thermal agitation are illustrated in Fig. 38. If, for example, we dissolve in water some Na_2HPO_4, obtaining Na^+ ions and doubly charged $(HPO_4)^=$ ions, the thermal agitation can throw a proton from a solvent molecule into the vacant level of any $(HPO_4)^=$ ion, forming thereby a singly charged $(H_2PO_4)^-$ ion, as indicated by the arrow at the bottom of Fig. 38; this process is called the hydrolysis of the sodium salt. Each proton so transferred from H_2O leaves behind a hydroxyl ion. Since the energy gap between the occupied level of H_2O and the vacant level of $(HPO_4)^=$ is rather large, the thermal agitation at room temperature is not sufficient to maintain more than a few protons in the higher level—that is to say, is not sufficient to convert more than a small fraction of the $(HPO_4)^{=}$ ions into $(H_2PO_4)^-$. The number of protons transferred from water molecules would be still smaller in an aqueous solution of NaH_2PO_4, containing Na^+ ions and $(H_2PO_4)^-$ ions, because in this case the energy gap between the occupied level of H_2O and the vacant level of the negative ion is still wider.

In Fig. 38 it will be seen that for the $(H_2PO_4)^-$ ion there are two entries, one for its occupied proton level and one for its vacant proton level. In the aqueous solution of NaH_2PO_4 under consideration the thermal agitation can throw a proton from one $(H_2PO_4)^-$ ion into the vacant level of another $(H_2PO_4)^-$ ion in the same solution, forming thereby a neutral H_3PO_4 molecule, according to the process:

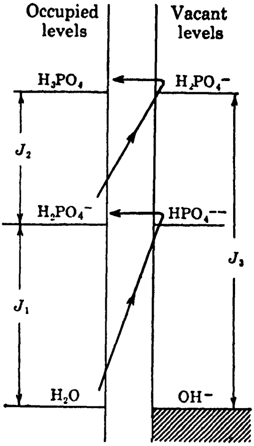

FIG. 38

$$(H_2PO_4)^- + (H_2PO_4)^- \rightarrow H_3PO_4 + (HPO_4)^{=} \tag{144}$$

In a solution containing such particles, the conditions for equilibrium in all possible proton transfers must be satisfied simultaneously. In terms of these proton energy levels, we may say that this is made possible by the additivity of the J values. In Fig. 38 the values of J for the three proton transfers have been labeled J_1, J_2, and J_3. From the relation $J_3 = (J_1 + J_2)$ we may obtain at once a relation between the values of K_x, and hence between the equilibrium constants K. In the proton transfer labeled J_2 the number of solute particles remains unchanged, whereas in J_1 and J_3 the number of solute particles is increased by unity.

Hence, in accordance with (88), we have

$$\begin{aligned} J_1 &= -kT \ln K_x = -kT \ln K_1 + kT \ln M \\ J_2 &= -kT \ln K_x = -kT \ln K_2 \\ J_3 &= -kT \ln K_x = -kT \ln K_3 + kT \ln M \end{aligned}$$

From the equality of J_3 and $(J_1 + J_2)$ we obtain the relation

$$K_3 = K_1 K_2 \tag{145}$$

Hence in the solution containing these species the conditions for equilibrium for all these proton transfers are satisfied at the same time; and the argument could be extended to include other species. Although in Fig. 38 we have discussed a diagram where one species, the $(H_2PO_4)^-$ ion, occurs twice, both on the left and on the right, and where a solvent molecule was involved, neither of these features is essential; and we might equally well have derived (145) for proton transfers involving six different solute species.

Problems

1. Derive the recipe, given in the footnote to Sec. 66, for finding the value of J in electron-volts from the value of log K for a weak acid in aqueous solution.

2. From the data given in Table 9 find the value of J for the proton transfer (125) in water at 10°C.

3. Find the value of J for the proton transfer (128) in water at 0°C.

4. The following table gives the values of K for the first dissociation constant of

Temperature, °C	0	10	20	30	40	50
$K \times 10^7$	2 64	3 44	4 16	4.71	5 04	5.19

carbonic acid; obtained by H. S. Harned and R. Davis [*J. Am. Chem. Soc*, **65,** 2030 (1943)]. Find the values of J at these temperatures, and compare the rate of variation of J with temperature with those given in Table 12.

5. For a certain weak acid HA in aqueous solution the value of J for the proton transfer

$$HA + H_2O \rightarrow (A)^- + (H_3O)^+$$

is equal to 0.50 electron-volt at 25°C. Find approximately what percentage of this solute would remain in the form of neutral molecules in a solution where the molality is equal to 10^{-6}.

CHAPTER 8

The Dissociation Constant of Nitric Acid. Moderately Weak Acids. The Variation of J with Temperature. Proton Transfers between Solute Particles. A Proton Transfer in Methanol Solution. Proton Transfers with a Negative Value for J_{non}. The Hydrolysis of Salts. Molecules with Symmetry. Substituted Ammonium Ions. Deuteron Transfers in D_2O. The Dissociation of Molecular Ions.

70. The Dissociation Constant of Nitric Acid. The largest value of K in Table 9 is that for the $(HSO_4)^-$ ion. In Fig. 36 there is a gap of more than 0.2 electron-volt below the level of the $(H_3O)^+$ ion. As is well known, several acids exist which in aqueous solution fall in the intermediate region between the very weak acids and the recognized strong acids; the proton levels of these acids will fall in this gap. The values of K for these acids obtained by different methods seldom show close agreement. Results obtained by various methods were compared in 1946 by Redlich,[1] who discussed the difficulties encountered.

In this connection we should first recognize that, if an acid is to behave as a strong acid in a moderately dilute aqueous solution, it is not necessary that in Fig. 36 the occupied proton level of the particle should lie above the vacant proton level of the H_2O molecule. For suppose that we have a species of acid molecule HA, whose proton level in aqueous solution is such that no work is required to transfer the proton to a distant water molecule—that is to say, J is equal to zero for this proton transfer—in this case the protons from the HA molecules will distribute themselves indiscriminately among the available vacant proton levels Now in a 0.001-molal solution, for example, the number of H_2O molecules is 55,510 times greater than the number of HA molecules dissolved in this solvent. Hence when the protons have distributed themselves at random among the available levels, the chance of finding one vibrating within an A^- ion

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[1] O. Redlich, *Chem. Rev.*, **39**, 333 (1946).

to form a neutral HA molecule is obviously very small. We can go further, and say that this chance will be small, even if J has a small positive value. In a moderately dilute solution the relative number of H_2O molecules is so great that, even if a small amount of work has to be done to transfer the proton to a distant H_2O molecule, nearly all the protons will be transferred.

This is illustrated by the case of nitric acid, which, according to the usual criteria, is classed among the strong acids. Nevertheless, there is evidence from more than one source that a considerable number of neutral HNO_3 molecules are present in moderately dilute solutions. A study of the ultraviolet absorption spectrum of aqueous solutions of nitric acid and of nitrates such as KNO_3 leads to the conclusion that the absorption bands of the $(NO_3)^-$ ion are different from those of the HNO_3 molecule. Unfortunately the intensity of absorption is weak, arising presumably from forbidden transitions, and accurate measurements have not been made at concentrations of nitric acid lower than 0.5 molal, at which concentration a few per cent of the solute appears to be in the form of neutral HNO_3 molecules. Results obtained by Goldring[1] at 25°C are shown in Fig. 39. As will be seen from the diagram, extrapolation to infinite dilution gives $K = 7$. The diagram also shows results calculated by Goldring from absorption data of von Halban and Eisenbrand,[2] using an extinction coefficient of Jones and Thorn.[3] It will be seen that this curve extrapolates to $K = 9$.

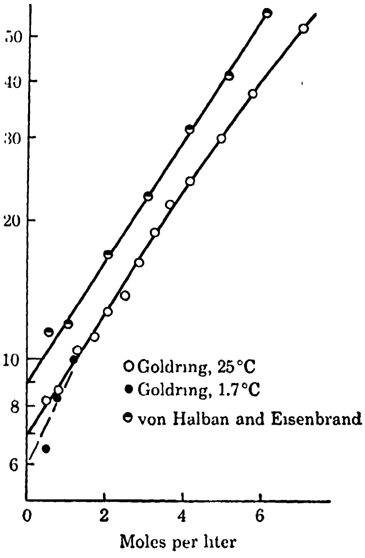

FIG. 39

At higher concentrations the Raman spectra of aqueous solutions of alkali nitrates and of nitric acid have been investigated. Nitric acid was found to be incompletely dissociated, though for the alkali nitrates no evidence of incomplete dissociation was found. Since accurate measurements on solutions of nitric acid have not been made at concentrations below 4.0 molar, it is not certain how the extrapolation to infinite

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[1] L. S. Goldring, Ph.D. Thesis in Chemistry, M.I.T., June, 1950.

[2] H. von Halban and J. Eisenbrand, *Z. physik. Chem.*, **132**, 433 (1928).

[3] R. N. Jones and G. D. Thorn, *Can. J. Research*, **272**, 580 (1949).

solution should be made. The results of Redlich and Bigeleisen[1] were extrapolated to give $K = 21 \pm 4$, while the results of Smith, Maranville, and Young[2] were extrapolated to $K = 24$.

When we come to calculate the value of J for the transfer of a proton from a HNO_3 molecule to a water molecule, we find that all these values of K agree in giving a *positive* value of J. In other words, a certain amount of work is required to transfer a proton from HNO_3 to a distant H_2O molecule, just as in the case of a weak acid. At 25°C, from $K = 7$ we calculate

$$\begin{aligned} J &= -kT \ln K_x \\ &= -kT \ln \frac{7}{M} \\ &= +0.052 \text{ electron-volt} \end{aligned}$$

Using this value, the positions of the proton levels of HNO_3 and of the $(NO_3)^-$ ion are shown in Fig. 40; the vacant level of the $(NO_3)^-$ ion lies 0.052 electron-volt below the vacant level of the H_2O molecule. (If we were to use the value $K = 21$, derived from measurements of Raman spectrum at high concentrations, the gap between these two levels in Fig. 40 would be about half as wide.)

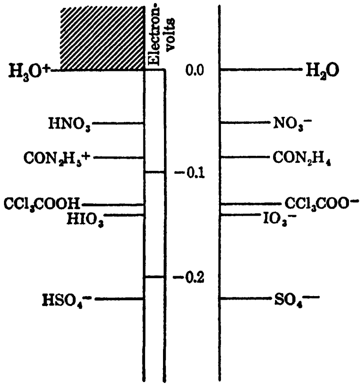

FIG. 40

71. Moderately Weak Acids. It has been recognized that, for moderately weak acids (K greater than 10^{-3}) the evaluation of reliable dissociation constants from measurements of electrical conductivity is more difficult than had previously been supposed. It is agreed that Shedlovky's method of extrapolation to infinite dilution is both simpler and, in some cases, more reliable than earlier methods.[3] Some values of K obtained by various methods are given in Table 14. The proton levels for HIO_3 and $(IO_3)^-$ and for trichloracetic acid are included in Fig. 40. The position of the vacant proton level of the urea molecule has been calculated from the value $K = 10^{-14}$ for the proton transfer[4]

$$CON_2H_4 + H_2O \rightarrow (CON_2H_5)^+ + (OH)^- \qquad (146)$$

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[1] O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 1883 (1942).

[2] H. M. Smith, L. F. Maranville, and T. F. Young, American Chemical Society Meeting, Atlantic City, 1949.

[3] R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1469 (1949).

[4] L. P. Hammett and N. Dietz, *J. Am. Chem. Soc.*, **52**, 4806 (1930).

72. The Variation of J with Temperature. Although each proton transfer has its own characteristic value of Θ, the variation of K near the maximum shows a marked degree of uniformity, as already mentioned in Sec. 64. If a parabola of the form $p(T - \Theta)^2$ is fitted to the experimental results, a single value of p, namely 5×10^{-5}, reproduces the variation of log K, not only for proton transfers of class III, but also for those of class II and class IV. If we accept (140) as providing a qualitative theory of the phenomena, we have at once a physical explanation of the observed uniformity. Whether we are concerned with the removal of a proton from a negative ion, such as $(HCO_3)^-$, or from a neutral molecule, or from a zwitterion, the increase of J_{el} with temperature is in each case due to the changing environment and so leads to a similarity in the variation of K, because the changing environment is the same in each case.

TABLE 14. DISSOCIATION CONSTANTS IN AQUEOUS SOLUTION

Acid	K	Temperature	Method	Reference
HIO_3. . . .	0.16	25	Conductivity	a
	0.167	25	Indicator	b
	0.163	25	Solubility	c
	0.262	0	Freezing point	d
H_3PO_2.	0 085		Potentiometric	e
	0 10		Conductivity	f
H_2SO_3	0 017	25	Conductivity	g
Trichloracetic	0 232	25	Indicator	b

[a] R. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1469 (1949).
[b] H. von Halban and J. Brull, *Helv. Chim. Acta*, **27** (1947).
[c] S. Naidich and J. E. Ricci, *J. Am. Chem. Soc.*, **61**, 3268 (1939).
[d] E. Abel, O. Redlich, and P. Hersch, *Z. physik. Chem.*, **A170**, 112 (1934).
[e] C. Morton, *Quart. J. Pharm.* **125**, 102 (1930).
[f] A. D. Michell, *J. Chem. Soc.*, **117**, 1957 (1920).
[g] H. V. Tartar and H. H. Garritson, *J. Am. Chem. Soc.*, **63**, 308 (1941).

Since, according to (77) we have $\Delta H = J - (dJ/dT)$, it follows that, if J_{el} is proportional to $1/\epsilon$, then the value of ΔH at any temperature should be proportional to $\frac{1}{\epsilon} - \frac{d}{dT}\left(\frac{1}{\epsilon}\right)$. Using the empirical values of $1/\epsilon$ for water, and its temperature coefficient, Baughan[1] tested the proportionality between the observed and calculated rates of variation of ΔH. Sur-

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[1] E. C. Baughan, *J. Chem. Phys.*, **7**, 952 (1939).

prisingly good agreement was obtained, an example of which is given in Table 15.

In equation (140) the magnitude of the electrostatic energy is contained in the constant C; and the variation of K with temperature is determined by the factor $e^{-T/\vartheta}$, which is common to all proton transfers of classes II, III, and IV.

TABLE 15. ΔH FOR PROTON TRANSFER FROM HCOOH IN AQUEOUS SOLUTION

Temperature, °C	0	10	20	30	40	50	60
ΔH_{obs}	931	573	189	−221	−657	−1118	−1602
ΔH_{calc}	931	584	206	−205	−652	−1129	−1650

An example of the use of (140) is shown in Fig. 41. The small circles in Fig. 41 give the experimental values of log K_x for acetic acid in aqueous solution. The theoretical curve marked 219 is calculated from (140), with $a = 1.35$, $C = 850.2$, and $\vartheta = 219$. It will be seen that the agreement is better than might have been expected. To obtain still closer agreement, a somewhat larger value of ϑ is required. The other curve in Fig. 41, calculated with $\vartheta = 240$, gives almost perfect agreement.

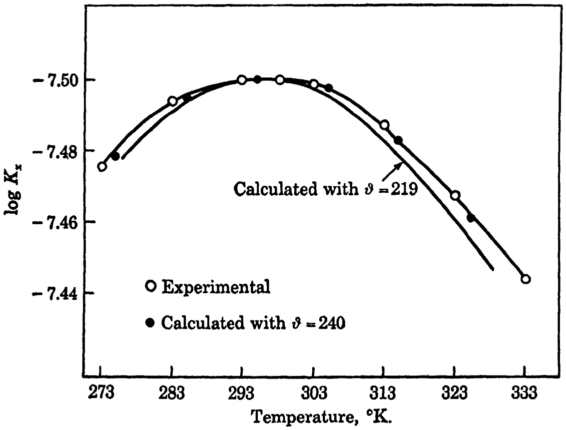

FIG. 41. Ionic dissociation of the acetic acid molecule in water.

73. Proton Transfers between Solute Particles. In each of the types of proton transfer discussed in Secs. 58 and 71, a solvent molecule is involved. In dilute solution the solvent molecules are present in great excess, and therefore an equilibrium is observed only if a considerable amount of work is required to transfer the proton; otherwise the solute will be almost completely dissociated. In aqueous solution electrostatic forces of attraction are not sufficient to give even a moderately weak acid; a contribution from quantum-mechanical forces is required in addition. Only in this way does one obtain a dissociation energy that is large enough to compensate for the large excess of solvent.

Consider now the transfer of a proton from a solute particle to another species of solute particle. Here the concentrations of both are under our control, and the above limitations do not apply. By adjusting the solute concentrations, one can observe an equilibrium, even if the work to transfer the proton has a value in the neighborhood of zero; a zero value can come about if the contributions from electrostatic and non-electrostatic forces happen to be of opposite sign. When the proton is transferred from one particle to the other, the binding energy of the proton in the latter may be greater than in the former; the difference in the binding energy may compensate for the energy that is put into the electrostatic fields, when ions are created and separated against the forces of mutual attraction, with the result that the net amount of work done is small, or even zero.

As pointed out at the end of Sec. 64, such a compensation can be exact only at a particular temperature, seeing that the electrostatic energy varies with temperature. In fact, with rise of temperature there will, in such a case, be a change in sign for J, the work to transfer the proton. J will change sign from negative to positive, as the temperature rises; and $\ln K_x$ will change sign from positive to negative. This will also be true of $\ln K$, since no solvent particle is involved in the proton transfer. An example of this behavior is recorded in Table 16.

74. A Proton Transfer in Methanol Solution. Although in non-aqueous solutions several proton transfers have been studied at room temperature, very few investigations have been made over a wide range of temperature in very dilute solution. Table 16 gives some results obtained in methanol solution by Nisonoff and Kuhn[1] for a proton transfer of the following type:

$$(\mathrm{AH})^- + \mathrm{B} \rightarrow \mathrm{A}^= + (\mathrm{BH})^+ \tag{147}$$

where the molecule B was trimethanolamine and $(\mathrm{AH})^-$ was the ion of bromcresol green. The measurements were made by the spectrophotometric method in very dilute solutions.

The character of the results is very different from any of those given in Tables 9 or 11. It will be seen that in Table 16, as the temperature falls below 0°C, the value of $\log K$ changes sign from negative to positive. Since $K = K_x$ in this proton transfer, this implies, according to (132),

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[1] A. Nisonoff, L. P. Kuhn, and R. W. Gurney, *J. Chem. Phys.*, **20**, 985 (1952).

that just below 0°C the value of J passes through a zero value; that is to say, at this temperature the vacant proton level of a B molecule in solution has exactly the same energy as the occupied proton level in a distant $(AH)^{-}$ ion. This must be due to the fact that, at this temperature, the values of J_{non} and J_{env} happen to be exactly equal and opposite. In (147) the work to set up the additional ionic fields will certainly be positive at all temperatures. The constant value of J_{non} must be negative here. At low temperatures, where the dielectric constant is large, the magnitude of J_{env} is smaller than that of J_{non}.

TABLE 16. VALUES OF LOG K FOR THE PROTON TRANSFER (116) IN METHANOL SOLUTION

Temperature, °C.	−0 62	+0.1	10 1	20.0	30 1	40.1	50 2
log K....... ..	+0.137	−0.048	−0 270	−0 484	−0.719	−0.924	−1.16

But with rise of temperature, as the dielectric constant decreases, the magnitude of J_{env} becomes greater than that of J_{non}, and a net amount of work is required to transfer the proton.

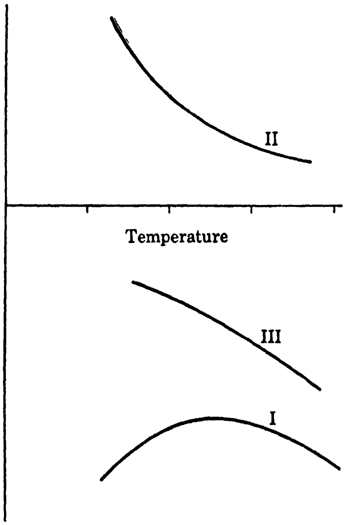

FIG. 42

75. Proton Transfers with a Negative Value for J_{non}. Although experimental results for many different proton transfers in aqueous solution are included in Tables 9, 10, and 11, those investigations were limited to proton transfers of only one type, namely, where both J_{non} and J_{env} are positive. We shall find that the different character of the results given in Table 16 is not due to the change of solvent from water to methanol but is due to the fact that the investigations dealt with a proton transfer with a large negative value for J_{non}. Widening the scope of the discussion, we may now use the equation

$$\ln K_x = -C\frac{a + e^{T/\vartheta}}{T} \qquad (148)$$

to predict the behavior in proton transfers for various negative values of J_{non}.

It will be convenient to deal with aqueous solutions as well as methanol solutions. In this connection we may refer again to Fig. 35, where curve I was a plot of $(-e^{T/\vartheta}/T)$, and curve II was a plot of $-a/T$ with $a = +1.5$. The effect of taking a J_{non} of opposite sign is shown in Fig. 42, where curve I is the same as in Fig. 35, but where curve II is a plot of $-a/T$ with $a = -1.5$, instead of $+1.5$. This represents a negative value of J_{non}. It so happens that in this case the concave curvature of the upper curve is nearly equal and opposite to the convex curvature of the lower curve, with the result that, when ordinates are added to give curve III, the latter is, over a wide range of temperature, almost a straight line. Curves of this type are included in Fig. 43, which shows a family of curves calculated with $\vartheta = 219$, and various values of a between $+1.5$ and -4.0. Near the bottom of Fig. 43 the row of circles reproduces the experimental results for acetic acid in aqueous solution. We have already seen that with a equal to $+1.35$ and C equal to 850.2, we obtain rather good agreement.

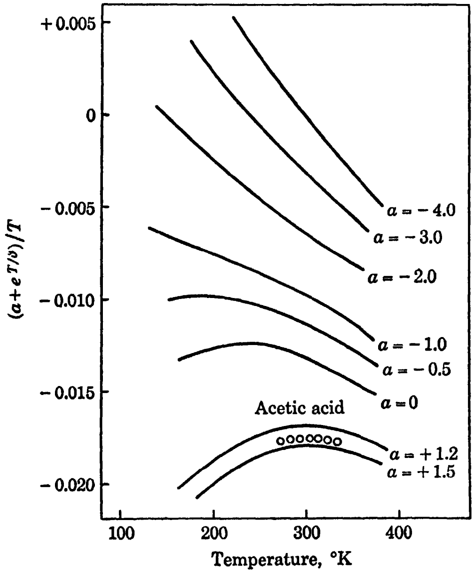

FIG. 43. Family of curves with $\vartheta = 219$ and various values of a

Returning now to proton transfers in methanol solution, we see that the family of curves in Fig. 44, calculated with $\vartheta = 185.4$ is very similar to those for aqueous solution. The curve for $a = 0.0$ passes through its maximum at the characteristic temperature 185.4°K. We now find that we can interpret the experimental results recorded in Table 16; for we see in Fig. 44 that curves drawn for values of a between -3 and -4 pass through zero near room temperature. The row of circles give values of ln (K/C) with $C = 645$ and experimental values of K taken from Table 16. Agreement with (140) is found if a is taken equal to -4.32.

76. The Hydrolysis of Salts. As shown in Table 41, the NH_3 molecule has a dipole moment almost as large as that of the H_2O molecule. When ammonia has been dissolved in water the electrostatic interaction of an NH_3 dipole with an adjacent solvent dipole is of the same order of magnitude as the interaction between two adjacent H_2O dipoles. At the same time, when ammonia has been dissolved in water, the solution has a feeble electrical conductivity, due to the fact that a certain number of protons have been transferred from water molecules to the solute particles;

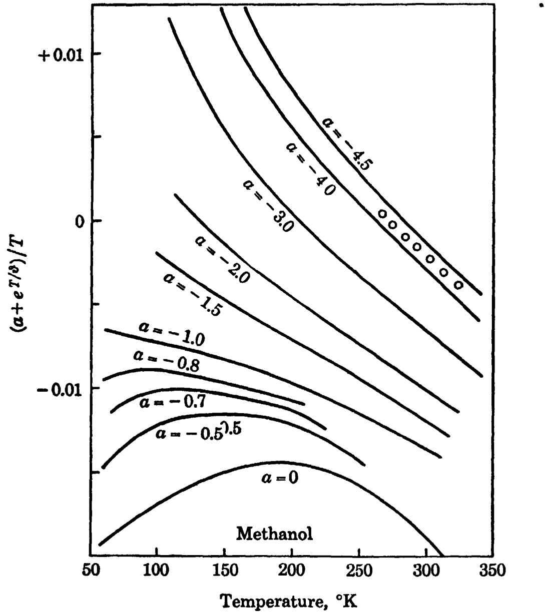

FIG. 44. Family of curves with $\vartheta = 184$ and various values of a

$$H_2O + NH_3 \rightarrow (OH)^- + (NH_4)^+ \qquad (149)$$

Formerly, it was thought that the NH_3 entered into chemical combination with the water to form NH_4OH molecules, some of which then dissociated into positive and negative ions. It is true that at low temperatures a solid compound NH_4OH is known. "But it melts with decomposition at $-79.3°C$, and the amount present in aqueous solution can hardly be important."[1]

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[1] L. P. Hammett, "Physical Organic Chemistry," p. 45, McGraw-Hill, 1940.

In Table 11 data were given on the proton transfer from the ammonium ion to a water molecule

$$(NH_4)^+ + H_2O \rightarrow NH_3 + (H_3O)^+ \tag{150}$$

When this takes place in the aqueous solution of a salt, such as NH_4Cl, the process is known as the hydrolysis of the salt. Formerly, this hydrolysis was regarded as due to the self-dissociation of the water

$$H_2O \rightarrow H^+ + (OH)^-$$

followed by

$$(NH_4)^+ + (OH)^- \rightarrow NH_4OH \tag{151}$$

Even recent textbooks mention only the traditional view that "if water were not dissociated at all, hydrolysis would not occur." From Fig. 36, however, it is quite clear that in the proton transfer (150) we are concerned with the gap between the occupied proton level of the $(NH_4)^+$ ion and the vacant level of the H_2O molecule near the top of the diagram. The existence of the vacant proton level of the $(OH)^-$ ion, near the bottom of the diagram, is irrelevant.

In contrast to this, consider next a solution of sodium acetate. From Sec. 69 we know that in such a solution the thermal agitation raises a certain number of protons from the solvent molecules to the vacant proton levels of the $(CH_3COO)^-$ ions. In the aqueous solution of such a salt, this process is known as the hydrolysis of the salt and is traditionally regarded as a result of the self-ionization of the water. In Fig. 36, however, it is clear that in the proton transfer

$$H_2O + (CH_3COO)^- \rightarrow (OH)^- + CH_3COOH \tag{152}$$

we are concerned only with the gap between the vacant level of the $(CH_3COO)^-$ ion and the occupied level of the H_2O molecule, near the bottom of Fig. 36. The existence of the vacant proton level of the H_2O molecule, near the top of the diagram, is irrelevant here.

Suppose now that the proton transfer (152) is followed by the transfer of the same proton to another distant water molecule:

$$CH_3COOH + H_2O \rightarrow (CH_3COO)^- + (H_3O)^+ \tag{153}$$

In this second step the $(CH_3COO)^-$ ion, to which the proton had been transferred in (152), is recovered, and the same would be true, whatever species of particle is involved. This will be clear from Fig. 45, which shows a close resemblance to Fig. 38. The final result of (152) followed by (153) is evidently

$$2H_2O \rightarrow (H_3O)^+ + (OH)^-$$

The equilibrium constant of (152), omitting the H_2O, is known as the hydrolysis constant and is often denoted by K_h. As in (145), it is related to J_1 in Fig. 45 by

$$J_1 = -kT \ln K_h + kT \ln M$$

Similarly

$$J_2 = -kT \ln K_A + kT \ln M$$

and

$$J_3 = -kT \ln K_W + 2kT \ln M$$

From Fig. 45 it is clear that $J_3 = J_1 + J_2$, from which we derive at once the relation

$$K_h = \frac{K_W}{K_A} \tag{154}$$

A corresponding relation exists for the equilibrium constant of (150) in the hydrolysis of an ammonium salt.

In non-aqueous solution the process corresponding to hydrolysis is known as "solvolysis"; and corresponding relations must hold for the solvolysis constants.

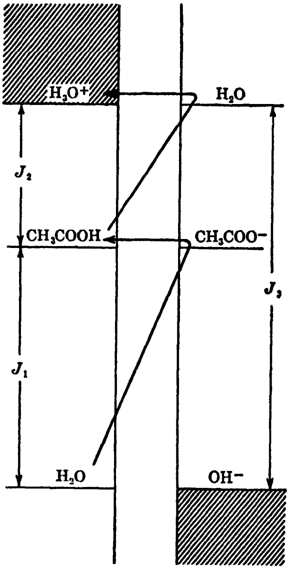
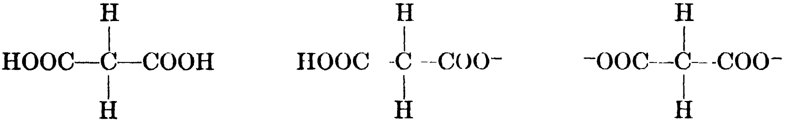


FIG. 45

77. Molecules with Symmetry. In discussing diatomic solute molecules in Sec. 44, the difference between the homonuclear and heteronuclear types was mentioned. If a homonuclear molecule in any position is rotated through 180°, the final state is indistinguishable from the initial state; and this must be taken into account in evaluating W_{of}. A similar situation arises in certain acid molecules containing two carboxyl groups. Figure 46*a* shows the malonic acid molecule. Consider the line which bisects the angle between the two COOH groups. If, about this line as axis, the molecule is rotated through 180°, the final state will be indistinguishable from the initial state—there will be no difference in the wave function describing the molecule. In any solution, this must be taken into consideration in counting the number of *different* ways in which the molecule may be placed.

If a proton is removed from one COOH group, as shown in Fig. 46*b*, and transferred to a distant water molecule to form $(H_3O)^+$, the symmetry of the molecule is lost. On the other hand, if the proton is now removed from the other COOH group and transferred to a water molecule, the symmetry is regained by the molecular ion, as shown in Fig. 46*c*. In each case the symmetry or asymmetry of the solute particle is obviously independent of the amount of solvent present; and hence each change of symmetry makes, through $\ln W_{cf}$, a contribution to the unitary term in (59). In fact, when the first proton is removed, the loss of symmetry makes in (59) the contribution $+kT \ln 2$; and when the second proton is removed, the restoration of symmetry makes the contribution $-kT \ln 2$.

Let us consider now the work required to remove the first proton and the second proton. When the doubly charged ion of Fig. 46*c* has been formed, a certain amount of energy has been put into the electrostatic field of the ion; this total amount differs, owing to the proximity of the two negative charges, from twice the amount put into the electrostatic field of the singly charged ion of Fig. 46*b*. Although in Fig. 46 only one CH_2 group separates the two carboxyl groups, malonic acid is the shortest of a series of dicarboxylic acids of the type $COOOH(CH_2)_nCOOH$, in which the length of the chain increases with n. We may take the point of view that, when the chain is long, the two COOH groups tend to become independent, both as regards electrostatic energy and as regards the binding of the proton. When these protons are to be transferred to distant solvent molecules, let J_1 and J_2 denote the values of J for the first and second protons, respectively. It would be a mistake to suppose that, when the molecular chain is long, J_1 and J_2 tend to become equal. In Sec. 52 we defined J as the total change in the unitary part of the free energy. Hence we can only anticipate that, when the molecular chain is long, the values of J_1 and J_2 may be related by expressions of the form



$$\mathrm{HOOC{-}\overset{H}{\underset{H}{C}}{-}COOH} \qquad \mathrm{HOOC{-}\overset{H}{\underset{H}{C}}{-}COO^-} \qquad \mathrm{^-OOC{-}\overset{H}{\underset{H}{C}}{-}COO^-}$$

(*a*) (*b*) (*c*)

FIG. 46

$$J_1 = J_0 + kT \ln 2$$
$$J_2 = J_0 - kT \ln 2$$

This means that, with increasing length of chain, the equilibrium constants K_1 and K_2 (the first and second dissociation constants at infinite dilution of the acid) should not tend to equality; rather their ratio K_1/K_2 should tend toward the value 4, as recognized by Adams.[1]

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[1] E. G. Adams, *J. Am. Chem. Soc.*, **38**, 1503 (1916); R. Gane and C. K. Ingold, *J. Chem. Soc.*, **1931**, 2153.

78. Substituted Ammonium Ions. Like NH_4Cl the substance $NH_3(CH_3)Cl$, where a CH_3 group has been substituted for one hydrogen, forms a crystalline solid; and so do the substances $NH_2(CH_3)_2Cl$ and $NH(CH_3)_3Cl$. When one of these substances is dissolved in water, it is completely dissociated into Cl^- ions and molecular positive ions corresponding to $(NH_4)^+$. Suppose now that such a solution contains an NH_3 molecule, and consider the following proton transfer

$$[NH(CH_3)_3]^+ + NH_3 \rightarrow N(CH_3)_3 + (NH_4)^+ \qquad (155)$$

Here the number of ions remains unchanged; only the smaller $(NH_4)^+$ ion replaces the initial larger ion. Although in Sec. 19 we discussed the transfer of a charge from a larger sphere to a smaller sphere, the situation here is different.

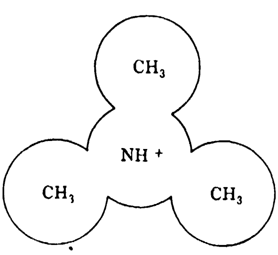

FIG. 47

Figure 47 shows schematically the structure of the $NH(CH_3)_3^+$ ion. We must suppose that the positive charge is associated with the proton which lies embedded in the nitrogen atom. Thus, in contrast to the case of Fig. 15, the proton transfer (155) does not imply the concentration of the charge upon a smaller sphere. When the ion is situated in a polar solvent, we must suppose that the three CH_3 groups will prevent adjacent solvent dipoles from lying as near to the positive charge as they would in the case of the $(NH_4)^+$ ion. This will mean that, at any temperature, the total amount of free energy lost by the solvent in the ionic co-sphere of $(NH_4)^+$ will be considerably greater than the amount of free energy lost by the solvent in the co-sphere of the $[NH(CH_3)_3]^+$ ion As a result, in the proton transfer

$$N(CH_3)_3 + (NH_4)^+ \rightarrow [NH(CH_3)_3]^+ + NH_3 \qquad (156)$$

although the number of ions remains unchanged, a positive amount of electrostatic work is done; and this amount will vary with temperature. The variation of J with temperature should be smaller for the dimethylammonium ion, where only two methyl groups prevent the solvent dipoles from approaching near to the positive charge; and smaller still for the monomethylammonium ion. The experimental results on these ions[1] show that these predictions are fulfilled.

79. Deuteron Transfers in D_2O. As shown in Table 1 the characteristic temperature ϑ for the dielectric constant of D_2O is almost the same as for H_2O. The values of the dielectric constant of D_2O are given with

[1] D. H. Everett and W. F. K. Wynne Jones, *Proc. Roy. Soc.*, **177A**, 499 (1941).

good approximation by the expression[1]

$$\log \epsilon = 1.9433 - 0.00199t \tag{157}$$

as compared with the expression for H_2O

$$\log \epsilon = 1.9446 - 0.00198t \tag{158}$$

Near room temperature there is scarcely any difference between the two. When a deuteron has been removed from a molecule in D_2O, the electrostatic energy associated with the negative ion will scarcely differ from that associated with the field of a similar ion in H_2O from which a proton has been removed. Furthermore, the energy associated with the electric field surrounding a $(D_3O)^+$ ion in D_2O will scarcely differ from that of the field surrounding a $(H_3O)^+$ ion in H_2O. We must conclude then that the observed differences between the degrees of dissociation of weak acids in D_2O and H_2O are due entirely to a difference in the quantum-mechanical forces.

Consider the quantized energies of vibration associated with a molecular potential energy such as that depicted in Fig. 7. It is well known that the three or four lowest vibrational energy levels have nearly uniform spacing—that is to say, the intervals between successive allowed values of the vibration energy are nearly equal, as in a harmonic oscillator. We may say that this is because, near its minimum, the potential-energy curve of Fig. 7 is approximately a parabola, the potential-energy characteristic of a harmonic oscillator. In a diatomic molecule containing nuclei of mass m and M the interval between successive levels is proportional to $\sqrt{(m + M)/mM}$. Writing down the corresponding expression for a similar molecule containing nuclei of mass m' and M, we find that, when M is large compared with either m or m', the spacing of the levels in the second molecule differs from that in the former approximately in the ratio $\sqrt{m/m'}$. If then we take m and m' to denote the mass of the proton and deuteron, respectively, and M to denote the mass of a nucleus several times larger than either, we conclude that the spacing of the vibrational levels for the deuteron will be narrower than those for the proton, nearly in the ratio $1/\sqrt{2}$. This reduction in the spacing of the levels is accompanied by a difference in the position of the lowest vibrational level.

We may fix our attention on the minimum of the potential-energy curve in Fig. 7 and ask how much higher the lowest vibrational level will lie. This energy gap between the potential minimum and the lowest vibrational level is equal to the vibrational energy of the molecule at the absolute zero of temperature and is known as the *zero-point energy of*

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[1] J. Wyman and E. N. Ingalls, *J. Am. Chem. Soc.*, **60**, 1184 (1938).

vibration. In the harmonic oscillator the zero-point energy is equal to half the spacing between successive levels. Since the spacing of the levels is narrower for a deuteron than for a proton, this means that the zero-point energy will likewise be smaller. If we consider a molecule where a proton has been replaced by a deuteron, the lowest quantized state for the deuteron will lie nearer to the potential minimum; and since the depth of the potential minimum is the same for both, being determined by the electric charge, we conclude that the binding energy will be greater for the deuteron than for the proton. This increment in the binding energy can be expressed as a fraction of the interval between successive levels. In the harmonic oscillator this fraction will be $\frac{1}{2}[1 - (1/\sqrt{2})]$, or about 15 per cent of the spacing between successive energy levels of the proton.

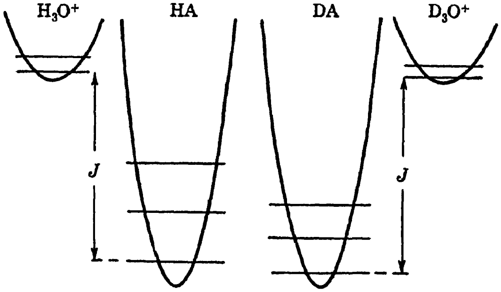

FIG. 48

We want now to ask what effect this will have on the difference between the work J required to transfer a proton from the molecule of a weak proto-acid HA to an H_2O molecule and the corresponding work J required to transfer a deuteron from the corresponding deutero-acid DA to a distant D_2O molecule to form a $(D_3O)^+$ ion. Since J is positive, the binding forces in the molecules HA and DA must be considerably stronger than in the ions $(H_3O)^+$ and $(D_3O)^+$; and we must here make use of the fundamental idea that in a molecule or molecular ion where the binding forces are strong the spacing of the energy levels is wider than where they are weak. The situation is shown schematically in Fig. 48, from which we conclude that the value of J for the deuteron will be greater than the value of J for the transfer of a proton from the corresponding proto-acid in aqueous solution.

We expect that the dissociation constant of a weak deutero-acid in D_2O solution will be smaller than that of the corresponding proto-acid in aqueous solution; and we may say at once that in all six cases that have been measured the value of the dissociation constant K_d of the deutero-acid is less than half that of K_p for the corresponding proto-acid.

The difference in the value of J that we have predicted is a difference in the quantum-mechanical binding energy J_{non} and not in the environmental part J_{env}. In fact, the replacement of a proton by a deuteron enables us to carry out the ideal experiment of increasing J_{non} without at the same time changing J_{env}. It therefore provides a convenient method of testing the theory put forward in Sec. 67. In connection with the parabolas of Figs. 35 and 43 it was pointed out that increasing the positive value of J_{non}, while leaving the value of J_{env} unchanged, has the effect of moving the parabola downward and to the right. That is to say, in the case of the deutero-acid the dissociation constant K should pass through its maximum value at a *higher* temperature than the corresponding proto-acid. Fortunately, in the case of deuteroacetic acid measurements have been made over a wide range of temperature.[1] Through the experimental points it is possible to draw a parabola having the same shape as that of Fig. 41, but passing through a maximum at a temperature some 10° higher. This is in the direction predicted.

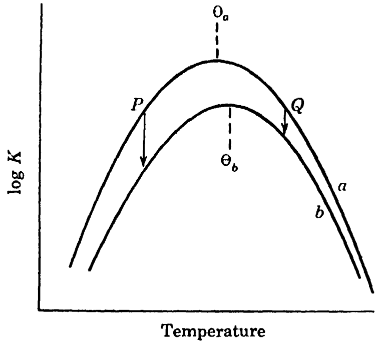

FIG. 49

For other acids measurements were not made over a wide range of temperature, but the value of the ratio K_p/K_d was determined at a single temperature—a temperature which in some cases lay above and in other cases below the temperature at which the value of K passed through its maximum value. Under these circumstances the situation needs to be looked into more carefully.

Curve b in Fig. 49 shows the situation that arises if curve a is shifted downward and slightly to the right. Suppose that at one particular temperature measurements are made to determine the value of K_a/K_b.

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[1] F. Brescia, V. K. La Mer and F. C. Nachod, *J. Am. Chem. Soc.*, **62,** 616 (1940).

The result will clearly depend on whether the maxima of the curves lie below or above or near the temperature at which the measurements are made, since the vertical distance between the curves is the logarithm of K_a/K_b. The arrow P in the diagram, for a temperature lying below the maxima, is considerably longer than the arrow Q for a temperature lying above the maxima.

When, for example, measurements of the value of K_p/K_d have been made at 25°C for a number of acids, we expect that the value of K_p/K_d will be larger when 25°C lies below the temperature Θ than when it lies above Θ. That such a trend is present is shown by the experimental results given in Table 17.

The question arises whether measurements made over a wide range of temperature would or would not show that the ratio of the *maximum* value of K_p to the *maximum* value of K_d would vary in the same way. For we have reason to believe that it would be so. In Table 17 the molecules and molecular ions have been arranged in the order of decreasing K_p, that is to say, in the order of increasing J, or of increasing strength of the binding forces. This means wider spacing of the energy levels, and greater zero-point energy, and hence—according to the situation depicted in Fig. 48—increasing difference between the binding energy of the deuteron and the binding energy of the proton. As pointed out by Halpern,[1] this leads us to expect that the value of K_p/K_d increases as we go from a moderately weak to a very weak acid. Rule and La Mer[2] found that, when the observed values of K_p/K_d at 25°C are plotted against log K_p, the points lie on a curve; and Martin and Butler[3] found that the values of K_p/K_d at 25° for six nitrophenols lie almost on the same

TABLE 17. DISSOCIATION CONSTANTS OF DEUTERO-ACIDS AND PROTO-ACIDS[a]

Acid	K_p/K_d	K_p	Θ, °C
Chloracetic	2.74	1.738×10^{-3}	−5.4
Benzoic	3.13	6.09×10^{-5}	
Acetic	3.33	1.754×10^{-5}	22.6
$(H_2PO_4)^-(D_2PO_4)^-$	3.62	6.226×10^{-8}	43.1
$(HCO_3)^-(DCO_3)^-$	3.95[b]	5.61×10^{-11}	>60
Hydroquinone	4.16	2.66×10^{-11}	>60

[a] C. K. Rule and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 1981 (1938).
[b] J. Curry and Z. Z. Hugus, *J. Am. Chem. Soc.*, **66**, 653 (1944).

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[1] O. Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

[2] C. K. Rule and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 1981 (1938).

[3] D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, **1939**, 1366.

curve. Unfortunately, when measurements have been made only at a single temperature, the effect obviously has to be disentangled from that depicted in Fig. 49.

80. The Dissociation of Molecular Ions. In Chapter 4 we introduced in Fig. 27 the idea of simultaneous long-range and short-range forces of attraction between a pair of ions of opposite sign in solution. When quantum-mechanical forces of attraction are superimposed upon the electrostatic forces, a neutral molecule or a molecular ion in solution may be formed. In Sec. 29 we gave as examples the formation of TlCl in aqueous solution from Tl^+ and Cl^-, and the formation of $(FeCl)^{++}$ from Fe^{+++} and Cl^-. For any such molecule or molecular ion in solution we use the letter D to denote the work required to break up the molecule or molecular ion and to separate the ions in the solvent. Since the strength of the long-range forces depends on the environment, D must clearly be regarded as consisting of two parts D_{non} and D_{env}, which will play a role similar to that of the J_{non} and J_{env} of Chapter 7. From the observed values of the dissociation constant K at room temperature we can estimate the value of the total dissociation energy D for various species. But, unfortunately, there have been few thorough investigations of the variation of K with temperature, comparable with those which have been made for proton transfers over a wide range of temperature.

By a spectrophotometric method Rabinowitch and Stockmayer[1] studied the dissociation of the molecular ions $(FeCl)^{++}$ and $(FeBr)^{++}$ between 25 and 45°C, and likewise the dissociation of the molecular ion $(FeOH)^{++}$ into Fe^{+++} and $(OH)^-$. Let us consider what different kinds of behavior are to be expected. In studying proton transfers, we found that, with rise of temperature, the value of K would either increase or decrease, according to the relative magnitude of J_{non} and J_{env}. So here, similar behavior is to be expected according to the relative magnitudes of D_{non} and D_{env}; the possibility of their being of opposite sign does not arise.

The crystallographic radius assigned to the ion Fe^{+++} is comparable with that assigned to the scandium ion Sc^{+++}. The ions K^+, Ca^{++}, and Sc^{+++} have the same number of electrons, and the same closed electronic shells as the argon atom. In aqueous solution there will be electrostatic forces of attraction between Ca^{++} and Cl^-, and between Sc^{+++} and Cl^-; but the quantum-mechanical forces between these ions will be forces of repulsion only. Between Fe^{+++} and Cl^-, on the other hand, there may be quantum-mechanical forces of attraction. In view of the rather intense electrostatic attraction between Fe^{+++} and a negative ion, a

[1] E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 341 (1942).

rather small D_{non} superimposed upon this D_{el} will be sufficient to give incomplete dissociation, comparable with that of the moderately weak acids that were listed in Table 14. On the other hand, when D_{non} as well as D_{env} is large, the dissociation constant K will have a very small value, like that of a very weak acid. The experimental data given in Table 18 include both of these types. For the $(FeOH)^{++}$ ion we obtain the value $D = 0.84$ electron-volt.

TABLE 18. DISSOCIATION OF MOLECULAR IONS IN AQUEOUS SOLUTION AT 25°C

Ion	K	ΔF	ΔH	Reference
$(FeOH)^{++}$	2×10^{-12}	$16{,}000 \pm 300$	$+1200 \pm 1000$	[a]
$(FeCNS)^{++}$	1.04×10^{-3}	4000	.....	[b]
$(FeCl)^{++}$	0.033	2000 ± 200	-8500 ± 200	[a]
$(FeBr)^{++}$	0.25	800 ± 300	-6100 ± 200	[a]

[a] E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 341 (1942). The equilibrium constants tabulated by these authors are association constants.

[b] S. Edmonds and N. Birnbaum, *J. Am. Chem. Soc.*, **63**, 1471 (1941).

If we make the approximation of replacing D_{env} by D_{el}, according to the equation analogous to (143), the dissociation constant of the molecular ion will pass through a maximum value at a certain temperature Θ, given by

$$\Theta = \vartheta\left(1 + \frac{D_{non}}{D_{el}^*}\right)$$

If Θ lies below the freezing point of the solvent, the value of the dissociation constant will fall over the whole range of temperature.

When D_{non}/D_{el} is large, the predominant effect will be the tendency for the thermal agitation to break up the molecular ions; and the degree of dissociation will increase with rise of temperature. On the other hand, when D_{non}/D_{el} is small, the predominant effect will, according to simple electrostatic theory, arise from the progressive increase in depth of the potential minimum of Fig. 8*b* with rise of temperature, so that the degree of dissociation actually decreases with rise of temperature, in spite of the increase of the thermal energy. Both types of behavior are found. In the case of the ions $(FeCl)^{++}$ and $(FeBr)^{++}$, where the value of $(D_{non} + D_{env})$ is relatively small, the value of K continually decreases with rise of temperature, whereas in the case of $(FeOH)^{++}$, for which the value of $(D_{non} + D_{env})$ is relatively large, the opposite behavior is found. It will be noticed that the value of ΔH for this ion, included in Table 18, has a positive value, in contrast to those for $(FeCl)^{++}$ and $(FeBr)^{++}$, which are negative. Thus the simple theory evidently predicts the right kind of behavior, which is all that should be expected of it.

We have discussed the triply charged ion Fe^{+++} in aqueous solution. Let us consider now the water molecules that are in contact with such an ion, and let Fig. 50*a* depict one such H_2O molecule. The protons in the H_2O molecule will be repelled by the large positive charge of the Fe^{+++} ion—will be so strongly repelled that it is possible that, sooner or later, the thermal agitation will be sufficient to transfer a proton to a more distant H_2O molecule, as depicted in Fig. 50*b*, to form an $(H_3O)^+$ ion; in which case it is likely that another proton, repelled by the Fe^{+++} ion, will be transferred from the $(H_3O)^+$ ion to a still more distant water molecule, as depicted in Fig. 50*c*.

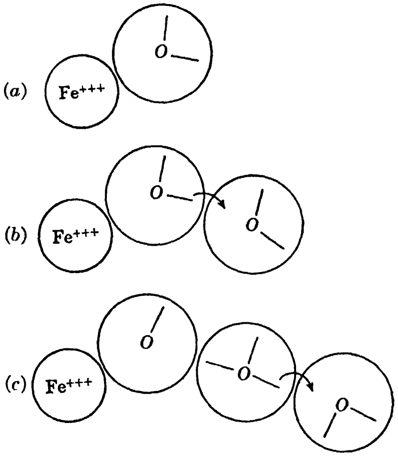

FIG. 50

This process leaves a hydroxyl ion in contact with the Fe^{+++} ion; and we have seen that these ions combine to form a molecular ion $(FeOH)^{++}$. The whole process may then be written

$$Fe^{+++} + H_2O \rightarrow (FeOH)^{++} + (H_3O)^+ \qquad (159)$$

We notice that, although there is only one solute species on the left-hand side, there are two on the right-hand side. The process is therefore accompanied by an increase in entropy, and the ΔF of the process will contain a term $-T\,\Delta S_{cratic}$. Let us first discuss the values of the unitary terms; to do this we may carry out the process in a different manner. Choosing two *distant* water molecules, we transfer a proton from one to the other. According to Table 12, at 25°C the work required amounts to 1.03 electron-volts. We then bring the hydroxyl ion up to, and allow it to combine with, the Fe^{+++} ion, thereby receiving energy equal to the dissociation energy D of the $(FeOH)^{++}$ ion. For this we have found the value to be $D = 0.84$. If we denote by U the work required to carry out the process (159), we find

$$\begin{aligned} U = J - D &= 1.03 - 0.84 \\ &= 0.19 \text{ electron-volt} \end{aligned}$$

Now this is smaller than any of the values of J given in Table 12, and since the cratic term is the same, Δq in (159) being equal to $+1$, we conclude that the process (159) should take place to a considerable extent. In this way we have another mechanism for the hydrolysis of a salt.

In the experiments described above no tendency was found for the $(ClO_4)^-$ ion to form a molecular ion by combination with Fe^{+++}. The absorption spectrum characteristic of the Fe^{+++} ion in aqueous solution was therefore determined by studying solutions of $FeClO_4$ as a function of the hydroxyl-ion concentration.

Problems

1. From the data given in Table 18 for the dissociation of the molecular ion $(FeCl)^{++}$, find in electron-volts the dissociation energy D at 25°C; and find in electron-volts per degree the value of dD/dT, the rate of variation of D with temperature; compare the result with values of dJ/dT taken from Table 12.

2. Taking from Tables 9 and 11 the values for the equilibrium constants for the proton transfers from the acetic acid molecule and from the anilinium ion, and using (145), find the value of $-kT \ln K_x$ for the proton transfer

$$CH_3COOH + C_6H_5NH_2 \rightarrow (CH_3COO)^- + (C_6H_5NH_3)^+$$

at the following temperatures: 0°, 20°, 40°, 60°. Plot the values of J against the temperature, and by comparison with Fig. 43, find approximately the value to be assigned to the constant a in equation (140).

CHAPTER 9

The Viscosity of Ionic Solutions. The B-coefficients. Assignment of B-coefficients to Separate Ions. The Acetate Ion. The Sign of the B-coefficient and the Magnitude of C_1^2. The Magnitude of the B-coefficient and of C_0^{18}.

81. The Viscosity of Ionic Solutions.

Random motion of the molecules of a liquid was discussed in Sec. 27; and the probable duration of contacts—the length of time during which two molecules were likely to remain neighbors—was examined. These considerations were for a liquid at rest or in uniform motion. When a velocity gradient exists in the moving liquid, each successive layer of molecules has to move over the adjacent layer, and the phenomena of viscosity enter. In this chapter we are concerned with the question of how the viscosity of a dilute ionic solution will differ from that of the pure solvent.

In a very dilute solution, between the co-spheres of the ions the interstitial solvent is unmodified and has the same properties as in the pure solvent. The co-sphere of each positive ion and the co-sphere of each negative ion, however, may contribute toward a change in the viscosity. We should expect to find, in a very dilute solution, for each species of ion present, a total contribution proportional to the number of ions of that species present in unit volume. At the same time, we may anticipate that the electrostatic forces between the positively and the negatively charged ions must be taken into account.

Accurate viscosity measurements have been made on dilute solutions containing atomic or small molecular ions, either water or methanol being the solvent. In 1929, Jones and Dole,[1] studying extremely dilute aqueous solutions, found that their results could be written in the form

$$\eta = \eta_0(1 + A\sqrt{c} + Bc) \tag{160}$$

where η_0 is the viscosity of the pure solvent, c is the concentration of the solute, and A and B are constants characteristic of the solute. They suggested that the $A\sqrt{c}$ term, which becomes predominant at low con-

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[1] Grinnell Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

centrations, might be due to the interionic electrostatic forces, like the analogous $\sqrt{c}$ term which occurs in expressions for electrical conductivity, and so on, derived from the Debye-Hückel theory. This suggestion has proved correct. When the contribution from these long-range forces was worked out, it was found that in very dilute solution they should yield an increment in viscosity, proportional to the square root of the concentration.[1] In agreement with the theory, the value of the coefficient A in (160) is found to be positive in every case that is examined. This leaves the Bc term in (160) to represent the expected contributions from the co-spheres of the ions.

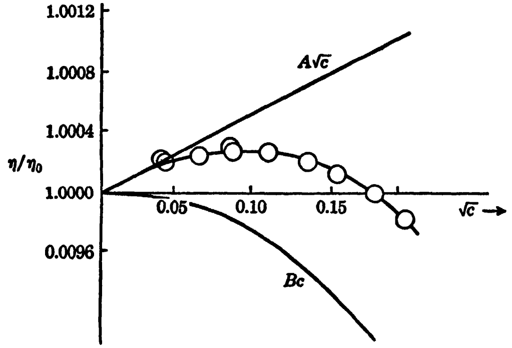

FIG. 51. Relative viscosity of aqueous solutions of KCl at 18°C plotted against the square root of the concentration. [*W. E. Joy and J. H. Wolfenden, Proc. Roy. Soc.*, **134A**, 424 (1932).]

In aqueous solution at room temperature the coefficient B is positive for the majority of electrolytes. For some, however, it is negative; in such a case the viscosity at moderate concentrations, where the B term is predominant, is less than that of pure water, while at lower concentrations, where the $A\sqrt{c}$ term becomes predominant, the value of the viscosity rises above that of pure water. An example of this is shown in Fig. 51, where abcissas are $\sqrt{c}$. The straight line is a plot of $A\sqrt{c}$ with $A = +0.0052$, while the lower curve is a plot of Bc with $B = -0.033$. On adding the ordinates of these two curves the middle curve is obtained, which reproduces, within the experimental error, the values of η/η_0 obtained for KCl in aqueous solution at 18°C.

82. The B-Coefficients. We may pass on now to discuss the B-coefficients. The experimental values in aqueous solution are given in Tables 21 and 22. The variation with temperature for various pairs of ions is shown in Fig. 52. It will be seen that with rise of temperature the

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[1] H. Falkenhagen, "Electrolytes," Chapter 10, Oxford, 1934.

TABLE 19. VISCOSITY A-COEFFICIENTS IN AQUEOUS SOLUTION[a]

Solute	Temp., °C	Eq. conductance		A calc.	A exp.
		Cation	Anion		
NaCl	25	50.11	76.34	0.0060	0.0067
	0	. .	41.3	0.0056	0.0045
KBr	0	40.4	43.1	0.0044	0.0045
$AgNO_3$	25	61.92	71.44	0.0056	0.0063
	0	32.9	40.4	0.00505	0.00515
K_2SO_4	25	73.52	79.8	0.0131	0.0141
	0	40.4	41	0.0122	0.0122
K_2CrO_4	25	73.52	79.3	0.0131	0.0133
	0	40.4	42.6	0.0119	0.0110
CsI	25	78.1	76.7	0.0048	0.0039
	0	44.4	43.4	0.0042	(0.0025)[b]
$KMnO_4$	25	73.52	61.7	0.0056	0.0058
	0	40.4	31.0	0.0052	0.0047
HNO_3	18	316.55	61.74	0.0021	0.0021

[a] Grinnell Jones and H. J. Fornwalt, *J. Am. Chem. Soc.*, **58,** 619 (1936); Grinnell Jones and J. H. Colvin, *J. Am. Chem. Soc.*, **62,** 338 (1940); Grinnell Jones and S. M. Christian, *J. Am. Chem. Soc*, **59,** 484 (1937), W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc.*, **134A,** 424 (1932).

[b] Value very uncertain because the $A\sqrt{c}$ term is masked by an unusually large negative Bc term; see Table 21.

TABLE 20. VISCOSITY A-COEFFICIENTS AT 25°C

Solute	Eq. conductance		A calc.	A exp.
	Cation	Anion		
In methanol solution:[a]				
KCl	53.8	51.3	0.0173	0.0151
KBr	53.8	55.5	0.0165	0.0142
KI	53.8	61.0	0.0158	0.0159
NHCl	59.0	51.3	0.0165	0.0183
In ethanol solution:[b]				
NaI			0.0255	0.027

[a] Grinnell Jones and H. J. Fornwalt, *J Am. Chem. Soc.*, **54,** 4244 (1932).

[b] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.*, **145A,** 475 (1934).

negative coefficients tend to become positive. It appears that above 50°C the B-coefficients for most pairs of ions will have become positive. At the same time, with rise of temperature the coefficients which are positive below room temperature increase in value, but more slowly.

It is likely that the occurrence of negative B-coefficients is a peculiarity of aqueous solutions, since the few accurate measurements that have been made in non-aqueous solvents have yielded only viscosities greater than that of the pure solvent. Some results from solutions in methanol and ethanol are given in Table 23. On comparing these values with those given in Table 21, it will be seen that solutes which have negative *B*-coefficients in water have large positive *B*-coefficients in methanol.

If the *B*-coefficients represent the contributions from the co-spheres of the ions, we should expect that in very dilute solution the contributions from the positive and the negative ions would be independent and therefore additive. In Table 21 the values for uni-univalent solutes in aqueous solution have been arranged so that one can see whether this additive property is present. It will be noticed that, for example, when the positive ion is Li$^+$ the value in each case is larger than when the positive ion is Na$^+$ in a solution at the same temperature. In most cases when the positive ion is K$^+$, the value is negative, while for Cs$^+$ at the same temperature the coefficients have still larger negative values. Not only do the values in the various columns lie in the order Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, but there are nearly constant differences between the rows, and likewise between the vertical columns. This means that at any temperature it is possible to assign a coefficient to each species of positive and of negative ion, such that the sum of two such coefficients gives in each case a value near to the observed *B*-coefficient for the pair of ions. We can conclude that at the concentrations at which the measurements

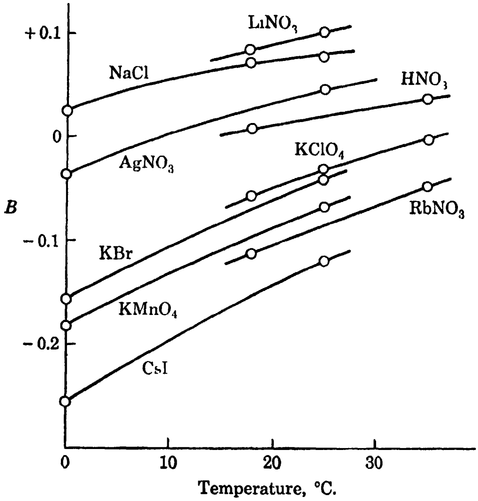

FIG. 52. Viscosity of *B*-coefficients plotted against the temperature centigrade.

have been made the contributions from the co-spheres of the positive and negative ions are, at least, approximately additive and independent.

It will be noticed that the value of the B-coefficient for HNO_3 at 18°C, given in Table 21, lies intermediate between those of KNO_3 and $NaNO_3$, while that of HCl lies intermediate between those of KCl and NaCl. On the other hand, the calculated value of the A-coefficient for HNO_3, given in Table 19, is abnormally small. This is because the ionic cloud surrounding the $(NO_3)^-$ ion has an abnormally small time of relaxation, owing to the high mobility of the proton that arises from proton jumps, and because the resultant drag due to the electrostatic interionic forces is small. It will be seen that the experimental value of the A-coefficient

TABLE 21. VISCOSITY B-COEFFICIENTS FOR ION PAIRS IN AQUEOUS SOLUTION[a]

	Temp., °C	Cl^-	Br^-	I^-	NO_3^-	IO_3^-
Li^+	25	0.139	0.106	0.081	0.101	0.299
	18				0.084	0.283
Na^+	25	0.07866				
	18	0.074			0.033	0.23
	0	0.2438				
K^+	35	+0.009				
	25	−0.0140	−0.0480		−0.0531	+0.132
	18	−0.033		−0.102	−0.074	+0.11
	0		−0.15377			
Rb^+	35			..	−0.047	
	25	−0.037	−0.061	−0.11		
	18	−0.065			−0.111	
Cs^+	25	−0.050		−0.1184	−0.092	
	18	−0.075			−0.126	
	0			−0.2543		
Ag^+	25				+0.04517	
	0				−0.03542	
H^+	35				+0.0365	
	25	+0.06	+0.029			
	18				+0.008	

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[a] Grinnell Jones and S. K. Talley, *J. Am. Chem. Soc.*, **55**, 624 (1933); Grinnell Jones and R. E. Stauffer, *J. Am. Chem. Soc.*, **62**, 336 (1940); V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.*, **1144** (1934); and references to Table 19.

agrees with this calculated value. On the other hand, the *B*-coefficient which belongs to the $(H_3O)^+$ ion is quite normal; it is unaffected by proton jumps and has a value intermediate between those of the K^+ ion and the Na^+ ion.

TABLE 22. VISCOSITY *B*-COEFFICIENTS NOT INCLUDED IN TABLE 21[a]

	Temp., °C	*B*
NaOH	18	+0 196
KOH.	18	+0 091
$KClO_3$.	35	−0 0035
	25	−0 031
	18	−0 056
$KMnO_4$	25	−0 066
	0	−0 18
$KBrO_3$	25	−0 001
NH_4Cl	25	−0 0144
	18	−0 05
NH_4Br.	25	−0 037
NH_4I...	25	−0 08
NH_4NO_3.	25	−0.034
K_2SO_4.....	25	+0 1935
	18	+0 08
	0	+0 0339
$LaCl_3$	25	+0.5672
	0	+0.4744

[a] Grinnell Jones and R. E. Stauffer, *J. Am. Chem. Soc.*, **62,** 337 (1940); and references to Tables 19 and 21.

TABLE 23. VISCOSITY *B*-COEFFICIENTS IN DILUTE METHYL AND ETHYL ALCOHOLS AT 25°C

In methanol:[a]	
KCl	0 7635
KBr	0 7396
KI	0 6747
NH_4Cl	0 6610
In ethanol:[b]	
NaI .. .	1 15

[a] Grinnell Jones and H. J. Fornwalt, *J. Am. Chem. Soc*, **54,** 4244 (1932).
[b] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.*, **145A,** 475 (1934).

The question arises as to how the *B*-coefficient for any solute is to be divided among the cation and anion. Before attempting to solve this problem, we could, of course, begin by assigning an arbitrary value to some species of ion (we could, for example, assign the value zero to K^+); then the values to be assigned to all the other monovalent ions can readily be worked out from Tables 21 and 22. Instead of this arbitrary scale, it would be much more satisfactory to decide, if possible, what contribution is actually being made by the cation and anion, separately.

For some of the solutes in Table 21 (for example, $NaNO_3$ and KCl) the *B*-coefficient has a value not far from zero. In such a case it might be that the viscosity of the solvent is very little modified either by the presence of the positive ion or by the presence of the negative ion. On the other hand, the correct explanation may be quite different: it may be that the co-sphere of the positive ion causes a local increase in the viscosity, while the co-sphere of the negative ion causes a nearly equal decrease in the viscosity, or vice versa; whenever such a cancellation occurs, the *B*-coefficient for the solute will have a value not far from zero, and we need other evidence before we can decide how contributions should be assigned to the individual ions. When the *B*-coefficient for a solute is negative, we know that at least one of the ions is diminishing the viscosity. The largest negative value in Table 21 is for cesium iodide. We may suspect that in this case both the positive and negative ion are diminishing the viscosity. But this will remain a speculation until we bring forward some evidence or argument to justify this interpretation.

In 1906, Einstein worked out a theory of the viscosity of a liquid which contains, in suspension, spherical particles which are large compared with the size of molecules of the liquid. The predictions of the theory are found to be in good agreement with the measured values of the viscosity of liquids containing colloidal particles in suspension. The presence of these obstacles increases the apparent viscosity of the liquid, and Einstein found[1] that the increment is proportional to the *total* volume v of the foreign particles in unit volume, that is to say, the sum of the volumes of the particles that are present in unit volume of the liquid; thus,

$$\eta = \eta_0(1 + 2.5v) \tag{161}$$

If we tentatively extend this theory to particles of smaller size, that is, to large molecules in solution, we should again expect to find an increment in the viscosity. It is, in fact, found that both the acetic acid molecule[2] CH_3COOH and the urea molecule[3] CON_2H_4 in aqueous solution at room temperature have positive *B*-coefficients, the values being 0.117 and 0.03784, respectively.

If we next try to extend the theory to particles that are not electrically neutral, that is, to large molecular ions, we must distinguish between two

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[1] A. Einstein, *Ann. Physik.*, **19**, 289 (1906); *ibid.*, **34**, 591 (1911).

[2] V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.*, **1144** (1934).

[3] Grinnell Jones and S. K. Talley, *J. Am. Chem. Soc.*, **55**, 641 (1933).

types—the same two types which were mentioned in Sec. 59, namely, (1) where the electric charge is distributed fairly uniformly over the whole solute particle, and (2) where the ionic charge is located on one atom or small group of atoms in the molecular ion. In the former class the electrostatic field of the ion is so weak that we may expect the large molecular ion to have an effect very similar to that of a neutral molecule of about the same size. When tetraethyl ammonium picrate is dissolved in water it is dissociated into ions, the tetraethyl ammonium positive ion and the picrate negative ion. At 18°C the solute is found to have a positive B-coefficient equal to 0.74. It seems then that a large ion behaves as an obstacle, in a way similar to that of a colloidal particle.

It is only when we come to examine ionic solutes in aqueous solution that we meet ionic solutes that decrease the viscosity of the solvent.

It will be recalled that in Fig. 28 we found that for the most mobile ions the mobility has the smallest temperature coefficient. If any species of ion in aqueous solution at room temperature causes a local loosening of the water structure, the solvent in the co-sphere of each ion will have a viscosity smaller than that of the normal solvent. A solute in which both anions and cations are of this type will have in (160) a negative viscosity B-coefficient. At the same time the local loosening of the water structure will permit a more lively Brownian motion than the ion would otherwise have at this temperature. Normally a certain rise of temperature would be needed to produce an equal loosening of the water structure. If, in the co-sphere of any species of ion, there exists already at a low temperature a certain loosening of the water structure, the mobility of this ion is likely to have an abnormally small temperature coefficient, as pointed out in Sec. 34.

A negative B-coefficient for a solute implies that, in the co-sphere of the positive ion, or in that of the negative ion, or in both, there is an increase in fluidity. Writing in 1934, Cox and Wolfenden[1] stated that the generally accepted explanation of these negative viscosity coefficients was that they were due to "depolymerization" of the water; in a footnote to their paper, referring to the hypothesis of Bernal and Fowler,[2] they added that, if water is a pseudo-crystalline liquid, the word depolymerization might be replaced by "rise of structural temperature." This problem can be more easily discussed if one first makes a tentative division of the B-coefficients between the anions and cations of each solute. Such a tentative separation was made by Cox and Wolfenden and appears to reach the correct result, although in their argument they used concepts which are more difficult to accept today.

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[1] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.*, **A145**, 486 (1934).

[2] J. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933)

83. Assignment of *B*-Coefficients to Separate Ions. As explained in Sec. 32, the term "electrolytic ion" in aqueous solution was often used, not for the solute particle itself, but for the solute particle surrounded by a quantity of attached solvent, which was supposed to form a permanent rigid spherical "hydrated ion." The next step was to suppose that such a "hydrated ion" is large enough to obey Stokes's law, even when the solute particle itself is as small as Li^+. It will be noticed that in Table 2 the mobility of Li^+ is less than 3 per cent larger than the mobility of the iodate ion $(IO_3)^-$. From this fact Cox and Wolfenden argued that the radius of the hydrated Li^+ ion must, in accordance with Stokes's law, be less than 3 per cent larger than the radius of the hydrated $(IO_3)^-$ ion. In support of this contention they cited the fact that the temperature coefficient of the mobilities of these two ions is not far from the value demanded by Stokes's law, as will be seen from Fig. 28. If the hydrated ions are spherical with the above radii, the *volume* of the hydrated Li^+ ion would be nearly 10 per cent greater than the *volume* of the hydrated $(IO_3)^-$ ion. Since the Einstein expression (161) is derived from Stokes's law (and since it is assumed that these two hydrated ions obey Stokes's law), the argument leads directly to the prediction that the *B*-coefficient of Li^+ must be nearly 10 per cent greater than that of $(IO_3)^-$. As the viscosity of aqueous solutions of lithium iodate had been measured, this conclusion permitted *B*-coefficients to be allotted to the Li^+ and $(IO_3)^-$ ions. In Table 21 the total *B*-coefficient of $LiIO_3$ in aqueous solution at 18°C is 0.283, the accuracy not being high enough to give the last figure with certainty. Cox and Wolfenden, making the separation in the required ratio, assigned 0.14_6 to Li^+ and 0.13_6 to $(IO_3)^-$. The values of the *B*-coefficients to be ascribed to the other ions at 18°C followed at once. At the same time, they tentatively assigned the value 0.14_6 to Li^+ at 25°C also; the values to be ascribed to the other ions at 25°C followed from this choice.

Before discussing these results, we may inquire whether there is not a plausible way of separating the *B*-coefficients without making use of the concept of hydrated ions obeying Stokes's law, or anything of that nature. Let us reconsider the whole problem from the beginning. It was pointed out in Sec. 34 that the mobility u and its temperature coefficient are almost the only quantities for which experimental values can be obtained for anions and cations separately. The information contained in Fig. 28 in Sec. 34 should be a more reliable guide for our purpose than any calculation based precariously on theory, seeing that the data of Fig. 28 appear to be relevant to the problem under discussion. Since the points plotted in Fig. 28 are a guide to the behavior of the individual ions, the question arises whether we cannot, by inspection, allot *B*-coefficients to the ions in such a way as to correspond rather closely to the behavior depicted. We notice, for example, that the point for K^+ in Fig. 28 lies very near to the point for Cl^-.

In Sec. 82 it was mentioned that the *B*-coefficient for KCl has a value near zero; and it was pointed out that this *could* arise from the fact that a considerable positive contribution from the cation was being nearly canceled by a similar negative contribution from the anion (or vice versa). According to this interpretation the ions K^+ and Cl^- would be showing opposite behavior. The points plotted in Fig. 28 would incline us to reject this view, to believe that the ions K^+ and Cl^- are alike, and to interpret the *B*-coefficient of KCl as meaning that each ion has very little effect on the viscosity of water at room temperature. From Table 21 we see that at 25°C the *B*-coefficient for KCl is −0.0140; we must split this into two nearly equal parts, each of which will be negative in sign. If we divide −0.0140 in two equal halves, and allot the value −0.007 to both the K^+ and the Cl^- ions, the values to be ascribed to all the other ions at this temperature follow at once. These *B*-coefficients for the separate ions are given in Table 24.

TABLE 24. VISCOSITY *B*-COEFFICIENTS IN AQUEOUS SOLUTION AT 25°C

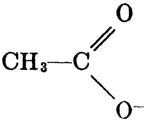
Li^+	$+0.14_7$	Cl^-	-0.00_7
Na^+	$+0.08_6$	Br^-	-0.03_2
K^+	-0.00_7	I^-	-0.08_0
Rb^+	-0.02_9	NO_3^-	-0.04_6
Cs^+	-0.04_5	MnO_4^-	-0.05_9
H^+	$+0.07_0$	ClO_3^-	-0.02_4
NH_4^+	-0.00_7	BrO_3^-	$+0.00_6$
Ag^+	$+0.09_1$	IO_3^-	$+0.15_2$
		OH^-	$+0.12$

The question arises whether this assignment of coefficients to the individual ions conflicts with that proposed by Cox and Wolfenden. In Table 24 it will be seen that the value allotted to Li^+ by the new method is +0.147, which is in surprisingly good agreement with the value 0.146 assigned to Li^+ by the method of Cox and Wolfenden. It follows that there is no significant difference between the values of Table 24 and the earlier values.

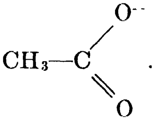
84. The Acetate Ion. For the *B*-coefficients of lithium acetate and potassium acetate, which are of course completely dissociated in aqueous solution, Cox and Wolfenden obtained at 25°C the values +0.397 and +0.238. These large values could be due entirely to the large size of the molecular ion or could be due partly to the fact that the anion produces order in its co-sphere. To test this, Laurence and Wolfenden measured the *B*-coefficient of acetic acid in aqueous solution at 25°C.

It is of especial interest to have coefficients for a neutral molecule and for a molecular anion of the same size. For the neutral molecule they found that the B-coefficient was equal to only 0.117. Since the values for lithium and potassium acetates are so much greater than for the chlorides, we cannot ascribe them merely to the large size of the anion but must suppose that it is an order-producing ion. This is not altogether surprising, since the oxygen atom that bears the negative charge may resemble $(OH)^-$, which is likewise an order-producing anion. From the B-coefficients $+0.147$ and -0.007 that have been allotted to Li^+ and K^+ in Table 24, we obtain for the acetate ion the value 0.250 or else 0.245.

In a vacuum an isolated acetate ion will resonate between the form



and the form



. If this were also true in solution, the negative charge would appear to be spread out over an unusually large volume. The ionic field would be weak, like that of (MnO_4) and $(NO_3)^-$; but the fact that the viscosity B-coefficient of the acetate ion has a greater positive value than that of the acetic acid molecule suggests that this is not so. If we consider the acetate ion in solution, at any moment it is extremely unlikely that the solvent dipoles that are in contact with the two oxygen atoms happen to produce identical polarizations, and provide for the negative charge states of equal energy, between which the electron can resonate. On one oxygen atom the energy will be the lower; and the negative charge will be localized on one oxygen atom or the other.

85. The Sign of the B-Coefficient and the Magnitude of C_1^{r2}. We come now to the important fact, pointed out by Cox and Wolfenden, that there is a correlation between the sign of the viscosity B-coefficient of an ion in aqueous solution and the temperature coefficient of the electrical mobility of the ion. They drew attention to the fact that ions to which they had assigned a negative B-coefficient for viscosity had the lowest values of the temperature coefficient of electrical mobility; and they gave an explanation in terms of depolymerization of the solvent. In pure water, with rise of temperature the liquid gradually becomes depolymerized. But if the presence of a certain ion has produced a partial local depolymerization already at a low temperature, "the temperature coefficient of viscosity of the solvent in the neighbourhood of the ion will be lower than that of the solvent as a whole. Since the mobility of an ion depends on the viscosity of the solvent immediately surrounding it, the temperature coefficient of mobility of an ion must be determined by the (lower) temperature coefficient of viscosity of the partially depolymerized solvent and not by the temperature coefficient of the macroscopic viscosity."[1] This convincing explanation can easily be put into terms of local order-disorder in the liquid. In pure water, with rise of temperature the average degree of local order becomes everywhere smaller. But if in the co-sphere of a certain species of ion,. the ionic field has produced a certain amount of disorder, already at a low temperature, one can say that the viscosity of the solvent in the ionic co-sphere will have a lower temperature coefficient than in the bulk of the solvent outside. At any rate, the freedom of the random Brownian motion of this ion at any temperature is determined by the local degree of order-disorder in its ionic co-sphere, and this Brownian motion will have a lower temperature coefficient than that calculated from the viscosity of the pure solvent. Since both the diffusion coefficient of the ion, and in an external electric field the electrical mobility of the ion, are determined by the freedom of its random motion, both these quantities will have an abnormally small temperature coefficient. There does not seem to be sufficient evidence as to how the diffusion coefficients of various ionic solutes vary with temperature. But it is true that those ions to which a negative viscosity coefficient have been assigned have the smallest values of C_0^{18}.

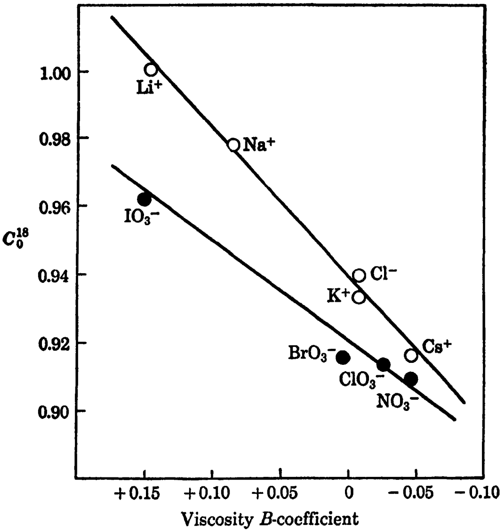


FIG. 53. Values from Table 4 plotted against viscosity B-coefficients from Table 24.

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[1] Cox and Wolfenden, *op. cit.*, p. 486.

86. The Magnitude of the *B*-Coefficient and of C_0^{18}. It will be recalled that in Fig. 28 in Sec. 34 we plotted values of C_0^{18} for various ions against the values of the ionic mobility; and we found that the values for atomic ions lay about one straight line, while the values for small molecular ions lay about another straight line. We may now try the effect of plotting values of C_0^{18} for the same ions against their viscosity B-coefficients. The values are plotted in Fig. 53, which shows the striking correlation between the values of C_0^{18} and the B-coefficients. The ordinates in Fig. 53 are the same as those of Fig. 28, while the abscissas are the values from Table 24. It will be seen that the diagram reproduces the main features of Fig. 28. The atomic ions fall near a straight line, and the molecular ions likewise fall in positions roughly similar to those of Fig. 28. One cannot resist the conclusion that for the various species of ions in aqueous solution there is a rather close connection between the mobility, the temperature coefficient of the mobility, and the effect on the viscosity of the water.

CHAPTER 10

Conventional Partial Molal Ionic Entropies. Correlation between Ionic Entropy and Viscosity. Conventional Partial Molal Entropy of $(H_3O)^+$ *and* $(OH)^-$. *The Conventional and the Unitary Entropy of Solution. Solutes in Aqueous Solution. Solutes in Methanol Solution.*

87. Conventional Partial Molal Ionic Entropies. In discussing the partial molal entropy of AgCl and AgI in Sec. 51, we succeeded in comparing the unitary term for the ion pair $(Ag^+ + Cl^-)$ with the unitary term for the ion pair $(Ag^+ + I^-)$. We found that the value of the latter is 12 entropy units greater than the former. To obtain this result, we had to take into account the fact that the concentration of a saturated solution of AgCl is more than a thousand times greater than for AgI. Only when the difference between the cratic terms had been eliminated could we make a comparison between the unitary terms. Experimental data are available from which similar results for many different solutes may be calculated; and it is obviously desirable to adopt some standard procedure and a standard way of expressing the results. The values obtained from saturated solutions of various substances are not comparable, so long as these contain widely different cratic terms. The method that has been adopted in the electrochemical literature is to choose an arbitrary standard and to tabulate values each of which contains the same cratic term.

When this has been done, the next step is to follow a procedure similar to that used in Sec. 83. When discussing the viscosity *B*-coefficients for ion pairs, we saw that, if a certain value is assigned to any one species of ion, the values to be ascribed to the other species of ions follow at once. The same will be true here.

Suppose that we arbitrarily set the partial molal entropy of the K^+ ion equal to zero. This means that we assign to the Cl^- ion the whole of the partial molal entropy of the ion pair $(K^+ + Cl^-)$; that is to say, we assign to the Cl^- ion, not only the unitary term for the Cl^- ion, but also the cratic term for both ions, and also the unitary term for the potassium ion.

A procedure like this has been adopted in the literature, except that it is the value for the hydrogen ion that has been set equal to zero. This involves a slightly more difficult concept; for, when a proton is added to water, it converts an H_2O molecule into an $(H_3O)^+$ ion. The entropy of the original water molecule is replaced by the entropy of the $(H_3O)^+$ ion and its co-sphere. When the partial molal entropy of HCl in aqueous solution has been determined, the whole is assigned to the Cl^- ion; that is to say, the value for the hydrogen ion is set equal to zero, and the values for all other species of ions are expressed relative to this zero.

Values expressed in this way, taken from a long list published by Latimer, Pitzer, and Smith, are given in Table 25. It will be seen that the value assigned to the iodide ion I^- is nearly 12 e.u. greater than that for the Cl^- ion (in agreement with the conclusion reached in Sec. 49). Adding together the values assigned to Ag^+ and Cl^- in Table 25, we see that the value ascribed to this pair of ions is 31 e.u. In Sec. 48 we found for $(Ag^+ + Cl^-)$ in a saturated solution of AgCl the value 75.8 e.u. This value contained, of course, the rather large cratic term for the ions in this very dilute saturated solution. As will be explained later, the basis of the values in Table 25 is such that the value for each ion pair contains a smaller arbitrary cratic term. Enough has been said to make it clear that the difference between the values assigned to any two species of positive ions is a significant unitary quantity, and likewise between any two species of negative ions; but *not* between a positive ion and a negative ion. Before saying more about the way in which the values in Table 25 were obtained, or about the way in which they are expressed, we shall discuss the values, as they stand, in relation to the viscosity *B*-coefficients of the same solutes.

TABLE 25. CONVENTIONAL PARTIAL MOLAL ENTROPIES OF IONS IN AQUEOUS SOLUTION AT 25°C[a]

Ion	e.u.	Ion	e.u.
H^+	(0.00)	NH_4^+	26.4
Li^+	4.7	Cl^-	13.5
Na^+	14.0	Br^-	19.7
K^+	24.2	I^-	25.3
Cs^+	31.8	OH^-	−2.49
Ag^+	17.54		

For the probable error in these values, see Table 43.

[a] W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1831 (1938)

88. Correlation between Ionic Entropy and Viscosity.

In Chapter 9, when we noticed that certain ions in aqueous solution cause a decrease in viscosity, and asked how this should be explained, it seemed natural to interpret the effect in terms of order and disorder. In pure water at room temperature there is a considerable degree of short-range order;

and it appears that certain species of ions introduce a certain degree of disorder in the co-sphere. Now, since the entropy of any system is to be regarded as some measure of the *degree of disorder*, it occurred to the author to examine the available data, to see whether a *decrease* in viscosity is, in fact, accompanied by an *increase* in entropy, and vice versa. In the co-sphere of any ion the presence of disorder should manifest itself in two ways: as a negative *B*-coefficient in viscosity, and as an increment in the entropy. Those species of ions which behave in this way should be in marked contrast to those which, in aqueous solution, cause an *increase* in the viscosity.

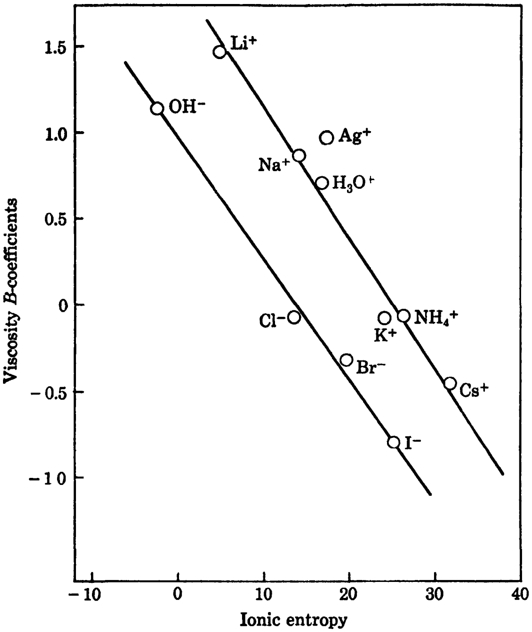

FIG. 54. Viscosity *B*-coefficients from Table 24 plotted against partial molal entropies from Table 25 (on scale of 0.0 for H^+).

Furthermore, we noticed in Table 23 that solutes which have negative *B*-coefficients in water have large positive *B*-coefficients when dissolved in methanol. The correlation will therefore be complete, if we find that these same solutes introduce an increase of entropy in water and a decrease in entropy when dissolved in methanol.

When we say that we might expect to find this correlation between viscosity and ionic entropy we are, of course, concerned only with the unitary part of the entropy—the part associated with the ionic co-sphere. If, however, such a correlation exists, it should be apparent in the values quoted in Table 25, in spite of the fact that these contain an arbitrary cratic term. In view of the fact that this cratic term has the same value for each ion pair, its presence will not mask the correlation with viscosity, if one exists. Let us then plot the viscosity *B*-coefficients from Table 24 against the values from Table 25. The result shown in Fig. 54 could hardly be more striking and convincing. It will be seen that the points for the positive ions lie about a straight line, while the points for the negative ions lie about a nearly parallel straight line. In both cases the ions with the greatest ionic entropies are those with negative *B*-coefficients for viscosity.

In view of the fact that the entropy values are all based on the arbitrary choice of zero for the H^+ ion, it is not surprising that the points for the positive and negative ions lie on separate straight lines; this fact is of no significance. If, instead of zero, we were to assign the value −5.5 to the H^+ ion, we should obtain the set of values shown in Table 26, where the value for each positive ion has been diminished by 5.5 e.u., while at the same time the value for each negative ion has been increased by the same amount, so that the sum for any ion pair retains the same value, namely, the value derived from the experimental data. Table 26 also includes entropy values for five of the larger molecular ions for which viscosity *B*-coefficients were given in Table 24.

TABLE 26

Ion	e.u	Ion	e.u
H^+	(−5.5)	Br^-	25.1
Li^+	−0.8	I^-	30.8
Na^+	8.5	OH^-	3.01
K^+	18.7	MnO_4^-	52.2
Cs^+	26.3	NO_3^-	40.5
Ag^+	12.04	ClO_3^-	44.9
NH_4^+	20.9	BrO_3^-	44.0
Cl^-	19.0	IO_3^-	33.5

When the values from Table 26 are plotted against the *B*-coefficients from Table 24, the result shown in Fig. 55 is obtained. The points for atomic ions of both signs now lie about a single straight line.

Further we may notice that there is a striking resemblance to Fig. 28 in Chapter 4, where the temperature coefficient of the ionic mobility was plotted against the mobility itself. This resemblance is more interesting when it is recalled that the experimental values plotted in Fig. 28 are obtained for each species of positive and each species of negative ion *separately* and do not contain any arbitrary factor (like the assignment of −5.5 to the H^+ ion). Six features of Fig. 28 may be enumerated as follows: (1) the values for K^+ and Cl^- lie close together; (2) the values for Cs^+ and I^- lie below; (3) the values for Na^+ and Ag^+ lie above; (4) the value for Li^+ lies still higher; (5) the values for the large molecular ions lie about a nearly parallel line; (6) their order is $(NO_3)^-$, $(ClO_3)^-$, $(IO_3)^-$. On comparing Fig. 55 with Fig. 28, it will be seen that all these six features are reproduced in Fig. 55. It is difficult to resist the conclusion

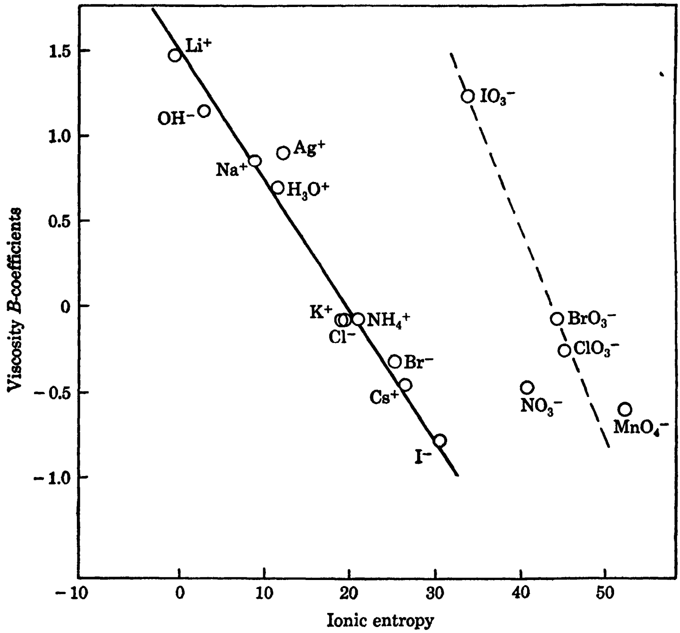

FIG. 55. Viscosity *B*-coefficients plotted against partial molal entropies from Table 26 (on scale of −5.5 for H^+).

that this striking resemblance is due to the fact that all four of the ionic properties that are involved in these diagrams depend largely on the same factor, namely, the degree of order or disorder in the ionic co-sphere.

It will be recalled that in Chapter 7, in dealing with the anions of weak acids, we found that we were able to obtain good qualitative agreement between theory and experiment, if we replaced J_{env} by the electrostatic J_{el}. As has been pointed out more than once, the use of simple electrostatic theory necessarily implies that there is an increment in the degree of order in the solvent subject to the electrostatic field. In the *B*-coefficients of Table 24, however, we have found that for 6 out of the

9 anions there appears to be a *decrease* in the amount of order in the ionic co-sphere; and we must ask whether the conclusions of Chapter 7 can be reconciled with this result. As a partial answer we can at once point out that every one of the 6 anions in question (Cl^-, Br^-, I^-, NO_3^-, MnO_4^-, ClO_3^-) is the anion of a strong acid and therefore did not come into question in Chapter 7 where we were discussing the anions of weak acids. Further, we can mention that the experimental evidence brought forward in Sec. 84 seems to show that, on the contrary, the acetate ion is an order-producing ion. As far as it goes, this is satisfactory, but it raises a new question—it leads us to inquire whether we should regard it as "accidental" that the anions of strong acids are order-destroying ions, while the anions of weak acids are order-producing ions; or whether there is some significance in this result. This question will be discussed in Sec. 99 of Chapter 12.

89. Conventional Partial Molal Entropy of $(H_3O)^+$ and $(OH)^-$. Let us now consider the partial molal entropy for the $(H_3O)^+$ ion and the $(OH)^-$ ion. If we wish to add an $(H_3O)^+$ ion to water, this may be done in two steps; we first add an H_2O molecule to the liquid, and then add a proton to this molecule. The entropy of liquid water at 25°C is 16.75 cal/deg/mole. This value may be "obtained (1) from the low temperature calorimetric data of Giauque and Stout,[1] combined with the zero point entropy predicted by Pauling, or (2) from the spectroscopic entropy of steam less the entropy of vaporization."[2] Values obtained by the two methods agree within 0.01 cal/deg.

The entropy per molecule of liquid water will therefore be 16.75 e.u., divided by Avogadro's constant. We have next to consider the change of entropy when a proton is added to a water molecule to give an $(H_3O)^+$ ion. It is this quantity that is arbitrarily put equal to zero in Latimer's scale. We see at once that the value that must be allotted to the $(H_3O)^+$ ion in Latimer's list is 16.75 e.u.

Let us now look at the viscosity B-coefficients for ion pairs containing the $(H_3O)^+$ ion. As far as the size of the ion is concerned, $(H_3O)^+$ should be similar to K^+. In Table 22 we see, however, that while the B-coefficients for KCl and KBr at 25° are negative, those for HCl and HBr are positive. The $(H_3O)^+$ more nearly resembles the Na^+ ion. For HCl the B-coefficient is 0.06 as compared with 0.07866 for NaCl; thus the value for HCl is smaller by nearly 0.019. The value for $NaNO_3$ given in Table 21 is 0.033 at 18°, while the value for HNO_3 at this temperature is 0.008; in this case the value for HNO_3 is smaller by 0.025 e.u.

It is of interest now to see where the point will fall in Fig. 55 if we plot

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[1] W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.*, **58**, 1144 (1936).

[2] K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **59**, 2639 (1937).

the entropy 16.75 against the *B*-coefficient, taking the value of the latter to be 0.022 e.u. less than that of Na^+. We see that the point in Fig. 55 falls quite near the line for positive ions.

The entropy of the $(OH)^-$ ion may be obtained from the value of ΔS^0 for the self-dissociation of water. Whether this process is written in the form

$$2H_2O \rightleftarrows (H_3O)^+ + (OH)^- \qquad (162)$$

or in the older form

$$H_2O \rightleftarrows H^+ + (OH)^-$$

in either case the number of solute species is increased by 2. We do not have to worry about the cratic term, since this will have the same value as when a uni-univalent solid dissolves. The initial entropy of $2H_2O$ is twice 16.75 e.u., that is to say, 33.50 e.u. From the measurements included in Table 9 the value of ΔS^0 for the process (162) was found to be -19.24 e.u. Adding this value to 33.50 e.u., we find $+14.26$ e.u. for the partial molal entropy of the ion pair $(H_3O)^+$ and $(OH)^-$. We have seen that assigning zero value to the proton is equivalent to assigning 16.75 e.u. to the $(H_3O)^+$ ion. We conclude then that the value to be allotted to $(OH)^-$ in Table 25 is $(14.26 - 16.75) = -2.49$ e.u. This value includes the same cratic term as the other anions in this table. The viscosity *B*-coefficient for $(OH)^-$ is plotted against this value in Fig. 54. It was pointed out in Sec. 24 that a hydroxyl ion may be regarded as an oxygen ion $O^=$ containing a proton inside the electronic cloud of the ion; and we see that in Fig. 54 the point for $(OH)^-$ falls almost on the line for the negative atomic ions.

90. The Conventional and the Unitary Entropy of Solution. In Sec. 55 we discussed the free energy of solution, by considering the quantity $(\Delta F - 2RT \ln x)$. Again taking a uni-univalent solute, let us now fix attention on the quantity

$$(\Delta H - \Delta F + 2RT \ln x) \qquad (163)$$

where ΔH is the heat of solution per mole, and ΔF is the corresponding free energy of solution at the same temperature T in that solution where the solute has the mole fraction x. As in Sec. 55 we shall ask two questions: (1) how does the value of this quantity vary with the concentration of the solution into which the additional ions are being introduced, and (2) how would the value vary with concentration, if the solution were an ideal solution? We may take question (2) first and may answer at once that the value would not vary with concentration at all. For according to (77) ΔH would not vary with concentration, and $-\Delta F$ would vary with concentration only because it contained the cratic part

$-2RT \ln x$. Since this cratic part is canceled by the third term in (163), we conclude that the value of (163) has a fixed value, characteristic of the solute dissolving in the given solvent.

Turning now to the non-ideal solution, we may answer question (1) by saying that the value of (163) will vary with concentration only insofar as the solution differs from an ideal solution; and we can proceed to ask a third question: how would the value of (163) vary with concentration for an ionic solution in the extremely dilute range? We must answer that in a series of extremely dilute solutions the value of (163) would be *constant* within the experimental error; it is, in fact, a unitary quantity, characteristic of the solute dissolving in the given solvent. As in Sec. 55, this constant value adopted by (163) in extremely dilute solutions may conveniently be written as the limiting value as x tends to zero; thus

$$\lim_{x \to 0} (\Delta H - \Delta F + 2RT \ln x) \tag{164}$$

If we now divide this by the constant temperature T, the result is obviously the unitary part of ΔS, the entropy of solution.

$$\lim_{x \to 0} \left(\frac{\Delta H - \Delta F}{T} + 2R \ln x \right) = \Delta S_{unitary} \tag{165}$$

Since in these extremely dilute solutions the mole ratio does not differ appreciably from x, (165) may equally well be written

$$\lim_{y \to 0} \left(\frac{\Delta H - \Delta F}{T} + 2R \ln y \right) \tag{166}$$

Finally, since $y = m/M$, we may add the constant quantity $2R \ln M$ to both sides of equation (166) and obtain

$$\lim_{m \to 0} \left(\frac{\Delta H - \Delta F}{T} + 2R \ln m \right) = \Delta S_{unitary} + 2R \ln M \tag{167}$$

The left-hand side of (165) or (166) gives the unitary part of the entropy of solution. In electrochemistry, however, it is the left-hand side of (167) which is the conventional "entropy of solution at infinite dilution" usually denoted by ΔS^0. Thus

$$\Delta S_{unitary} = \Delta S^0 - 2R \ln M \tag{168}$$

With the usual 1000 grams of solvent as the b.q.s. we have in aqueous solution $M = 55.51$; thus $2R \ln M$ is equal to 16 e.u. To obtain the unitary part of the entropy of solution of a uni-univalent crystal in water at any temperature, we have to subtract 16.0 e.u. from the conventional

ΔS^0. Similarly in methanol, whose molecular weight is 32, we have $M = 1000/32$; for any uni-univalent solute, we have then $2R \ln M$ equal to 14.0 e.u.

The molar entropy of solution of a crystal—the ΔS^0 of (168)—may be regarded as the difference between (1) the molar entropy of the crystal, and (2) the partial molal entropy of the solute in a solution of a certain concentration. The question arises: In a solution of what concentration? Now we notice that (168) may be written in the form

$$\begin{aligned}\Delta S^0 &= \Delta S_{unitary} - \left(2R \ln \frac{m}{M}\right)_{m=1} \\ &= \Delta S_{unitary} - (2R \ln y)_{m=1}\end{aligned} \tag{169}$$

Accordingly, the conventional partial molal entropies of ions in solution are often said to refer to the ions in a one-molal solution ($m = 1$); not in a real one-molal solution, but in a hypothetical ideal one-molal solution, where the contribution from the interionic forces is taken to be zero, and the cratic term replaces the communal term.

Actually the cratic term for an ideal solution of a uni-univalent solute, instead of $-2R \ln y$, would be $-2R \ln x$ with $x = 1/(M + 2)$; or if one imagines two ideal solutions, each containing only one species of ion, it would be twice $-R \ln x$, with $x = 1/(M + 1)$

In (167), in taking the value at the limit as m tends to zero, our aim was merely to eliminate the contribution from the interionic forces. In practice we may take for the molality m any value lying within the extremely dilute range, provided that in (167) we take the value of ΔF for the solute at the same concentration m. Now we know that in the case of a sparingly soluble solute the interionic forces make a negligible contribution, even in a saturated solution. In evaluating ΔS^0 for such a solute, it is convenient to take for m the molality of the saturated solution, since in this case the value of ΔF is zero. As an example, we may evaluate the conventional ΔS^0 for AgCl in water at 25°C. In Table 33 on page 205 the concentration of the saturated solution at 25°C is given as 1.337×10^{-5} mole per 1000 grams of water, and the corresponding value of $-\log K$ is given as 9.749. Multiplying this by 1.987×2.303, we find that $2R \ln m$ is equal to 44.6. Now in Sec. 48 we have already seen that for AgCl the value of $\Delta H/T$ is 52.8 e.u. Hence for the conventional ΔS^0 of AgCl we find

$$\begin{aligned}\Delta S^0 &= 52.8 - 44.6 \\ &= 8.2 \text{ e.u.}\end{aligned}$$

In the same way, for silver iodide we see that the value of $-\log K$ at 25° is given in Table 33 as 16.08. Multiplying this by 1.987×2.303, we find that the value of $2R \ln m$ is 73.6 e.u. Since the value of $\Delta H/T$ given in Sec. 48 was 89.6 e.u., we obtain for the conventional ΔS^0 of AgI at 25°C the value

$$\begin{aligned} \Delta S^0 &= 89.6 - 73.6 \\ &= 16.0 \text{ e.u.} \end{aligned}$$

For sodium hydroxide the value of ΔS^0 may be obtained by subtracting the entropy of solid NaOH (given in Table 44) from the values given in Table 45 for the Na^+ and OH^- ions, which are known independently; see Sec. 89.

91. Solutes in Aqueous Solution. As mentioned in Sec. 88, when we say that we expect to find a correlation between the *B*-coefficients of viscosity of various species of ions, and their entropy of solution, this refers only to the unitary part of the entropy, the part associated with the ionic co-sphere. We are inclined to adopt the view that a negative *B*-coefficient for a pair of ions should be accompanied by a positive increment in entropy, while a positive *B*-coefficient should be accompanied by a decrease in entropy. The values of ΔS^0, the conventional entropy of solution, to be found in the literature, do not give a direct answer to this question, since they contain the cratic term, which in water at room temperature amounts to 16 e.u. This must be subtracted.

TABLE 27. ENTROPIES OF SOLUTION[a] AND VISCOSITY *B*-COEFFICIENTS

1	2	3	4	
			B-coefficient	
Solute	ΔS^0	$(\Delta S^0 - 16.0)$	At 18°C	At 25°C
KI	+25.4	+9.4	−0.102	(≈ −0.09)
KCl	+18.1	+2.1	−0.033	−0.014
NaCl .	+10.3	−5.7	+0.074	+0.0787
NaOH.. ..	−2.3	−18.3	+0.196	(≈ +0.21)

[a] W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940); W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938)

Table 27 contains data for some uni-univalent solutes for which both the entropy of solution at 25°C and the viscosity *B*-coefficient in aqueous solution at 18 or 25° are known. In column 3 from the entropy of solution 16.0 e.u. have been subtracted for the cratic term.

In column 4 it will be seen that the *B*-coefficients for potassium iodide and potassium chloride are negative, in contrast to that for sodium chloride, which is positive. In all three cases the values of ΔS^0, given in column 2, are positive. When, however, the 16.0 e.u. are subtracted, we obtain the negative value −5.7 for NaCl, in contrast to +9.4 and +2.0 for KI and KCl. The *B*-coefficient for the ion pair ($Na^+ + OH^-$) has a positive value, larger than that of ($Na^+ + Cl^-$). In column 3 we see that the value obtained for NaOH is −18.3 as compared with −5.7 for NaCl. In each case a negative value in column 3, implying an increment in order in the ionic co-spheres, is accompanied by a positive viscosity *B*-coefficient. At the same time a positive value in column 3, indicating disorder in the ionic co-spheres, is accompanied by a negative value in column 4. Additional examples of the latter type, such as KBr, KNO_3, and $KClO_3$ could have been added; but before we do this, the large molecular anions need special attention.

TABLE 28

	ΔS^0	$(\Delta S^0 - 24)$	*B* at 18°C	*B* at 25°C
KIO_3.	+15.9	−8.1	+0.11	
$NaNO_3$	+21.5	−2.5	+0.033	
$KBrO_3$	+27.2	+3.2	(≈ −0.02)	−0.001
KNO_3	+27.4	+3.4	−0.074	−0.053
$KClO_3$	+29.4	+5.4	−0.057	−0.031
$KMnO_4$	+29.9	+5.9	−0.08	−0.066
	ΔS^0	$(\Delta S^0 - 16.0)$	*B* at 18°C	*B* at 25°C
NaOH	−2.3	−18.3	+0.196	
NaCl	+10.3	− 5.7	+0.074	
KCl	+18.1	+ 2.1	−0.033	−0.0140
KBr	+21.4	+ 5.4	(≈ −0.07)	−0.0480
KI ...	+25.4	+ 9.4	−0.102	

Consider an ionic crystal in which the anion is a molecular ion. The orientation of this anion in the crystal is completely determined, or determined to a large extent, by the crystal structure; and furthermore, its freedom of libration is severely limited by the intense fields of the adjacent ions. When this ion goes into solution, it will have a greater number of possible orientations, and its freedom of libration will be greater. Hence the ΔS^0 for a molecular anion will contain a considerable increment in entropy over and above the cratic term (which is all that we subtract in the case of an atomic ion). This additional increment in entropy is likely to be somewhat different for different species of anion. The best we can do at present is to subtract an amount that is of the right order of magnitude. The question is whether we can, by subtracting a certain amount for each of the large molecular anions, bring these solutes into line with those that consist of atomic ions. Allowing an additional 8 e.u. for this effect, in Table 28 we have subtracted 24 e.u., in place of the 16 e.u. used for a pair of atomic ions. We have seen in Fig. 55 that the small molecular ions $(OH)^-$, $(H_3O)^+$, and $(NH_4)^+$, which merely contain one or more protons within the electronic cloud, behave like atomic ions.

When the values in columns 3 and 4 of Table 28 are compared, it will be seen that the correlation is surprisingly good; in fact, there is not a single case of a positive value in column 3 being accompanied by a positive value in column 4 or of a negative value in column 3 being accompanied by a negative value in column 4. We should hardly expect to find this perfect correlation; and it is likely that, when accurate data for other solutes are available, cases will be found which fail to fit into this scheme.

92. Solutes in Methanol Solution. In Table 23 we have seen that for four solutes in methanol the viscosity B-coefficients are positive. This is the case even for KCl and KBr, for which the coefficients are negative in aqueous solution. In Sec. 88 it was pointed out that it would be of interest to see whether this inversion is likewise accompanied by a change in sign for the ionic entropy. Although no accurate values for the entropy of solution of salts in methanol are available, reliable estimates have been made for KCl, KBr, and NaCl.[1] Since the B-coefficients of KCl and KBr have been determined both in methanol and in water, all the required data are available for these two solutes. The values of ΔS^0 given in Table 29 have been taken from Table 34 in Chapter 12, where the method of derivation is explained. The cratic term included in each of these values is 14 cal/deg, as already mentioned in Sec. 90.

TABLE 29. ENTROPIES OF SOLUTION AND VISCOSITIES IN METHANOL AND IN WATER

In methanol	ΔS^0	$\Delta S^0 - 14$	B
KCl	−16.5	−30.5	+0.7635
KBr	−12.8	−26.8	+0.7396
In water	ΔS^0	$\Delta S^0 - 16$	B
KCl	+18.1	+2.1	−0.014
KBr	+21.4	+5.4	−0.018

It will be seen that the correlation that was found in aqueous solution is now extended to solutes in methyl alcohol. The large increment in the

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[1] W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940).

viscosity is accompanied by a large loss in entropy. It is only in water that negative *B*-coefficients have been found, and then only for certain species of ions. This is interpreted as due to a local breaking up or loosening of the water structure in the ionic co-sphere. In each case this mechanical disorder appears at the same time as thermodynamic disorder, or an increment in the entropy. The results from columns 3 and 4 of Table 29 are plotted in Fig. 56, together with the results for solutes in aqueous solution from Table 27.

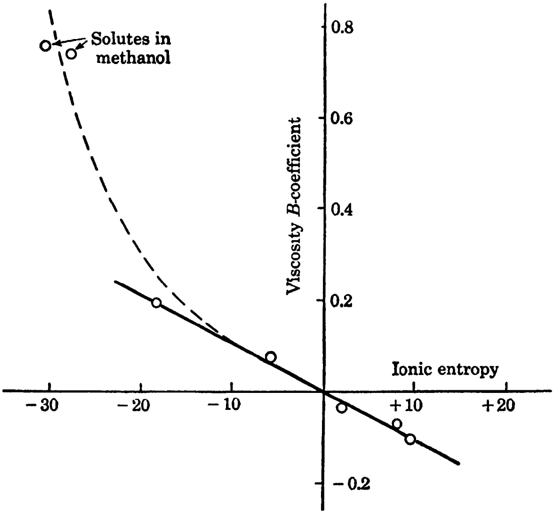

FIG. 56. Viscosity *B*-coefficients plotted against values from Tables 28 and 29.

As a postscript to this chapter we may return to the values for ions in aqueous solution given in Tables 25 and 26. We recall that each value contains the conventional cratic quantity $R \ln M$; that is to say, 8.0 e.u. per uni-univalent ion. Subtracting 8.0 e.u. from each of the values in Table 26, we obtain those given in Table 30, assigning −13.5 e.u. to

TABLE 30. THE UNITARY PARTIAL MOLAL ENTROPY IN AQUEOUS SOLUTION
($H^+ = -13.5$ e.u.)

Ion	e.u	Ion	e.u.
H^+	(−13 5)	Cl^-	11 0
Li^+ .	−8 8	Br^-	17.1
Na^+	+0 5	I^-	22 8
K^+	10 7	OH^-	−4 99
Cs^+	18 3	MnO_4^-	44 2
Ag^+	4 04	NO_3^-	32 5
NH_4^+.	12.9	ClO_3^-.	36.9
H_3O^+.	0.76	IO_3^-.	25.5

the H^+ ion, this being the value that brings together the points for positive atomic ions and negative atomic ions, to lie about the same straight line as in Fig. 55.

Problem

Taking the values for the Ag^+ ion and the Cl^- ion from Table 25, and adjusting the cratic term, find the value of the partial molal entropy of silver chloride in an aqueous solution having a molality equal to 10^{-6}.

CHAPTER 11

Properties of Different Solvents. Volumes in Aqueous Solution. The Increment in Volume for a Pair of Ions. Volumes in Different Solvents Compared. Thermal Expansion.

93. Properties of Different Solvents. In discussing molecular dipoles in Sec. 25, we estimated the force of attraction between an atomic ion and a dipole having the most favorable orientation and found this attraction to be very strong. In any ionic co-sphere those molecular dipoles which have a favorable orientation will be attracted, while those that have the opposite orientation will be repelled. Since the former are more numerous the solvent in the co-sphere is, on the whole, attracted toward the ion. Since the liquid is not incompressible, we must expect that this will lead to a contraction in each co-sphere. In any ionic solution the sum of the contractions that have taken place in the co-spheres of the positive and negative ions will be apparent if we measure accurately the volume of the solution.

At the same time, since there has been, in each co-sphere, an increment in the density of the solvent, we must expect some modification in other properties of the solvent, such as its compressibility. In a very dilute solution it may be difficult to detect such a change by measuring the compressibility of the solution. At higher concentrations, however, when a sufficient fraction of the total solvent lies within the ionic co-spheres, the sum of these local modifications can be detected by measuring the compressibility of the whole solution.

For this purpose, from the available solvents one would be inclined to choose first the liquid whose properties, in the pure state, are the simplest. In other words, one would not choose water, whose properties in the pure state are most complicated. Not only does the density of water show the familiar maximum at 4°C, but its compressibility passes through a minimum near 50°C; its thermal expansion is abnormal, and so on. If it were not for the extreme practical importance of the familiar aqueous solutions, one would prefer to study several other solvents first. But, as it is, aqueous solutions must be interpreted, and one may ask which of the other solvents is most suitable for comparison with water.

As methyl alcohol freezes in the neighborhood of −95°C, measurements at a temperature −70°C would be comparable with water at room temperature; at 25°C methyl alcohol is very unlike water, having a compressibility more than 2.5 times as large. Ethyl alcohol and liquid ammonia are likewise unsuitable for comparison with water.

On the other hand, ethylene glycol, $C_2H_4(OH)_2$, which has a dielectric constant equal to 38.66 at 20°C, has been investigated by R. E. Gibson and found to be a very suitable solvent for comparison with water, without the eccentricities of the latter. At room temperature the compressibility of ethylene glycol (for brevity often called glycol) is only 29 per cent smaller than that of water. The behavior of its energy-volume coefficient $(\partial E/\partial v)_T$ does not differ much from that of a normal nonpolar liquid. Ionic crystals dissolve in glycol almost as readily as in water; and, as described below, the solvation of the ions in this liquid seems to be almost free from the peculiarities shown in aqueous solution. Various comparative results obtained for ions in glycol, water, and in methyl alcohol will be described later in this chapter. But, since a greater mass of data is available in aqueous solutions, we shall first turn our attention to the latter.

94. Volumes in Aqueous Solution. In an extremely dilute solution, there will be a large quantity of solvent that is not near any ion or modified by any ion; and in this solution the co-spheres of the ions will not overlap, except in those very rare cases where two ions happen to be near to each other. If the volume of such a solution could be measured, the contributions from the co-spheres of the positive ions would be independent of the contributions from the co-spheres of the negative ions. In other words, the contributions would be additive; and if measurements were made on the solutions of a large number of ionic crystals, it should be possible to express each of the results as the sum of a contribution from the species of positive ion present and a contribution from the species of negative ion present. When the volume of a sufficiently dilute solution cannot be accurately measured, measurements can be made on a series of less dilute solutions, and the results extrapolated to infinite dilution. In attacking this problem, it looks at first sight as if one could obtain interesting and significant data for a series of ionic solutes by a simple straighforward procedure. Suppose we take a known amount of an ionic crystal, and a known large amount of solvent. Adding the volumes of solute and solvent, we call this the initial volume. After dissolving the crystal in the solvent, we measure the volume of the resulting solution, and compare it with the initial volume. The difference is the change of volume on mixing. By making measurements on a series of dilute solutions, the values can be extrapolated to infinite dilution—that is to say, to a solution where the co-spheres of the ions do not overlap. Such values for 15 alkali halides are given in column 2 of Table 31, together with the crystal volume in column 3. The values are shown by the circles in Fig. 57. In this diagram the scale used for ordinates and abcissas is the same, and a diagonal has been drawn at 45° to the axes. If, for the various pairs of ions in solution, the increment in volume follows the volume in the crystal, the experimental points will lie near this diagonal. Although nearly all the points are seen to lie below the diagonal, Fig. 57 shows clearly a rough correlation between the crystal volume and the volume in solution. The points for LiBr, LiI, CsBr, and CsI lie very near the diagonal. Only for LiI is the volume in solution greater than in the crystal; in all other cases there is a certain shrinkage, as we might expect, from the electrostatic attraction between ions and solvent dipoles.

TABLE 31. PARTIAL MOLAL VOLUME OF ION PAIRS AT INFINITE DILUTION IN WATER AT 25°C AND 1 ATMOSPHERE,[a] AND THE MOLAL VOLUME IN THE CRYSTALLINE SOLID, BOTH IN CM^3/MOLE

1	2	3	1	2	3
LiCl	17.1	20.4	KI. .	45.3	52.8
LiBr	24.0	24.9	RbCl	31.8	42.7
LiI. .	35.6	32.5	RbBr	38.7	48.8
NaCl	16.6	26.8	RbI	50.3	59.2
NaBr	23.5	31.5	CsCl	39.2	42.5
NaI	35.1	40.6	CsBr	46.1	48.0
KCl	26.8	37.3	CsI	57.7	57.8
KBr	33.7	42.9			

[a] B. B. Owen and R. S. Brinkley, *Chem. Rev.*, **29**, 461 (1942).

Although such a survey as that shown in Fig. 57 is useful as a first step, we find that the data do not bear a straightforward interpretation, when we come to look at the details. It is clear from Fig. 19 that, if each solvent molecule is regarded as a sphere, the total volume of any pure solvent is equal to the volumes of these spheres, together with the large amount of void space between the spheres. If to a quantity of water at room temperature we add *n* additional H_2O molecules, we thereby add the volumes of these *n* spheres together with the appropriate amount of void space, characteristic of water, where the average number of nearest neighbors is 4.4. Similarly, if to the same quantity of water we add *n* (spherical) solute particles of any species, we add not only the volumes of the particles themselves but also a certain amount of void space per particle.

Turning next to an ionic crystal, where the ions may be regarded as spheres, the total volume of the crystal is equal to the volumes of these spheres, together with the appropriate amount of void space between the spheres. To take the simplest case, it is convenient to discuss a set of substances, all of which have the same crystalline structure—for example, the 17 alkali halide crystals that have the NaCl structure.

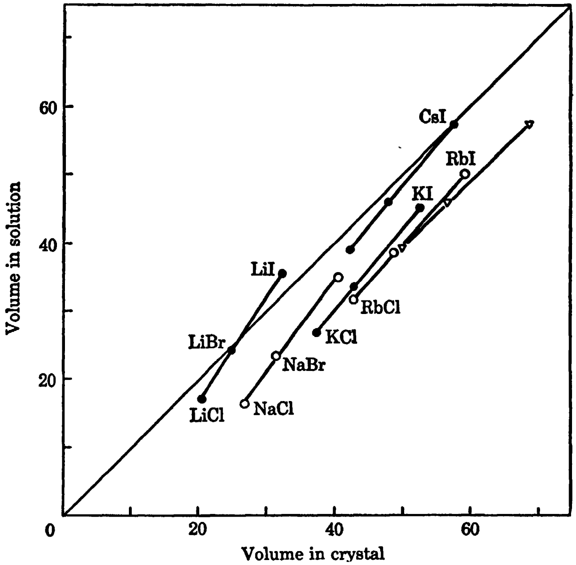

FIG. 57. Ion pairs in aqueous solution at 25°C. Partial molal volume at extreme dilution, plotted against the volume in the crystalline solid, both in cubic centimeters per mole.

But even in this case the fraction of the crystal that is "void space" between the spheres depends on the relative radii of the positive and negative ions and will have a different value for each of the 17 crystals. This being so, when we come to introduce the ions into a solvent, and wish to understand the increment in volume of the liquid, the volumes of the various crystals clearly do not provide a satisfactory basis of comparison.

Consider next the experimental points for CsI, CsBr, and CsCl which, as already pointed out, lie quite near the diagonal in Fig. 57. At room temperature neither of these substances crystallizes in the NaCl type of lattice, but in a lattice where each ion has eight neighbors, instead of six. From the observed distance between the cesium nucleus and the halogen nucleus in each of these three crystals, one can easily calculate what would be the molar volume of the substance, if it crystallized in the NaCl type of lattice. The three triangles plotted in Fig. 57 show the result of plotting the ionic volume in solution against these calculated values, instead of against the actual crystal values.[1] We see that in the positions of the three triangles the cesium salts fall in line with the salts of rubidium and potassium.

Returning to the observed values for these cesium salts, plotted as dark circles in Fig. 57, we must conclude that the position of the experimental points—nearer the diagonal than any salt of Rb, K, or Na—does not indicate anything unusual about the aqueous solution of the cesium salts, but merely arises from the fact that these cesium salts happen to crystallize in a more compact lattice structure, with less void space between the ions. We cannot make a similar remark about the points for the lithium salts, which lie astride the diagonal; the interpretation of these values will be discussed later.

We set out with the idea that, in the vicinity of each ion in solution there is likely to be a certain amount of electrostriction—a certain shrinkage of the solvent caused by the attraction between the ionic charge and the polar molecules. In order to estimate from experimental data how much shrinkage, if any, has taken place, we must start with a correct idea of what would have been the volume of the solution, if no shrinkage had taken place. In making a comparative study of various solutes, we need a common basis for comparison. Since this is not provided by the volumes of the crystalline solids, we may try a different approach. We may compare the addition of any pair of ions to the solvent with the addition of a pair of solvent molecules.

The molecular weight of H_2O being 18.0, 1 mole of water at room temperature occupies 18.0 cm^3. If several water molecules are added to a quantity of water, the increment in volume per molecule added will be 18.0 cm^3 divided by Avogadro's constant. In other words, omitting Avogadro's constant, the increment will be 18.0 cm^3/mole. As we shall be interested in ion pairs, we may remark that the increment in volume per pair of H_2O molecules will be 36 cm^3/mole; and we may use this value as a basis of comparison for a pair of atomic ions.

95. The Increment in Volume for a Pair of Ions. The type of solution that may be expected for atomic ions was considered in connection with Figs. 23 and 24. Let us discuss the ions K^+ and F^-, since the crystallographic radii assigned to these ions most nearly resemble that assigned to the H_2O molecule. Let us begin by supposing that, from the interior of water, we remove an H_2O molecule and insert a K^+ ion at the vacant site. We place the H_2O molecule on the surface of the liquid, causing

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[1] A. F. Scott, *J. Phys. Chem.*, **35**, 3379 (1931).

thereby an increment in the volume of the liquid. Let us suppose that, from a distant site, we remove another H_2O molecule, and insert a F^- ion, again placing the H_2O molecule on the surface of the liquid. We see that, if no disturbance of the water structure took place, the increment in volume for one pair of ions would amount to 36.0 cm^3 divided by Avogadro's constant; or 36.0 cm^3/mole of KF at extreme dilution.

Let us now ask how this value could be used as a basis from which to measure the local disturbance of the water structure that will be caused by each ionic field. The electrostriction round each ion may lead to a local increase in the density of the solvent. As an example, let us first consider the following imaginary case: let us suppose that in the neighborhood of each ion the density is such that 101 water molecules occupy the volume initially occupied by 100 molecules and that more distant molecules are not appreciably affected. In this case the local increase in density would exactly compensate for the 36.0 cm^3 increment in volume per mole of KF. The volume of the solution would be the same as that of the initial pure solvent, and the partial molal volume of KF at infinite dilution would be zero. Moreover, if we had supposed that in the vicinity of each ion 101 molecules occupy rather *less* than the volume initially occupied by 100 molecules, the partial molal volume of the solute would in this case have a negative value.

Turning now to the experimental value for KF in aqueous solution, we see from Table 44 that the value at 25°C at infinite dilution is 6.6 cm^3/mole. This is certainly much smaller than 36.0 cm^3/mole, but the value is at least positive.

It is well known in crystallography that, when spheres of equal radius are packed together, the closest type of packing is one in which each sphere has 12 other spheres in contact with it. In Sec. 24 it was mentioned that in water at room temperature each molecule has, on the average, only 4.4 other molecules in contact with it. If we wanted to place one or two additional H_2O molecules in contact with any H_2O molecule, there would be plenty of room to do this without seriously disturbing the neighbors that are already in contact with this molecule. Similarly, if this molecule is replaced by a solute particle of the same size, the same remark could be made about placing molecules in contact with the solute particle.

The crystallographic radius of the ion Ba^{++} is very nearly the same as that of the water molecule. For the solute BaF_2 we could carry through an argument similar to that given above for KF, inserting separately the three ions to replace three distant water molecules. Now the electrostatic attraction between the ion Ba^{++} and any molecular dipole will be twice as great as that exerted by a singly charged ion on a dipole having the same orientation. Authors who have discussed the subject[1] are agreed that, as a result, in dilute aqueous solution the average number of water molecules in contact with a Ba^{++} ion is at least as great as 6. In order to illustrate the effects of various increments in the number of nearest neighbors, it is scarcely necessary to draw diagrams depicting the situation in three dimensions. Diagrams showing the situation schematically in two dimensions will help to illustrate the various results.

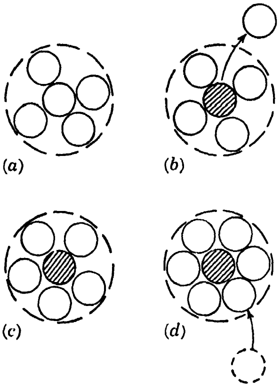

FIG. 58

Let Fig. 58*a* represent a molecule in the pure solvent, with four nearest neighbors; and let Fig. 58*b* represent the simple substitution of a solute particle for the central molecule. The displaced molecule is to be put on the surface of the liquid. In water, if there were no other disturbance of the liquid, this would lead to the value 18 cm^3/mole for the solute. Next let Fig. 58*c* represent the situation where the number of nearest neighbors has been increased by unity. In this case no solvent molecule has to be placed on the surface of the liquid; and if there were no other disturbance of the surrounding liquid, the observed molal volume for the solute would clearly be zero.

Figure 58*d* is intended to represent schematically the situation where the number of nearest neighbors has been increased by 2. If there has been no disturbance of the surrounding liquid, we are at liberty to suppose that the extra molecule has been brought from the surface of the liquid; this could lead to a negative molal volume for the solute; in water the value would be -18 cm^3 for each ion; that is to say, -36 cm^3 per ion pair. These are the values that would be obtained if there were no contraction in the surrounding solvent. In practice we must suppose that such electrostriction is present; superimposed on an increment in the number of nearest neighbors, the effect would clearly be to give still greater negative values for the partial molal volume of the solute. The interpretation of experimental values is not at present possible. An increment in the number of nearest neighbors produces a decrease in volume equal to that which would be produced by a certain degree of electrostriction. It is not possible to disentangle these two effects until we have evidence of a different kind that helps to throw light on the

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[1] J. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 536 (1933); E. J. W. Verwey, *Rec. trav. chim.*, **61**, 127 (1941).

problem. We shall therefore pass on to review the comparative studies that have been made on ionic solutes in different solvents.

96. Volumes in Different Solvents Compared. It has been mentioned above that at room temperature methanol is more than 2.5 times as compressible as water. This factor is so large that we should certainly expect that, when ions are dissolved in these liquids, the contraction caused by the ionic fields will be greater in methanol than in water. Some results in three different solvents are given[1] in Fig. 59. In each case the volume of the solid crystal is subtracted from the apparent volume in solution; and the difference is plotted against the square root of the concentration.

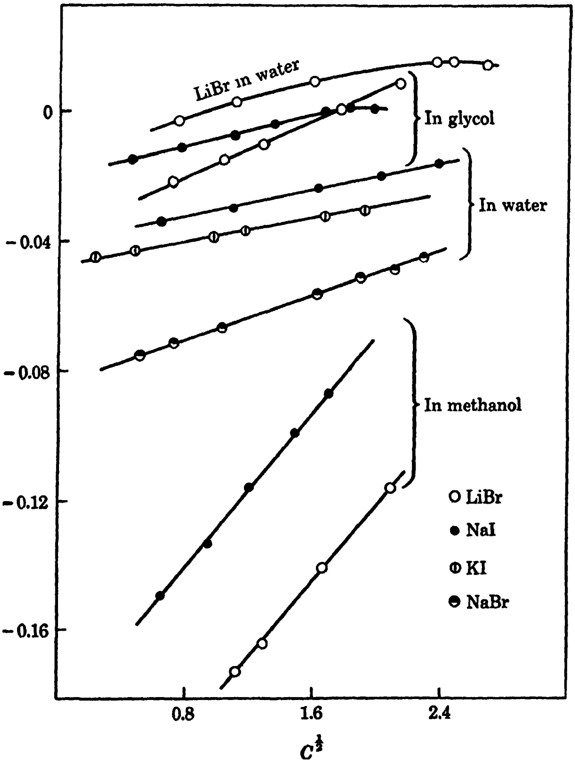

FIG. 59. Ordinates give in milliliters per gram the volume change accompanying the solution of the ionic crystal at 25°C; abscissas give the square root of the concentration in moles per liter.

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[1] R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **59**, 580 (1937).

We have pointed out above that the volume of the solid crystal is not a useful basis for comparing different salts in the same solvent. It is, however, quite satisfactory, when we are comparing the apparent volumes of the same salt in different solvents, as is being done in Fig. 59.

Near the bottom of Fig. 59 the large negative values obtained for salts dissolved in methanol agree with the large contraction expected in this solvent. Near the top of the diagram the values for four salts dissolved in glycol lie in a close group.[1] Since the compressibility of water has a value intermediate between that of glycol and that of methanol, we expect the values for salts in aqueous solution to fall in the diagram between these groups. It will be noticed that the curves for NaBr and KI in aqueous solution do, in fact, fall here. But the curve for LiBr in aqueous solution lies in anomalous position. Instead of falling below the curve for LiBr in glycol, it lies above all the glycol results. When measurements are made on LiBr and NaBr in aqueous solution at 0°C, the values are found to be still farther apart than the values for 25° shown in Fig. 59. Moreover, it will be noticed that the values for LiCl and LiI, given in Table 31, instead of being smaller than those of NaCl and NaI, are larger. Apparently when the Li^+ ion is introduced into water, it causes an abnormally small contraction of the surrounding solvent. Drawing attention to the comparison between LiBr in water and in glycol, Gibson and Kincaid wrote as follows: "The lithium ion in virtue of its small radius can approach close enough to a water molecule to polarize the molecule, thereby causing a strengthening of the electrostatic bonds which hold the water molecules in the less random open liquid structure (the 'quartz-like' structure of Bernal and Fowler with all its inference as to its exact nature removed). The effect is to cause an expansion of the water and hence to produce a smaller net contraction than if structural effects were absent. This also accounts for the fact that the compressions of lithium salt solutions are abnormally high." This interpretation obviously agrees with our opinion of the Li^+ ion as an order-producing ion in aqueous solution. It will be recalled that in Chapter 10 we found that, among the alkali ions, Li^+ has the largest positive B-coefficient in viscosity, accompanied by the largest loss of entropy (see Fig. 55).

At the same time we recall that, in an external field, the electrical mobility of the Li^+ ion is unusually small; and in this connection we should certainly discuss the passage just quoted. Although the Li^+ ion has the smallest radius of all the alkali ions, it has the smallest electrical mobility. According to the traditional explanation, described in Chapter

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[1] The curves for KI and NaBr, not shown in Fig. 59, lie just below the other two.

3, a number of water molecules are attached to each alkali ion, to form a large but compact "hydrated ion." The H_2O molecules attached to Li^+ were supposed to be more numerous than those attached to Na^+, which in turn were supposed to be more numerous than those attached to K^+. The data on the relative volumes, shown in Fig. 59, do not support this view; on the contrary, they suggest that this view is untenable.

It is clear, however, that, from the state of affairs envisaged by Gibson, we can obtain quite a different view of the ionic mobility of Li^+ and Na^+—a view in good agreement with the concepts of order-disorder already developed in this book. Let us first consider a Li^+ ion in aqueous solution in the absence of an external field. The ion executes a random Brownian motion, which becomes more lively as the temperature is raised. At each temperature this random movement is hampered by the amount of interlocking between the water molecules near the ion (see Fig. 20). If it is true that the average degree of interlocking is greater in the co-sphere of the Li^+ ion than in the co-sphere of the Na^+ ion—and greater for Na^+ than for K^+, this would be sufficient to account for the observed fact that the ionic mobilities stand in the order Li^+, Na^+, K^+.

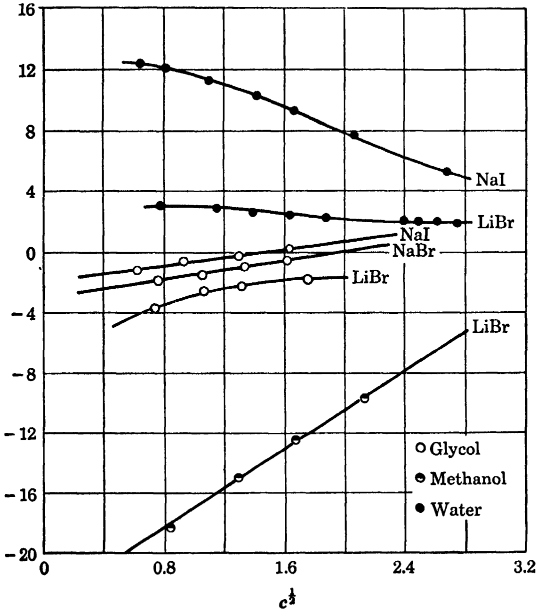

FIG. 60. Ordinates give 100 times the apparent molal expansibility of each solute at 25°C, while abscissas give the square root of the concentration in moles per liter.

97. Thermal Expansion. Turning next to the thermal expansion of solutions, results[1] obtained in the same three solvents, methanol, glycol, and water, are shown in Fig. 60. Ordinates give in each case the apparent molal expansibility of the salt in a solution at 25°C, and abscissas are again the square root of the number of moles of salt per liter of solution. The results in glycol and methanol may be regarded as normal behavior, the larger negative values in methanol being due to the much larger compression. In aqueous solution, on the other hand, we find positive values; in the case of NaI large positive values. Gibson is again inclined to interpret the results in terms of order-disorder. (From this point of view, however, the choice of solutes is unfortunate, since the data of Chapter 11 led us to regard the I^- and Br^- ions as among the strongest disorder-producing ions, in contrast to Li^+ and Na^+.)

Problem

Taking the ionic radii for Cs^+, Cl^-, Br^-, and I^- from Table 42, calculate in cubic centimeters per mole the volumes which the cesium halides would have if they crystallized in the sodium chloride structure, and compare with the values plotted in Fig. 57.

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[1] Gibson and Kincaid, *loc. cit.*

CHAPTER 12

The Number of Dipoles per Unit Volume. The Entropy Change Accompanying Proton Transfers. The Equilibrium between a Solid and Its Saturated Solution. Examples of Values of L and ΔF^0. *The Change of Solubility with Temperature. Uni-divalent and Other Solutes. Lithium Carbonate in Aqueous Solution.* H_2CO_3 *in Aqueous Solution. Comparison between* H_2CO_3 *and* Li_2CO_3 *in Aqueous Solution. Heats of Solution and the Conventional Free Energies and Entropies of Solution.*

98. The Number of Dipoles per Unit Volume. In the foregoing chapters a discussion of experimental data of various kinds has led us to develop some new ideas about ions in solution. We may now attempt to treat these ideas in a more systematic way. For this purpose we may make a fresh start, reexamining in greater detail the various concepts, beginning with those discussed in Chapter 1. It will be recalled that in Table 41 the permanent dipole moments of the CH_3OH and C_2H_5OH molecules have almost the same value as that of the H_2O molecule; and in Table 1 the empirical values of ϑ for the liquids methanol and ethanol do not differ by any large factor from the value of ϑ for water. In each case let us consider now n, the number of dipoles per unit volume. The values of n are given in column 2 of Table 32, together with the corresponding value of $(\epsilon - 1)$ in column 3. If the values in columns 2 and 3 are compared, it will be seen that the values of $(\epsilon - 1)$ are roughly proportional to the number of dipoles per cubic centimeter. In these liquids the dipole moment of each molecule is nearly the same, and the effect of the mutual interaction between these dipoles is roughly the same; but the number of dipoles per cubic centimeter is widely different, and this accounts for the rapid decrease in ϵ on going from water to the series methanol, ethanol, and so on.

Alternatively, starting with water, the number of dipoles per cubic centimeter may be progressively diminished by diluting the water with a nonpolar liquid, such as dioxane. Values for dioxane-water mixtures are included in Table 32; and it will be seen that the mixture resembles an artificial alcohol. The value of ϑ is reduced only a little, while the dielectric constant is reduced by a large factor.

In discussing the loss of entropy in an electric field, we may consider a charged sphere immersed either in an alcohol or in a dioxane-water mixture. In (19) in Sec. 8 we obtained an expression for the total amount of entropy lost by the dielectric lying outside any radius R. The expression was

TABLE 32. THE NUMBER OF MOLECULAR DIPOLES IN SOLVENTS AND SOLVENT MIXTURES AT 25°C

	n	$(\epsilon - 1)$	ϑ
Water	3.3×10^{22}	75.2	219
Methanol...	1.46×10^{22}	30.5	186
Ethanol	1.17×10^{22}	23.2	164
Propanol.	8.0×10^{21}	19.1	148

Water-Dioxane Mixtures[a]

Weight, % dioxane	Density	n	$(\epsilon - 1)$	ϑ
20	1.014	2.7×10^{22}	60	194
45	1.032	1.9×10^{22}	37.5	178

[a] G. Akerlof and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

$$\frac{q^2}{2R\vartheta\epsilon} \tag{170}$$

our purpose now is to ask how this total loss of entropy will depend upon n, the number of dipoles per unit volume. We have seen that, in the series of alcohols and in the dioxane-water mixtures, ϑ varies only slowly with n, while ϵ is roughly proportional to n.

Let us now consider the same charged sphere immersed in various liquids with widely different values of n. By diluting water with dioxane at constant temperature, we can reduce n from 3.3×10^{22} toward zero. Clearly when n, the number of dipoles per unit volume, approaches zero, the total entropy lost per unit volume must approach zero. From this point of view the expression (170) is seen to have a somewhat paradoxical appearance, since ϵ, which, according to Table 32, is roughly proportional to n, occurs in the denominator. This means that, as the number of dipoles per cubic centimeter *decreases*, the total amount of entropy lost progressively *increases*. The reason for this is that, when fewer dipoles are present, the dielectric reduces the intensity of the field to a smaller extent. Hence each dipole that is present is subject to control by a greater residual field, and hence there is a greater degree of order, and each dipole loses more entropy in the field. In fact, this loss of entropy is so much greater that it more than compensates for the smaller number of dipoles per unit volume—with the result that the total loss of entropy per unit volume is actually larger, roughly in inverse ratio to n. At the same time, it must remain true that, if n is reduced to zero, the loss of entropy eventually falls to zero. There is no reason to pursue the problem; for a more detailed discussion, see Note 4 of the Appendix.

The conclusions are evidently relevant to the amount of entropy lost by ions in methanol solution—see Table 29. If, however, the expression (170) is used for an atomic ion, we know that it is applicable only for values of R that are large compared with the ionic radius—that is to say, it will give quantitative results only when applied to the solvent dipoles in the outer parts of the co-sphere. The extent to which it applies also to the dipoles in the inner parts of the co-sphere must depend on the degree to which the behavior of these molecules simulates that of the more distant molecules. This can be determined only by experiment. In Table 29 we have seen that for the ion pair ($K^+ + Br^-$) and for the ion pair ($K^+ + Cl^-$) in methanol the unitary part of ΔS^0 amounts to a loss of 26.8 e.u. and 30.5 e.u., respectively, in contrast to the values for the same ions in aqueous solution, where the *loss* of entropy in the outer parts of the co-sphere is more than counterbalanced by a *gain* in entropy that has been attributed to the disorder produced by the ionic field.

Although the viscosity B-coefficients in methanol are known for very few solutes, the numerical values in Table 23 suggest that the values would be positive, even for such solutes as KNO_3 and CsI, which have the largest negative coefficients in aqueous solution.

99. The Entropy Change Accompanying Proton Transfers. If we compare potassium iodate with potassium nitrate, we find that entropy of crystalline KIO_3 given in Table 44 is 4.4 e.u. greater than that of KNO_3. This is doubtless, as usual, due to the fact that the mass of the iodine atom in KIO_3 is much greater than the mass of the nitrogen atom in KNO_3. For the same reason, it is likely that the entropy of the HIO_3 molecule in aqueous solution is greater than that of the HNO_3 molecule. Yet we know from the values given in Table 26 that the unitary part of the partial molal entropy of the $(IO_3)^-$ ion is 7 e.u. less than that of the $(NO_3)^-$ ion. This implies that, if we consider the formation of these anions by proton transfer, the loss of entropy in the process

$$HIO_3 + H_2O \rightarrow (IO_3)^- + (H_3O)^+$$

should be *more* than 7 e.u. greater than in the process

$$HNO_3 + H_2O \rightarrow (NO_3)^- + (H_3O)^+$$

Now loss of entropy, we recall, means gain of free energy, or work done, and the quantity $-T\,\Delta S_{unitary}$ makes a contribution to J. In fact, as we shall see, it may account for the whole difference between the values of J for HIO_3 and HNO_3.

In Table 24 the viscosity B-coefficient of the ion $(NO_3)^-$ is negative, while that of the ion $(IO_3)^-$ has a large positive value. We are led to entertain the idea of an unexpected correlation between *viscosity* and the *degree of dissociation* of the corresponding acids HIO_3 and HNO_3. The acid HIO_3 is a moderately weak acid, while HNO_3 is classed among the strong acids. In Secs. 70 and 71 we found for J the values 0.16 and 0.05 electron-volt, respectively. The difference between them thus amounts to $(0.16 - 0.05) = 0.11$ electron-volt per molecule, or 25,300 cal/mole. Now we concluded above that the value of $\Delta S_{unitary}$ for the proton transfer from the HIO_3 molecule at 25°C is more than 7 e.u. less than the corresponding quantity for the HNO_3 molecule. Multiplying this difference by the absolute temperature 298°, we find that the corresponding values of $T\,\Delta S_{unitary}$ differ by more than 20,000 cal/mole; and a difference of 9 e.u. in ΔS, arising from the order-destroying character of one anion and the order-producing character of the other, would be sufficient to account for the whole difference between the values of J for HIO_3 and HNO_3.

In recent years various attempts have been made to account for the observed differences between the dissociation constants of organic acids, whose molecules differ only slightly from each other. The proposed explanations have naturally been given in each case in terms of the structures of the respective neutral acid molecules.[1] In the tentative discussion of HNO_3 and HIO_3 that has just been given, the approach has been quite different; we focused attention, not on the neutral molecule or on the structure of the anion, but on the condition of the solvent in the vicinity of the anion.

In view of this result, it becomes almost imperative to inquire whether the same method might be given wider application—whether, in discussing the small differences between homologous organic acids, we should pay attention to the possible states of order-disorder in the co-spheres

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[1] The theory has been developed especially by F. W. Westheimer, *J. Am. Chem. Soc.*, **61**, 1977 (1939). A good account of this work is given by G. W. Wheland, "Advanced Organic Chemistry," 2d ed., Chapter 11, Wiley, 1949; see also M. Kilpatrick, *Chem. Rev.*, **30**, 159 (1942); J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

of the anions. Table 2 in Sec. 21 shows, for example, that at 18°C the electrical mobility of the formate ion is some 40 per cent greater than that of the acetate ion. This means that, in the absence of an external electric field, the Brownian motion of the former is more lively than that of the latter. Although this difference *may* be due entirely to the smaller size of the formate ion, let us, for the sake of argument, suppose that it is partly due to the fact that the solvent in the co-sphere of the formate ion has a smaller degree of order than in the co-sphere of the acetate ion. If this were so, the comparison would be similar to the tentative comparison that has been made between HNO_3 and HIO_3, the formate ion playing the part of NO_3^-, and the acetate ion that of IO_3^-.

We see from Table 13 in Sec. 68 that the value of Θ for formic acid falls at 24.7°C. Table 15 in Sec. 72 shows that for formic acid between 20 and 25° the magnitude of ΔH is less than ± 200 cal/mole; the same will be true for acetic acid whose Θ falls at 22.6°C. On the other hand, the value of J for formic acid, given in Table 12, is smaller than that of acetic acid by 0.0584 electron-volt, or 1344 cal/mole. Evidently, this large difference in J arises from a difference in the term $-T\,\Delta S_{unitary}$. The viscosity B-coefficient of the formate ion has not yet been measured; but its high mobility suggests that, compared with the acetate ion, it is a less strongly order-producing ion, and that, in discussing these weak acids, we are right in attempting to correlate the degree of dissociation with properties, such as viscosity and mobility, that depend on the state of order-disorder in the co-sphere of the anion.

We are led to reexamine the temperature coefficients of J, given in the last column of Table 12, in relation to the values of J itself, given in the preceding columns. It will be recalled that the striking result of Table 12 was that the temperature coefficients of J were found to fall (with the possible exception of boric acid) into four groups corresponding to the four types of proton transfer, irrespective of the value of J itself. We emphasized the absence of a correlation between dJ/dT and J; thus the ammonium ion has one of the largest values of J, but one of the smallest values of dJ/dT. In the main, we were undoubtedly right to stress the absence of correlation. But the tentative comparison that we have just made between formic acid and acetic acid, suggests that, on a small scale, a correlation should be found. In ascribing formic acid's smaller value of J to the presence of a greater entropy in the co-sphere of the formate ion, we thereby, according to (75), associate it with a smaller value of dJ/dT. Now, on looking at the last column of Table 12, we see that the value inserted for formic acid is, indeed, 15 per cent smaller than that for acetic acid. Furthermore we see that the values for propionic and n-butyric acids are larger than for acetic acid, and so are the values of J given in the preceding columns for these two acids. Thus on the broad classification into four types of proton transfer there may be superimposed a small-scale effect, arising from the various values of J_{env} for the different acids.

Turning now to Table 22, we see that the viscosity B-coefficients of NH_4Cl, NH_4Br, and NH_4NO_3 are all negative, while the values given in Table 21 for HCl, HBr, and HNO_3 are all positive. There thus appears to be less order in the co-sphere of the $(NH_4)^+$ ion than in that of the $(H_3O)^+$ ion. Using the same type of argument as we have used above, let us ask whether this enables us to make any prediction with regard to the proton transfer

$$(NH_4)^+ + H_2O \rightarrow NH_3 + (H_3O)^+ \tag{171}$$

We recall that the field of an ionic charge, in aligning the solvent dipoles, produces a certain amount of order; at a higher temperature the alignment is smaller, and a greater amount of energy is associated with the ionic field. This description disregards the order that already existed in the solvent and disregards the possibility that the ionic field may to some extent destroy this order—an effect that appears to be present in the co-sphere of $(NH_4)^+$, but not in that of $(H_3O)^+$. With rise of temperature, the amount of energy associated with the ionic field of $(NH_4)^+$ should thus show a smaller increment than that of $(H_3O)^+$. According to (75), although we expect the radii of the two ions to be nearly the same, we do not expect the value of J for the proton transfer (171) to be independent of temperature, but to increase slightly with temperature. In this way we account for the small increment recorded in the last column of Table 12.

100. The Equilibrium between a Solid and Its Saturated Solution. We shall discuss now in greater detail the process depicted in Fig. 11, where ions are taken from the surface of a solid into a solvent. In Sec. 52 we defined a unitary quantity L, which will play a role similar to that played by D and J. The equilibrium between a solid and its saturated solution is an example of the equilibria considered in Sec. 51. If a few additional pairs of ions are taken into this solution, the value of dF/dn is zero. We now say that this zero value can come about only when the communal part and the unitary part have values that are equal and opposite. A saturated solution is, in fact, the solution that *provides these equal and opposite values.* The communal term in the free energy differs from the cratic term by the value that $\mathbf{d}_x$ has in the saturated solution. When this value is known, ΔF^0 and L can be evaluated. Let m_{sat}, y_{sat}, and x_{sat} refer to the concentration of the saturated solution. Then, writing $\Delta F = 0$ in (108), we obtain for the standard free energy of solution

$$\Delta F^0 = -2RT \ln (\gamma_{sat} m_{sat}) \tag{172}$$

and likewise

$$L = -2kT \ln (\gamma_{sat} m_{sat}) + 2kT \ln M \tag{173}$$

where the value of γ_{sat} is adjusted so that

$$\gamma_{sat} y_{sat} = f_{sat} x_{sat} \tag{174}$$

When interpreting proton transfers in Chapter 7, we found that the experimental data showed that for most solute species in aqueous solution the values of J lay between 0.25 and 1.0 electron-volts. We shall now be interested in the values of L that are necessary to account for the observed solubilities of solids in water. We may expect the range of values of L to be rather similar; the main difference is that in the solution of a crystal the value of Δq in (86) is never less than 2, whereas in most of the proton transfers discussed in Chapter 7 the value of Δq was either unity or zero.

For any ionic crystal the conventional "free energy of solution" per mole ΔF^0 is often defined as the change in free energy accompanying the transfer of ions, comprising 1 mole, from the solid to a solution or solutions, where the positive ions and the negative ions are at unit activity. The case of a uni-divalent salt will be discussed in Sec. 103. Here we shall discuss a uni-univalent crystal, in contact with its saturated solution. The process of transferring a pair of ions to a solution of unit activity may be carried out in two steps—each pair of ions is taken from the surface of the crystal into the saturated solution and from there is transferred to a solution of unit activity. If a_{sat} is the activity of the solute in the saturated solution, the work done in transferring the pair of ions from this solution to a solution where $a = 1$ will be

$$2kT \ln \frac{1}{a_{sat}} = -2kT \ln (a_{sat}) \tag{175}$$

while the work done in the initial step is zero. Hence for 1 mole of a uni-univalent solute

$$\Delta F^0 = -2RT \ln (a_{sat}) = -2RT \ln (\gamma_{sat} m_{sat}) \tag{176}$$

which is the same expression as (172), which was derived from (108). Thus the operation of transferring the ions to a solution of unit activity on the molality scale has the effect of removing the communal part and subtracting, at the same time, the conventional quantity $2RT \ln M$, where M is the number of moles on the b.q.s.; for we have

$$-2RT \ln (\gamma_{sat} m_{sat}) = -2RT \ln (\gamma_{sat} y_{sat}) - 2RT \ln M \tag{177}$$

$$= -2RT \ln (f_{sat} x_{sat}) - 2RT \ln M \tag{178}$$

101. Examples of Values of L and ΔF^0. As a first example we may evaluate both L and ΔF^0 for a moderately soluble salt in aqueous solution. At 25° a saturated solution of potassium perchlorate has a concentration of 0.148 mole of $KClO_4$ in a 1000 grams of water; that is to say, $y_+ = y_- = 0.148/55.5$. The activity coefficient in the saturated solution has been taken[1] to be 0.70 ± 0.05. Using this value, we can estimate the work required to take a pair of ions from the crystal surface to mutually distant points, when the crystal is in contact with pure solvent at 25°C;

$$\begin{aligned} L &= -2kT \ln (0.7 \times 0.148/55.5) \\ &= 0.33 \text{ electron-volt per ion pair} \end{aligned}$$

Comparing this value with the values of J for proton transfers given in Table 12, we see that, for this moderately soluble crystal the value of L is similar to the value of J for a weak acid.

Turning next to the conventional free energy of solution of the same substance, we have

$$\begin{aligned} \Delta F^0 &= -2RT \ln (0.7 \times 0.148) \\ &= -2 \times 1364.3 \log (0.7 \times 0.148) \\ &= 2690 \text{ cal/mole} \end{aligned}$$

In order to obtain NL from this value, we should, according to (178), have to add $2RT \ln (55.5)$, which at 25° is 4760 cal.

As another example we may discuss silver iodide. As mentioned in Sec. 49 a saturated aqueous solution of this salt at 25°C contains only 9.08×10^{-9} mole in 1000 grams of water. At this low concentration the activity coefficient does not differ appreciably from unity; we have then

$$\begin{aligned} L &= -2kT \ln (9.08 \times 10^{-9}/55.5) \\ &= 1.158 \text{ electron-volts} \end{aligned}$$

This value is rather larger than the value of J for the self-dissociation of water, given in Table 12.

Finally, as an example of a highly soluble salt, we may take sodium chloride; at 25° the concentration of the saturated solution is 6.16 molal. The activity coefficient of NaCl, like that of NaBr plotted in Fig. 72, passes through a minimum at a concentration between 1.0 and 1.5 molal; and it has been estimated[2] that in the saturated solution the activity coefficient has risen to a value very near unity. Writing $\gamma = 1.0$, we find that the work required to take a pair of ions from the surface of NaCl into pure water at 25° has the rather small value

$$L = -2kT \ln (6.16/55.51) = 0.11 \text{ electron-volt}$$

[1] W. M. Latimer and J. E. Ahlberg, *J. Am. Chem. Soc.*, **52**, 549 (1930).

[2] W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940).

102. The Change of Solubility with Temperature. The solubilities of various salts have been measured in aqueous solution at various temperatures. But from these measurements we cannot derive values of L as a function of temperature, until the activity coefficients in the various saturated solutions have been accurately measured. In dilute solutions of a few salts measurements of activity coefficients have been made over a wide range of temperature; but not in saturated solutions; in fact, in most cases the activity coefficient of even the saturated solution at 25°C is not accurately known. Thus, we can obtain values of L as a function of temperature only in the case of sparingly soluble substances, where the activity coefficient is in the neighborhood of unity at all temperatures and so is independent of temperature within the experimental error.

Table 33. Solubilities of AgCl, AgBr, and AgI in Water

Temp., °C	moles/liter	$-\log K$	L, electron-volts
	AgCl		
5	0.506×10^{-5}	10.5945	0.777
15	0.842	10.1520	0.780
25	1.337	9.7492	0.784
35	2.038	9.3809	0.787
45	3.002	9.0425	0.791
	AgBr		
5	0.203×10^{-6}	13.3860	0.931
15	0.380	12.8021	0.932
25	0.704	12.3026	0.934
35	1.213	11.8280	0.936
45	1.997	11.3920	0.939
	AgI		
5	0.178×10^{-8}	17.4980	1.158
15	0.417	16.7598	1.159
25	0.908	16.0813	1.157
35	1.859	15.4562	1.157
45	3.599	14.8792	1.159

AgBr:

$$RT \log K = 72{,}776 + 4.90(t - 25) - 2.0 \times 10^{-2} (t - 25)^2$$

AgCl:

$$RT \log K = 57{,}671 + 3.4248(t - 25) - 2.581 \times 10^{-2}(t - 25)^2 + 9.948 \times 10^{-5} (t - 25)^3$$

Table 33 gives the solubilities and the values of $-\log K$ for AgI, AgBr, and AgCl from 5 to 45°C from the measurements of Owen and Brinkley.[1]

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[1] B. B. Owen and S. R. Brinkley, *J. Am. Chem. Soc.*, **60**, 2237 (1938).

The last column in the table gives the values of L, calculated from (173). It will be noticed that for AgCl and AgBr the value of L increases with rise of temperature. The sign of dL/dT is thus in agreement with that expected from simple electrostatic theory: the work to convey the ions from the solid into solution increases with rise of temperature. For AgI, on the other hand, we see that L is almost independent of temperature.

Now from Sec. 52 we recall that

$$\Delta S_{unitary} = -\frac{dL}{dT}$$

For AgCl and AgBr this quantity is negative (in agreement with a loss of entropy by solvent dipoles in the ionic fields). For AgI, on the other hand, it is zero. This implies, according to (168), that in this case ΔS^0 happens to be equal to $2R \ln M$; in other words, the value happens to be 16.0 e.u. On referring to Sec. 90 it will, in fact, be seen that the value of ΔS^0 calculated from the solubility of AgI at 25°C, and its heat of precipitation, was 16.0 e.u.

Turning next to AgBr, we see from Table 33 that the value of L increases from 0.931 electron-volt at 15° to 0.935 at 35°, a difference of 0.004. Dividing by 20, we find that the average value of dL/dT in the neighborhood of 25° is 2×10^{-4} electron-volt/deg. Multiplying by 23,060, we find this is equivalent to 4.6 cal/mole. It follows that the value of the conventional entropy of solution ΔS^0 in the neighborhood of 25°C is approximately

$$\begin{aligned}\Delta S^0 &= 16.0 - 4.6\\ &= 11.4 \text{ e.u.}\end{aligned}$$

In Table 33 are given equations that express the results for AgCl and AgBr. Multiplying by 2.303 to obtain $-RT \log_e K = \Delta F^0$, and differentiating with respect to the temperature, we find for AgBr at 25° the more accurate value $\Delta S^0 = 11.3$ e.u.

Similarly for AgCl at 25°C we find from Table 33 the value $\Delta S^0 = 7.9$ e.u. Owen and Brinkley regarded this value as probably more accurate than the value 8.2 obtained in Sec. 90 from the heat of solution.

103. Uni-divalent and Other Solutes. In Sec. 47 we were able to state that the heat of precipitation of silver iodide amounted to 1.16 electron-volts per ion pair. On the other hand, when the heat of precipitation of CaF_2 or Li_2CO_3 or $LaCl_3$ has been measured, we obviously cannot express the result in electron-volts per ion pair, since in each case three or four ions are involved; nor is there in use any recognized name for the group of ions. Since in Greek the word κῶμος was used for a mobile group (of doves, huntsmen, maidens), we propose to coin the word *kome* and to speak of a kome of ions when we wish to refer to that group of ions which, in any solution, is the smallest group that together form an electrically neutral unit. Thus in a solution of CaF_2, a kome of ions will contain one positive and two negative ions, while in a solution of Li_2CO_3 the kome will contain one negative and two positive ions, and so on. We can then, for example, in each case express the heat of precipitation in electron-volts per kome. A pair of ions is now a special case of a kome of ions. It will be shown below that the heat of precipitation of Li_2CO_3, for example, tends at extreme dilution to the value 0.18 electron-volt per kome.

Consider now the non-ideal solution of a completely dissociated uni-divalent salt, and its comparison with the corresponding ideal solution. In choosing the ideal solution, if we denote the two solute species by B and C, we must obviously take a solution that contains twice as many C particles as B particles. The mole fraction of B is $\dfrac{n_B}{n_A + n_B + n_C}$, where $n_C = 2n_B$. In the extremely dilute range we can take the mole ratios instead of mole fractions and may take the cratic terms in the free energy to be $-n_BkT \ln y_B$ and $-n_CkT \ln y_C$, where n_C is again equal to $2n_B$.

In the imperfect solution of an ionic solute, such as $BaCl_2$, the cratic terms are, of course, *the same as those of the corresponding ideal solution*, namely,

$$-n_+kT \ln y_+ - n_-kT \ln y_- \tag{179}$$

There is no difference between this expression and that of a uni-univalent solute; only n_- is equal to $2n_+$. In practice, however, it is convenient to express the concentration of the positive and negative ions in terms of the amount of neutral solute that has been dissolved in a given amount of solvent. If y denotes the mole ratio of $BaCl_2$, and if the solution contains n komes, each consisting of ($Ba^{++} + 2Cl^-$), we have in (179)

$$\begin{aligned} n_+kT \ln y_+ &= nkT \ln y \\ n_-kT \ln y_- &= 2nkT \ln 2y \end{aligned}$$

Substituting in (179), and using (59), we obtain

$$\begin{aligned} \frac{dF_{\text{cratic}}}{dn} &= -kT \ln 4y^3 \\ &= -3kT \ln m + kT \ln \frac{M^3}{4} \end{aligned} \tag{180}$$

since $y = m/M$.

Proceeding as in Sec. 55, we can consider ΔF, the free energy change per mole accompanying the solution of this crystal in a certain solvent at temperature T, and we can fix attention on the quantity

$$\left(\frac{\Delta F}{N} - kT \ln 4y^3\right) \tag{181}$$

and can ask how the value of this quantity will vary with the concentration of the solute. We can answer that, for any concentrations lying within the extremely dilute range, it will not vary appreciably with concentration but will have a constant value, characteristic of this solute dissolving in this solvent. But, as soon as we leave the extremely dilute range and go to progressively higher concentrations, the value of (181) will no longer remain constant; it is now the quantity

$$\left(\frac{\Delta F}{N} - \mathbf{d}_y - kT \ln 4y^3\right) \tag{182}$$

that remains constant.

In Sec. 56, where we said, let $\mathbf{d}_y/kT$ be equal to 2 ln γ, the factor 2 was introduced, because 2 was the number of ions in the kome. In general, if the kome contains N ions, we say, let

$$\frac{\mathbf{d}_y}{kT} = \mathrm{N} \ln \gamma \tag{183}$$

In the uni-divalent or di-univalent solute, to which (181) refers, N is equal to 3, and (182), when multiplied by Avogadro's constant, takes the form

$$(\Delta F - 3RT \ln \gamma y - 2RT \ln 2) \tag{184}$$

The conventional free energy of solution is greater than this by the amount $3RT$ ln M; adding this quantity, we obtain

$$(\Delta F - 3RT \ln \gamma m - 2RT \ln 2) = \Delta F^0 \tag{185}$$

In particular, if the crystal is in contact with its saturated solution, in (185) we may write $\Delta F = 0$, whence

$$\Delta F^0 = (-3RT \ln \gamma_{sat} m_{sat} - 2RT \ln 2) \tag{186}$$

Finally, the conventional entropy of solution ΔS^0 may be written

$$\Delta S^0 = \lim_{m \to 0} \left(\frac{\Delta H - \Delta F}{T} + 3R \ln m + 2R \ln 2\right) \tag{187}$$

There is no ambiguity as to the value of the cratic term, as this must be the same as in the corresponding ideal solution that contains the same number of particles of each of the species present.

104. Lithium Carbonate in Aqueous Solution. As an illustration, we shall evaluate the conventional ΔF^0 and ΔS^0 for lithium carbonate in aqueous solution. At 25°C the concentration of the saturated solution is 0.169 molal.[1] In this solution the molality of the Li^+ ion is of course 0.338. The activity coefficient of the Li_2CO_3 in the saturated solution is not accurately known, but its value is not far from $\gamma_{sat} = 0.59$. Substituting in (186) we have then

$$\begin{aligned} \Delta F^0 &= -RT[3 \ln (0.59 \times 0.169) + 1.38] \\ &= 3280 \text{ cal/mole} \end{aligned}$$

The heat of solution of solid Li_2CO_3 in water at 25°C has been measured;[2] the value is found to tend to -4200 cal/mole at infinite dilution equivalent to -0.18 electron-volt/kome. We have then

$$\begin{aligned} T\,\Delta S^0 = \Delta H^0 - \Delta F^0 &= -4200 - 3280 \\ &= -7480 \text{ cal/mole} \end{aligned}$$

Hence for the conventional entropy of solution at 25° we obtain

$$\Delta S^0 = -\frac{7480}{298.1} = -25.1 \text{ e.u.}$$

As mentioned in Sec. 90 we may think of this ΔS^0 as being the difference between the molar entropy of solid Li_2CO_3 and the partial molal entropies of one $(CO_3)^=$ ion and two Li^+ ions, each in its hypothetical standard aqueous solution. We propose now to compare the ΔS of the reaction

$$Li_2CO_{3(solid)} \rightarrow (CO_3)^= + 2Li^+$$

that we have been discussing, with the ΔS of the process

$$H_2CO_{3(aq)} \rightarrow (CO_3)^= + 2H^+$$

likewise carried out in aqueous solution at 25°C. Our purpose will be to show that eventually the comparison may be made to yield the difference between the unitary part of the partial molal entropy of the lithium ion and the corresponding unitary quantity for the proton.

105. H_2CO_3 in Aqueous Solution. Before discussing the ionic dissociation of H_2CO_3 in aqueous solution, let us first consider its formation from gaseous CO_2 and liquid H_2O

$$CO_2 + H_2O \rightarrow H_2CO_{3(aq)}$$

The entropy of CO_2 in its standard state is 51.08 e.u., while that of water at 25° is 16.75 e.u. From the experimental data it has been found that

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[1] C. A. Seyler and P. V. Lloyd, *J. Chem. Soc.*, **111**, 994 (1917).

[2] L. I. Brown and W. M. Latimer, *J. Am. Chem. Soc.*, **58**, 2229 (1936).

the value of ΔS^0 to give H_2CO_3 in aqueous solution is -22.7 e.u. Subtracting 22.7 from 67.8, we obtain 45.1 e.u. as the partial molal entropy of H_2CO_3 in a solution of unit activity.

When H_2CO_3 reacts with another molecule of water by proton transfer, we have the first stage of the dissociation:

$$H_2CO_3 + H_2O \rightleftarrows (HCO_3)^- + (H_3O)^+ \tag{188}$$

The value for the equilibrium constant at 25°C given in the last column of Table 10 is 4.52×10^{-7}. Multiplying $\log_e K$ by RT, we find for ΔF^0 the value 8683 cal/mole. The heat of dissociation has been measured calorimetrically[1] and found to be 1843 cal/mole. By subtraction we find

$$\begin{aligned} T\,\Delta S^0 = \Delta H^0 - \Delta F^0 &= 1843 - 8683 \\ &= -6840 \\ \Delta S^0 &= -22.9 \text{ e.u.} \end{aligned}$$

When a proton is transferred from the $(HCO_3)^-$ ion, we have the second stage of dissociation:

$$(HCO_3)^- + H_2O \rightleftarrows (CO_3)^= + (H_3O)^+ \tag{189}$$

Values for the equilibrium constant at temperatures between 0 and 60°C were included in Table 9. From the value at 25° we find $-\log_e K = 23.8$. Multiplying by RT, we obtain $\Delta F^0 = 13{,}983$ cal/mole. From the temperature coefficient of ΔF^0 we obtain for the heat of dissociation the value $\Delta H^0 = 3500$ cal. Hence

$$\begin{aligned} T\,\Delta S^0 &= \Delta H^0 - \Delta F^0 \\ &= 3500 - 13{,}983 = -10{,}483 \\ \Delta S^0 &= -35.2 \text{ e.u.} \end{aligned}$$

Adding together the values for the two stages, we may obtain the entropy change for the whole process

$$H_2CO_3 + 2H_2O \rightarrow (CO_3)^= + 2(H_3O)^+ \tag{190}$$

It amounts to $-(22.9 + 35.2) = -58.1$ e.u.

106. Comparison between H_2CO_3 and Li_2CO_3 in Aqueous Solution. If we subtract two H_2O molecules from either side of equation (190), we may take the ΔS to refer to the simpler process

$$H_2CO_{3(aq)} \rightarrow (CO_3)^= + 2H^+ \tag{191}$$

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[1] K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2368 (1937).

We are now in a position to compare this quantity with the ΔS for the process

$$Li_2CO_{3(solid)} \rightarrow (CO_3)^{=} + 2Li^+ \tag{192}$$

In both processes the ions are supposed to be introduced into solutions where the interionic forces are negligible. When in (191) the $CO_3^=$ ion is formed, the solvent in the co-sphere of this ion loses a certain amount of entropy. Likewise, in (192) when the $CO_3^=$ ion is formed, the solvent in the co-sphere of the ion loses precisely the same amount of entropy. At the same time, the amount of entropy associated with the thermal energy of the $CO_3^=$ ion in aqueous solution is, of course, the same in (192) as in (191). In the process (192) we shall be concerned with the unitary term for the two Li^+ ions in contrast to (191) where two protons are added to two H_2O molecules.

In each case the values of ΔF^0 and ΔS^0 discussed in this chapter contain, of course, the cratic term appropriate to the change in the number of solute particles that are mixed with the solvent. In the reaction (191) we have, on the left-hand side, a species of solute particle H_2CO_3 mixed with M moles of solvent, where M is the number of moles in the b.q.s. On the right-hand side we have three solute particles, each supposed to be mixed with M moles of solvent. The ΔF^0 and ΔS^0 for this reaction must therefore, if correctly calculated, contain the cratic term appropriate to the change from one to three solute particles; the value $\Delta S^0 = -58.1$ does, in fact, contain this contribution, namely, $+16.0$ e.u. In the process (193), on the other hand, the ΔS^0 must contain a greater cratic term, namely, 24.0 e.u., appropriate to the mixing of three particles with the solvent; the values obtained in Sec. 104 contain, in fact, this cratic contribution.

From Table 44 it will be seen that the molar entropy of solid Li_2CO_3 amounts to 21.60 cal/degree. In Sec. 104 it was pointed out that, if the ΔS^0 for the process (192) is added to the entropy of solid Li_2CO_3, the sum will be equal to the partial molal entropies of the $CO_3^=$ ion and two Li^+ ions. For this sum then we obtain

$$\begin{aligned} S_{CO_3^-} + 2S_{Li^+} &= 21.6 - 25.1 \\ &= -3.5 \end{aligned} \tag{193}$$

Similarly, for (191)

$$\begin{aligned} S_{CO_3^-} + 2S_{H^+} &= 45.1 - 58.1 \\ &= -13.0 \end{aligned} \tag{194}$$

We can now ask the question to which the whole of this discussion has been leading: By subtracting (194) from (193) can we obtain the difference between the unitary term for two Li^+ ions and the unitary term for two protons? We have already seen that for the $CO_3^{=}$ ion the unitary contribution in (194) must be identical with that in (193). Furthermore, the discussion of the different cratic contributions to ΔS^0 just given has shown that these different contributions are exactly what is required to ensure that the cratic term in (194) is the same as that in (193). We can conclude then that the difference between (194) and (193) lies entirely in the difference between the unitary term for two Li^+ ions and that for two protons. Thus, when we write

$$\begin{aligned} 2S_{Li^+} - 2S_{H^+} &= -3.5 + 13.0 \\ &= 9.5 \end{aligned}$$

we have obtained a quantity that is independent of the choice of a certain concentration as standard state. In Sec. 104 it was mentioned that the activity coefficient of Li_2CO_3 in its saturated solution is not accurately known; so there may be a considerable error in the value −3.5. Latimer adopted[1] the value

$$S_{Li^+} - S_{H^+} = 4.7 \pm 1 \text{ cal/mole/deg}$$

The value 4.7 was included in Table 25.

107. Heats of Solution and the Conventional Free Energies and Entropies of Solution. Table 34 gives for various common salts the observed values of the heat of solution, and the conventional free energy

TABLE 34. CONVENTIONAL FREE ENERGIES AND ENTROPIES OF SOLUTION AND HEATS OF SOLUTION AT 25°C

	ΔF^0	ΔS^0	ΔH^0	Reference
In water:				
KCl	−1,258	18.1	+4,120	[a]
KBr	−1,620	21.4	4,780	[a]
NaCl . . .	−2,156	10.3	920	[a]
NaBr	−4,231	14.0	−44	[b]
AgI.	21,940	16.0	26,710	
KIO_3	1,770	15.3	6,340	[b]
$PbCl_2$	6,483	−4.8	5,060	[b]
$BaSO_4$	13,718	−27.7	5,455	[b]
Li_2CO_3. .	3,280	−25.1	−4,200	
In methanol:				
KCl	+6,000	−16.5	+1,080	[a]
KBr	4,700	−12.8	870	[a]
NaCl	3,420	−18.2	−2,000	[a]

[a] W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62,** 2019 (1940).

[b] W. M. Latimer, *Chem. Rev.*, **18,** 350 (1936).

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[1] W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60,** 1829 (1938).

and entropy of solution calculated from experimental data. In all columns both positive and negative values are represented; and on comparing values or different substances, it will be seen that positive and negative values of ΔH^0, ΔF^0, and ΔS^0 appear to be combined in a capricious manner. In order to display these various combinations, the signs of ΔH^0, ΔF^0, and ΔS^0 are listed in Table 35. Although NaCl and KCl are alike in aqueous solution, they are unlike in methanol. Moreover, neither NaCl nor KCl shows the same type of behavior in methanol as in water.

Table 35. Sign of the Conventional Free Energy, Entropy, and Heat of Solution

	ΔF^0	ΔS^0	ΔH^0
In water:			
KCl	Negative	Positive	Positive
KBr			
NaCl			
NaBr	Negative	Positive	Negative
AgCl	Positive	Positive	Positive
KIO_3			
$PbCl_2$	Positive	Negative	Positive
$BaSO_4$			
Li_2CO_3	Positive	Negative	Negative
$CaCO_3$			
In methanol:			
KCl	Positive	Negative	Positive
KBr			
NaCl	Positive	Negative	Negative

Altogether five types are included in Table 35; and the question arises whether there are any other possible combinations that are not represented here. Examples of the types that follow are not found in

ΔF^0	ΔS^0	ΔH^0
Negative	Negative	Negative
Positive	Positive	Negative
Negative	Negative	Positive

Table 35; and though the first of these is possible, the last two are logically impossible. When ΔF^0 and ΔS^0 are of the same sign, ΔH^0

must likewise be of this sign; this clearly follows at once from the relation $\Delta F = \Delta H - T\,\Delta S$.

Confronted by the wide variety shown in Table 35, we are led to inquire whether we can do something to account for this variety. For this purpose, we must evaluate the unitary part of each quantity. As pointed out in Sec. 101, to obtain the unitary part of ΔF^0 in aqueous solution, one must add to ΔF^0 4760 cal/mole for a uni-univalent and 7140 for a uni-divalent solute; or, respectively, 0.2064 and 0.3097 electron-volt per kome. In methanol solution the corresponding quantities to be added are 4080 and 6120 cal/mole. The results of doing this for the substances of Table 34 are shown in Table 36 under the column headed NL. All the values are positive in both solvents. It will be seen that the division into solutes with ΔF^0 positive and solutes with ΔF^0 negative, shown in Table 35, arises merely from the fact that for some solutes NL happens to be greater than 4760 cal, while for others it happens to be less.

Turning next to the unitary part of ΔS^0, this is given in Table 36 under the heading $-N(dL/dT)$. It was pointed out in Secs. 90 and 106 that, to obtain the unitary part of ΔS^0 in aqueous solution, one must subtract 16.0 e.u. for a uni-univalent solute, and 24.0 e.u. for a uni-divalent solute. In methanol solution the corresponding quantities are 14.0 and 21.0 e.u. In Table 36 it will be seen that, except for the first two solutes KBr and KCl, the values are all negative, in both solvents. It will be recalled that for KBr and KCl the B-coefficients in viscosity are negative, and we associate the positive values for the unitary part of the entropy, shown in Table 29, with the creation of disorder in the ionic co-spheres. In every solvent the dielectric constant decreases with rise of temperature; and this leads us to expect that L will increase. For KBr and KCl in methanol solution, we see from Table 36 that dL/dT has indeed a large positive value. On the other hand, when these crystals dissolve in water, these electrostatic considerations appear to be completely overbalanced by other factors.

In the last column of Table 36 we come finally to the values of ΔH^0 under the guise of $N[L - T(dL/dT)]$. Since the two quantities in brackets are of the same order of magnitude, the value of ΔH^0 may be either positive or negative.

It is of interest to compare the values of ΔF and ΔH in Table 34 with the values of ΔF and ΔH given in Table 18 for the dissociation of molecular ions. We notice that in the dissociation of the ions $(FeCl)^{++}$ and $(FeBr)^{++}$ the value of ΔF is relatively small and is accompanied by a ΔH that is negative; on the other hand, in the dissociation of $(FeOH)^{++}$ the value of ΔF is very large and is accompanied in Table 18 by a ΔH

that is positive. This correlation is, of course, to be expected. The large amount of work required to break up the $(FeOH)^{++}$ into separate ions is due to the presence of a large D_{non} superimposed on a smaller D_{env}. A large amount of heat is absorbed in the dissociation, whereas in the case of $(FeCl)^{++}$ and $(FeBr)^{++}$ the D_{non} is sufficiently small for its effect to be swamped by the effect of the D_{env}, with the result that ΔH is negative and heat is evolved.

TABLE 36. VALUES OF NL AND $-N\frac{dL}{dT}$ AND $N\left(L - T\frac{dL}{dT}\right) = \Delta H°$

	NL	$-N\frac{dL}{dT}$	$N\left(L - T\frac{dL}{dT}\right)$
In water			
KCl	3,502	+2.1	4,120
KBr	3,140	+5.4	4,780
NaCl	2,604	−5.7	920
NaBr	529	−2.0	−44
AgI	26,700	~0.0	26,710
KIO_3	6,530	−0.7	6,340
$PbCl_2$	13,623	−28.8	5,060
$BaSO_4$	18,478	−43.7	5,455
Li_2CO_3	10,420	−49.1	−4,200
In methanol:			
KCl	10,080	−30.5	+1,080
KBr	8,780	−26.8	870
NaCl	7,500	−32.2	−2,000

The same factors are present in Table 34, though in a more complicated form. The largest values of ΔF in the table, namely, those for $BaSO_4$ and AgI, are accompanied by large positive values of ΔH. We can say that the large value of L arises from the presence of a large L_{non} superimposed on a smaller L_{env}. It has, in fact, long been recognized that the lattice energy of silver iodide possesses a considerable homopolar component; the observed lattice energy is larger than that calculated theoretically for a purely ionic crystal.[1] We expect then that the ΔH for AgI will have a large positive value. The situation is complicated by the fact, noted in Sec. 102, that, owing to the disorder in the co-sphere of the iodide ion, the value of L does not appreciably increase with temperature. In this exceptional case we have ΔH approximately equal to NL.

Problems

1. The saturated solution of silver sulfate in water at 25°C has a molality equal to 0.02689, and the activity coefficient γ of the solute in this saturated solution is 0.533.

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[1] J. E. Mayer, *J. Chem. Phys.*, **1**, 327 (1933).

The heat of solution tends at extreme dilution to the value +4207 cal/mole. Calculate the conventional free energy of solution at 25°C and the conventional entropy of solution.

2. The saturated solution of potassium iodate in water at 25°C has a molality equal to 0.43. Taking the activity coefficient γ in this saturated solution to be 0.52, find the conventional free energy of solution at 25°C, and calculate in electron-volts per ion pair the value of L for the removal of the ions K^+ and $(IO_3)^-$ into water at 25°C.

3. What is the solubility in water at 0°C of a uni-univalent crystal for which the value of L at this temperature is 0.90 electron-volt?

4. The saturated solution of silver iodate in water at 25°C has a molality equal to 0.00179, and the activity coefficient γ in this saturated solution may be taken to be 0.989. The heat of solution tends at extreme dilution to the value +13,200 cal/mole Find in electron-volts per ion pair the value of L, and also the value of dL/dT in water at 25°C.

5. Taking the values for the Ag^+ ion and the SO_4^{--} ion from Table 45, find the value of the partial molal entropy of silver sulfate in an aqueous solution at 25° having a molality equal to 10^{-6}; see the discussion of (179).

6. Discuss the sign and the magnitude of all the quantities given in Tables 34 and 36 for the solution of lithium carbonate, in comparison with the values for other substances.

CHAPTER 13

Electrodes and Galvanic Cells. The Silver–Silver Chloride Electrode. The Hydrogen Electrode. Half-cells Containing an Amalgam Electrode. Two Cells Placed Back to Back. Cells Containing Equimolal Solutions. The Alkali Chlorides as Solutes. HCl *in Methanol or Ethanol Containing a Trace of Water. The Alkali Chlorides in Methanol-Water Mixtures. The Heat of Solution of* HCl. *Proton Transfer Equilibrium from Measurements of E.M.F.*

108. Electrodes and Galvanic Cells. In connection with Fig. 9 in Sec. 11 we discussed the removal of a positive atomic core from a metal. The same idea may be applied to any alloy that is a metallic conductor. When, for example, some potassium has been dissolved in liquid mercury, the valence electron from each potassium atom becomes a free electron, and we may discuss the removal of a K^+ core from the surface of the amalgam. The work to remove the K^+ into a vacuum may be denoted by Y_{vac} When this amalgam is in contact with a solvent, we may consider the escape of a K^+ into the solvent. The work Y to remove the positive core into the solvent is much smaller than Y_{vac}.

When a metal (or an alloy) is in contact with a solvent, the escape of positive cores into the solvent leaves a negative charge on the metal. An electrical double layer is set up at the surface of contact between the metal and the solvent; and the work required to take an additional positive core into the solvent becomes greater than Y. This increment opposes the further escape of positive cores into the solvent; in fact, the strength of the double layer quickly reaches a value that establishes an equilibrium such that the number of ions leaving the metal per second is equal to the number returning to the metal. The part played by such electrical double layers has been discussed in some detail by the author.[1] In any galvanic cell the e.m.f. is the algebraic sum of the double layers present at the surfaces of contact between the conductors.

Any galvanic cell may be regarded as consisting of two half-cells, each

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[1] R. W. Gurney, "Ions in Solution," Cambridge, 1936.

of which contains a metallic electrode in contact with an ionic solution. In electrochemistry a half-cell is usually called an electrode; thus the silver–silver chloride half-cell is known as the silver–silver chloride electrode. In addition to this electrode we shall discuss in this chapter only two other types, namely, the hydrogen electrode, and the alkali amalgams of the type mentioned above.

When two reversible half-cells are coupled together to form a cell, a current may be caused to flow through the cell in either direction if a source of e.m.f. is introduced into the external circuit. When a current passes, electrons will flow into the external circuit from the metallic electrode of one half-cell, and from the external circuit into the metallic electrode of the other half-cell. In each half-cell electrical neutrality must be preserved by the simultaneous motion of ions.

109. The Silver–Silver Chloride Electrode. In the Ag/AgCl half-cell the electrode itself is of metallic silver, and the solution contains some solid silver chloride, so that the solvent is saturated with AgCl. In the Ag/AgCl half-cells to be discussed in this chapter the solvent will be either water or in some cases methanol or a mixture of methanol and water. In each case the solution in the half-cell will contain two solutes, namely, silver chloride and some other chloride, either HCl or an alkali chloride. In the reversible half-cell to which the Ag/AgCl half-cell is to be coupled there will in each case be a solution differing from the above by the absence of the AgCl, but containing the other chloride at the same concentration in the same solvent.

It has already been mentioned that, in addition to the metallic silver electrode, the Ag/AgCl half-cell contains some solid AgCl. Consequently, when one of these cells generates a current, not only must the usual requirement of electrical neutrality be preserved, but in the Ag/AgCl half-cell the solubility product of the ions Ag^+ and Cl^- must be maintained constant, to preserve the equilibrium between the saturated solution and the solid AgCl. When a steady current passes, either additional solid AgCl will be formed, or else an equivalent amount of solid AgCl will dissolve away, according to the direction in which the current is caused to flow. When electrons flow from the metallic silver into the external circuit, the Ag/AgCl half-cell receives an equal number of Cl^- ions from the other half-cell. At the same time, an equal number of Ag^+ ions from the metallic silver become superfluous. Deposition of Ag^+ and Cl^- ions to form additional solid AgCl prevents the solution from becoming supersaturated. The net result is that, for every electron entering the external circuit from the metallic silver, one Ag^+ ion is transferred from the metallic electrode to the solid AgCl, the number of Ag^+ ions in the solution remaining constant. When the current flows in the reverse direction, Ag^+ ions from the AgCl build up additional metallic silver, their positive charge being neutralized by the electrons that arrive from the external circuit.

Provided that the solution in a reversible half-cell contains the requisite solutes, it may also contain one or more other solutes which do not react with the electrode at all; the electrode will still function properly. The Ag/AgCl half-cells mentioned in Sec. 118 will contain one or two such subsidiary solutes. These solutes, which will also be present in the other half-cell to which the Ag/AgCl half-cell is coupled, react with the electrode there; they are included in the Ag/AgCl half-cell at the same concentration in order to avoid the electrical double layer which would otherwise be set up at the junction between the two solutions—at the liquid junction between the two half-cells.

110. The Hydrogen Electrode. In the reversible hydrogen half-cell the solution contains a strong or a weak acid; the solution is also saturated with H_2 at atmospheric pressure, pure hydrogen being continuously bubbled through the solution. The electrode is usually of platinum foil, covered with finely divided platinum. The latter provides a medium from which protons can go into solution, or into which protons can be deposited from solution, just as a potassium amalgam provides a medium from which K^+ ions can go into solution, or into which K^+ ions can be deposited from solution. When the solvent is water, and the electrode is on open circuit, the state of affairs in a hydrogen half-cell may be described by saying that both the following reactions are taking place at the surface of the metallic electrode.

$$H_2 + 2H_2O \rightarrow 2(H_3O)^+ + 2 \text{ electrons}$$
$$2(H_3O)^+ + 2 \text{ electrons} \rightarrow H_2 + 2H_2O$$

At the surface of contact between the platinum and the solution an electrical double layer spontaneously arises of that magnitude which suffices to make these reactions take place at the same rate, thereby yielding equilibrium. The strength of the double layer that is sufficient for this purpose depends on the concentration, or rather on the activity, of the $(H_3O)^+$ ions. When the half-cell has been coupled to another suitable half-cell, such as an Ag/AgCl half-cell, the value of the e.m.f. generated by the complete cell will accordingly depend on the activity of the hydrogen ions. A measurement of e.m.f. may therefore be used to make an accurate determination of the hydrogen-ion activity in a solution of unknown composition, provided that the cell has been standardized by a series of measurements on solutions of known composition. For example, one may measure the hydrogen-ion activity in the solution of a weak acid whose dissociation constant is not accurately known. It was, in fact, by this method, as already mentioned in Sec. 63, that all the dissociation constants in Table 9 were obtained. The solutions in the cells used for those measurements were somewhat complex, since they contained no less than five solute species, not counting the molecular H_2 with which the solution in the hydrogen half-cell was saturated. Those measurements will be described later in Sec. 118. We shall first discuss some measurements with cells containing fewer solute species.

111. Half-cells Containing an Amalgam Electrode. We return now to the type of half-cell already mentioned in Sec. 108. When the electrode is a potassium amalgam in contact with the dilute solution of a potassium salt, K^+ ions are continually passing into the solution from the amalgam, and from the solution to the amalgam. At the surface of contact between the solution and the amalgam an electrical double layer will spontaneously arise, whose magnitude gives equilibrium. The strength of this double layer will depend on the concentration of the potassium, both in the solution and in the amalgam. It will also depend on the liquid that is used as solvent.

In the experiments to be described, in each case the half-cell was coupled to a Ag/AgCl half-cell, which in each case formed the positive electrode of the cell; that is to say, on closing the external circuit, electrons flowed in the external circuit from the amalgam electrode to the silver electrode. This was the situation whether the solvent was water, or methanol, or a mixture of methanol and water.

112. Two Cells Placed Back to Back. In Sec. 57 of Chapter 6 we discussed the e.m.f. of two cells placed back to back. Both cells contained the same solute in aqueous solution, but at different concentrations. We saw that, when a current flows, the net result is simply to transfer an amount of solute from one solution to the other. Hence the observed resultant e.m.f. of the pair of cells is a measure of the change in free energy on transferring a pair of ions from one solution to the other; in fact, this change of free energy expressed in electron-volts is numerically equal to the e.m.f. expressed in volts.

In the cells discussed in Sec. 57 the solvent in every case was water. But in this chapter we shall discuss cells placed back to back, where one solution contains a solute dissolved in water, while the other contains the same solute dissolved in ethanol, or in methanol, or in a methanol-water mixture. When, for example, a hydrogen electrode containing HCl dissolved in ethanol is coupled to a Ag/AgCl electrode, also containing HCl dissolved in ethanol, the cell may be written

$$H_2\ (\mathrm{Pt})\ |\ \mathrm{HCl\ in\ ethanol}\ |\ \mathrm{AgCl/Ag} \qquad (195)$$

If now we have a similar cell with HCl in aqueous solution, and we put the two cells back to back, by placing the two hydrogen electrodes in contact with each other, the resulting arrangement may be written

$$\mathrm{Ag/AgCl} \mid \mathrm{HCl\ in\ water} \mid \mathrm{H_2\ (Pt)} \mid \mathrm{HCl\ in\ ethanol} \mid \mathrm{AgCl/Ag} \qquad (196)$$

since there is no need to write down the hydrogen electrode twice.

On closing the external circuit between the two Ag electrodes, when a current flows, the net result will be simply to transfer an amount of solute from one solvent to the other, and the measured e.m.f. will be equal to the change in free energy associated with the transfer of a kome of ions from one solvent to the other. This quantity will contain, in addition to the usual communal term, a unitary term arising from the fact that, in the co-sphere of each positive ion and each negative ion, the amount of free energy lost by the dipoles of one solvent will be different from that lost by the dipoles of the other solvent.

We shall be interested in pairs of cells, in which the mole fraction of the solute in one solvent is equal to its mole fraction in the other solvent. Suppose then that a series of such pairs of cells is made up, with the solute at progressively greater dilutions. When the members of these pairs of cells are placed back to back, the resultant e.m.f.'s will contain progressively smaller contributions from the interionic forces; and, on extrapolation to extreme dilution, this contribution will be negligibly small. Since the mole fraction on each side is the same, the difference between the cratic terms will be zero. In any such series of cells, the measured e.m.f.'s when extrapolated to extreme dilution thus yield the unitary part of the change in free energy.

113. Cells Containing Equimolal Solutions. In the literature values of the e.m.f. of the cells (196) are given, not when the HCl has the same mole fraction in either solvent, but when it has the same molality—an arbitrary choice. A thousand grams of water contain 2.555 times as many molecules as 1000 grams of ethanol; so, when we consider the number of different ways in which the protons from the HCl can be distributed among the vacant levels provided by the solvent molecules, we have a greater value of W_{cf} in (59) for water than for an equimolal solution in methanol. The difference between the cratic terms would give rise to an e.m.f., even if the unitary terms gave rise to none. The magnitude of this e.m.f. would clearly be equivalent to

$$2kT \ln 2.555 = 1.88kT = 0.048 \text{ electron-volt}$$

The e.m.f. would thus be 0.048 volt, and its sign would be such that the spontaneous current transfers HCl from ethanol to water. This is the sign that the resultant e.m.f. of equimolal cells, placed back to back, is found to have; the value, extrapolated to infinite dilution, is either 0.296

volt, according to Harned and Fleyscher, or 0.310 volt according to the measurements of Woolcock and Hartley.[1] Subtracting 0.048 electron-volt, we find that the work required to transfer one Cl^- ion and one proton from aqueous solution to ethanol amounts to either 0.248 or 0.262 electron-volt.

Passing on now to cells containing HCl at equal molality in *methanol* and in water, we find for the difference between the cratic terms, since the molecular weight of methanol is 32,

$$2kT \ln \tfrac{32}{18} = 1.15kT = 0.030 \text{ electron-volt} \tag{197}$$

The cells with equimolal solutions of HCl, placed back to back, were found to yield an e.m.f. of 0.232 volt. Converting to electron-volts, and subtracting 0.030, we find 0.202 as the value of the work required to transfer one Cl^- ion and one proton from water to methanol. This value, 0.202, has been plotted on the right-hand side of Fig. 61; the other points plotted give values obtained with methanol-water mixtures. These will be discussed below.

114. The Alkali Chlorides as Solutes. In order to make a similar study of the transference of KCl, NaCl, and LiCl between water and methanol-water mixtures, the hydrogen electrode was replaced by an amalgam electrode, as described in Sec. 111. The arrangement when two cells having potassium amalgam electrodes are placed back to back may be written

$$\text{Ag/AgCl} \;\Big|\; \text{KCl in water} \;\Big|\; \text{K(Hg)} \;\Big|\; \begin{array}{l}\text{KCl in methanol or in}\\ \text{methanol-water mixture}\end{array} \;\Big|\; \text{AgCl/Ag} \tag{198}$$

since there is no need to write down the K(Hg) electrode twice. When the external circuit between the Ag electrodes is closed, and the cells generate a current, on one side K^+ and Cl^- ions go into solution in the water, while at the same time K^+ and Cl^- ions are deposited from solution in the methanol or in the methanol-water mixture. The net result is that, for every electron that flows round the external circuit, one pair of ions, K^+ and Cl^-, is transferred to the water from the other solvent. When the e.m.f. of the cells, placed back to back, has been extrapolated to infinite dilution of KCl, and when the cratic term has been subtracted, we expect to find a residual e.m.f. characteristic of the transfer of the pair of ions from one solvent to the other. In addition to potassium amalgams, lithium amalgams in contact with lithium chloride solutions were used, and sodium amalgams in contact with sodium chloride solutions.

Before discussing the results of the experiments, it will be convenient

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[1] *Phil. Mag.*, **5**, 1142 (1928).

to inquire into the magnitude of the effect that would be expected from simple electrostatic theory. If we consider the introduction of any species of atomic ion into two different solvents, we see from (16) that the loss of free energy by the solvent lying outside any radius R will be smaller in the solvent that has the lower dielectric constant. Whether this is still true for a value of R comparable with an ionic radius depends on the degree to which the contribution from those solvent molecules that are in contact with the ion resembles the contribution to be expected from (18). We may say at once that in every case, for the ions of KCl, NaCl, LiCl, and HCl, the unitary part of the observed e.m.f. has the sign to be expected from (18); that is to say, the spontaneous e.m.f. corresponds to a transfer of ions to the water from the methanol (or from the mixed solvent).

Fixing attention on this difference between ions in methanol and ions in water, we may next ask whether the difference should be greater for an atomic ion of large or of small radius. The answer is clearly that, according to (18), if we take R equal to or proportional to the ionic radius a, between any two solvents the difference should be greater for the smaller ion; greater for Li^+ than for K^+ or Cs^+, for example. If ϵ_1 and ϵ_2 denote the dielectric constants of the two solvents, the difference, according to (18), would amount to

$$\frac{e^2}{2a}\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) \tag{199}$$

which is inversely proportional to the radius. In accounting for this result, we make use of the same idea that was used near the end of Sec. 14, where, in considering an ion in a vacuum, it was pointed out that in the field of a *small* ion there is initially more energy to lose, and consequently, when the ion is plunged into a solvent, more energy is lost. So here, when a small ion is transferred from methanol to water, according to (199) more free energy should be lost than in the case of a larger ion, because there is more free energy to lose. If the galvanic cells of Sec. 111 are set back to back, the current should in every case be observed to flow in the direction that corresponds to transfer of solute from methanol to water; and the e.m.f. should be the larger, the smaller the ionic radius.

Nothing has been said about obtaining a numerical value from (199); such a calculation, of course, could not be expected to give a correct result. We have only suggested that, in comparing ions of markedly different sizes, use of (199) might give relative values lying in the right direction. We must next inquire whether we are entitled to expect even this; we must ask whether the above effect may not be entirely masked by the order-disorder change in water in comparison with methanol or other solvent.

As seen from Tables 23 and 21 the ion pair ($K^+ + Cl^-$) increases the viscosity of methanol but diminishes that of water. We recall that the values for the entropy of solution in Table 29 show a parallel trend; in the galvanic cells of Sec. 112 placed back to back, this difference in ionic entropy between aqueous and methanol solutions would *alone* be sufficient to give rise to an e.m.f. We must ask whether this e.m.f. would be in the same direction, or in the direction opposite to the e.m.f. that would result from a use of (199).

Owing to the minus sign in $\Delta F = \Delta H - T\,\Delta S$, a gain in entropy implies a loss of free energy. On transferring the ions ($K^+ + Cl^-$) from *methanol* to *water*, we go from order in the co-sphere (accompanied by a high viscosity) to disorder in the co-sphere (accompanied by a diminished viscosity); there is thus an increment in entropy. This means a loss in free energy. Looking back at (199), we see that the e.m.f. to be expected from this source is of the same sign as that to be expected from (199). We anticipate then that the order-disorder effect may change the magnitude but not the sign of the e.m.f. It has been already mentioned that for all four solutes the e.m.f.'s are of the expected sign.

In one of the two cells placed back to back, the solvent, as mentioned above, was pure water in each case. When the mixed solvent in the other cell contains only a small percentage of methanol, the resultant e.m.f. will obviously be small, and it should progressively increase with increasing difference between the solvents. In Fig. 61 abscissas are values of $1/\epsilon$ for the mixed solvent, running from 0.0126 for pure water to 0.0301 for pure methanol. Ordinates give the unitary part of the e.m.f. extrapolated to infinite dilution. It will be seen that for KCl, NaCl, and LiCl the curves differ only slightly from straight lines, but the curve for HCl has quite a different shape. From the experimental results on the electrical conductivity depicted in Fig. 31 we expect the curve for HCl to take this form. In Sec. 115 we shall discuss this result for HCl, and in Sec. 116 we shall return to the interpretation of the results obtained with the alkali chlorides.

115. HCl in Methanol or Ethanol Containing a Trace of Water. When a little HCl is dissolved in methanol, nearly all the protons are transferred to solvent molecules to form $(CH_3OH_2)^+$ ions. If now a certain amount of water is mixed with this solution, each water molecule provides for a proton a vacant level that lies considerably deeper than that occupied in the $(CH_3OH_2)^+$ ion. Consequently, as we saw in Sec. 36, many of the protons are transferred, to form $(H_3O)^+$ ions. If a hydrogen electrode is dipping into this solution, the falling of the protons will be accompanied by a change in the strength of the electrical double layer at the metal surface. When the protons have fallen to the lower levels provided by the added water molecules, the tendency for protons to be deposited on the metal surface is much reduced. Escape of protons from the surface into the solution is no longer compensated by an equal deposition of protons from the solution; and this will quickly leave an additional negative charge on the metal. The strength of the electrical double layer will thereby quickly change to a new value which will give equilibrium.

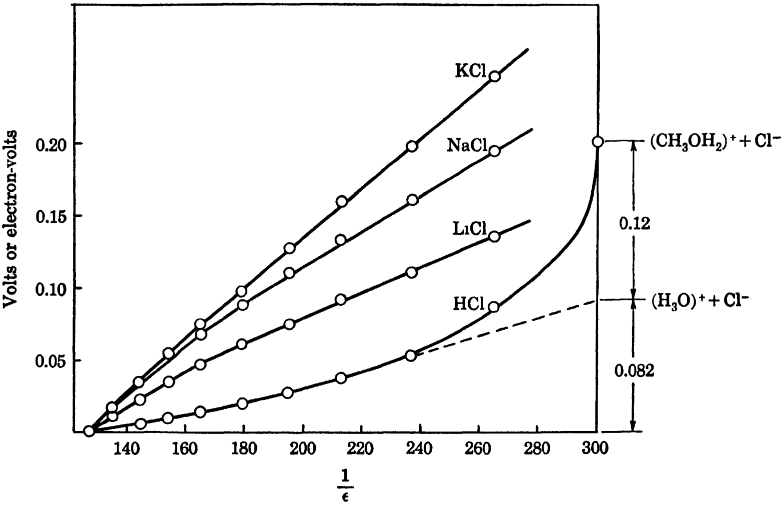

FIG. 61. Abscissas give the reciprocal of the dielectric constant of the methanol-water mixture.

If the said hydrogen half-cell is part of a cell, the change in the electrical double layer will mean a change in the e.m.f. of the cell.

In their measurements with the cell (195) containing methanol, Nonhebel and Hartley[1] verified by direct experiment that the addition of a small drop of water to either side of the cell, sufficient to give a mole fraction of H_2O equal to about 0.001, produced a change in the e.m.f. equal to a few millivolts. This was attributed mainly to the proton transfer (44). The curve for HCl in methanol-water mixtures must thus have a very steep slope, as has been sketched on the right-hand side of Fig. 61.

We can calculate the value of J for the proton transfers (43) and (44) from the measurements of conductivity depicted in Figs. 31 and 32.

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[1] *Phil. Mag.*, **50**, 734 (1925).

The simple analysis of their results, given by Thomas and Marum, was as follows.

When the added water has a molarity n, let a fraction g of positive ions be alcoholic ions, while the fraction $(1 - g)$ is in the form of $(H_3O)^+$ ions. On extrapolating to infinite dilution, the equilibrium constant of the reaction (43) may be written

$$\frac{(1 - g)N}{gn} = K \tag{200}$$

Here N is the molarity of the alcohol which does not vary appreciably when a trace of water is introduced. Writing $N/K = r$, we have

$$g = \frac{r}{n + r}; \qquad (1 - g) = \frac{n}{n + r} \tag{201}$$

If the conductivity of the HCl in pure alcohol is given by (37), one can try the following simple assumption: that, when a trace of water has been added, each $(C_2H_5OH_2)^+$ makes to the conductivity a contribution proportional to λ_+, while each $(H_3O)^+$ ion makes a contribution, which may be written λ'_+, proportional to its mobility in the nearly pure alcohol. In this case the total conductivity of the solution of HCl, when the added water has a molarity n, may be written

$$\Lambda_n = \lambda_+ \frac{r}{n + r} + \lambda'_+ \frac{n}{n + r} + \lambda_-$$

Hence we obtain

$$(\Lambda_0 - \Lambda_n)(n + r) = (\lambda_+ - \lambda'_+)n$$

which may be written in the form

$$n = -r + (\lambda_+ - \lambda'_+) \frac{n}{\Lambda_0 - \Lambda_n} \tag{202}$$

If, then, values of $n/(\Lambda_0 - \Lambda_n)$ obtained from experiment are plotted against the molarity of the water n, a straight line should be obtained, of which the slope is $(\lambda_+ - \lambda'_+)$ and the intercept $-r$. The results[1] in methyl and ethyl alcohol are shown in Fig. 62. It will be seen that from the intercept the value $r = 0.25$ is obtained in methyl, and $r = 0.06$ in ethyl. In each solvent the mobility of the $(H_3O)^+$ ion is found to be not very different from that of the Na^+ ion.

The equilibrium (43) has also been studied by a spectroscopic method, as already mentioned in Sec. 36. In ethanol solution picric acid is a weak acid; in other words, the negative picrate ion has a tendency to pick up a proton. This tendency is diminished when, according to (43), the

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[1] L. Thomas and E. Marum, *Z. physik. Chem.*, **143**, 213 (1929).

protons have fallen to a lower level. The change in the equilibrium is determined by measuring the change in the absorption spectrum of the solution.[1] In this way, the value $r = 0.052 \pm 0.001$ was obtained. There seems then no doubt that the value 0.06 obtained from the conductivity measurements is near to the truth; and we may take the same point of view with respect to the value 0.25 for methanol.

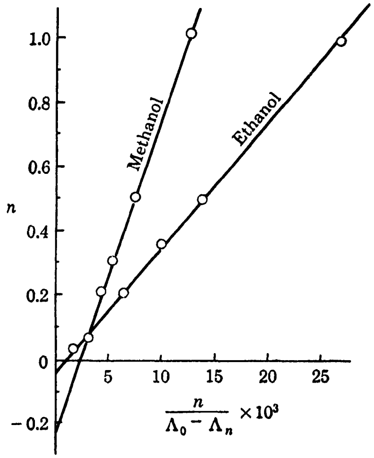

FIG. 62

In each case, from the value of r we can at once calculate the value of J for the proton transfer. At 25°C a liter of ethanol weighs 786 grams and contains 17.0 moles. We find then for the proton transfer (43)

$$\frac{J}{kT} = -\ln K_x = -\ln\frac{N}{r} = -\ln\frac{17.0}{0.052}$$

$$J = 5.78kT = 0.148 \text{ electron-volt} \tag{203}$$

Similarly, at 25°C a liter of methanol weighs 785 grams and contains 24.5 moles. We find then for the proton transfer (44)

$$J = -kT\ln\frac{24.5}{0.25} = 4.6kT = 0.12 \text{ electron-volt} \tag{204}$$

The contribution that this quantity makes to the e.m.f. of the cell containing HCl in Fig. 61 is indicated at the right-hand side of that diagram. The result, (204), implies that, when an H_2O molecule is present in methanol solution, its vacant proton level lies about 0.12 electron-volt lower

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[1] P. Gross, A. Jamoch, and F. Patat, *Monatsh.*, **63**, 124 (1933).

than that of a CH_3OH molecule. If then from an extremely dilute aqueous solution of HCl we transfer a Cl^- ion and a proton to a quantity of methanol that contains one or more H_2O molecules in solution, the work done (the unitary part) will be only (0.202 − 0.12) = 0.082 electron-volt if the proton is inserted into an H_2O molecule to form an $(H_3O)^+$ ion. An additional amount of work, in the neighborhood of 0.12 electron-volt is required to transfer the proton from the $(H_3O)^+$ ion to a methanol molecule to form a $(CH_3OH_2)^+$ ion. The broken line in Fig. 61 must then be taken to represent the effect of the changing environment on the ions Cl^- and $(H_3O)^+$.

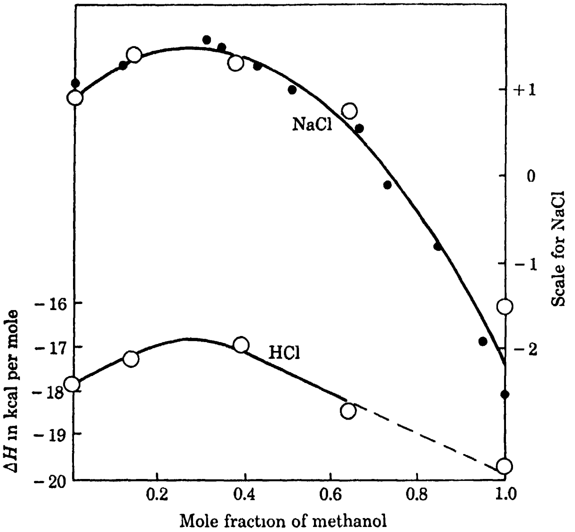

FIG. 63. Heat of solution of HCl and NaCl at 25°C (Slansky) and of NaCl at 20° (Moss and Wolfenden). Abscissas give the mole fraction of methanol in the methanol-water mixture. [*R. L. Moss and J. H. Wolfenden, J. Chem. Soc.*, **1939,** 118; *C. M. Slansky, J. Am. Chem. Soc.*, **62,** 2433 (1940).]

116. The Alkali Chlorides in Methanol-Water Mixtures. Turning to the results for KCl, NaCl, and LiCl, plotted in Fig. 61, we see that in each case the values are nearly linear with $1/\epsilon$, suggesting that the results may be simply interpreted in terms of electrostatic theory. This apparent simplicity is, however, illusory. In the first place, KCl gives greater e.m.f.'s than NaCl, while LiCl gives smaller e.m.f.'s; whereas in Sec. 114 we deduced from (199) that the contrary should be the case. In the second place, if a simple electrostatic interpretation is to be given for the variation of ΔF with the composition of the solvent, a similar simple trend should be found for ΔH, the heat absorbed when ions are transferred from water to the methanol-water mixture. That there is no simple trend is shown in Fig. 63, where the heats of solution of NaCl in methanol-water mixtures are plotted against the mole fraction of methanol. It will be seen that for a value of x_{meth} in the neighborhood of 0.6 the heat of solution of NaCl has the same value as in pure water; in other words, the heat of transferring the ions from water to this mixed solvent is zero. In the left-hand half of the diagram the ΔH for this proton transfer is positive, while in the right-hand half it is negative. According to simple electrostatic theory the sign ΔH should be the same everywhere; and the question arises, in which half of the diagram is the sign of ΔH in accordance with simple electrostatic theory? The answer is: in the right-hand half. As in (24), we expect ΔF and ΔH to be opposite in sign.

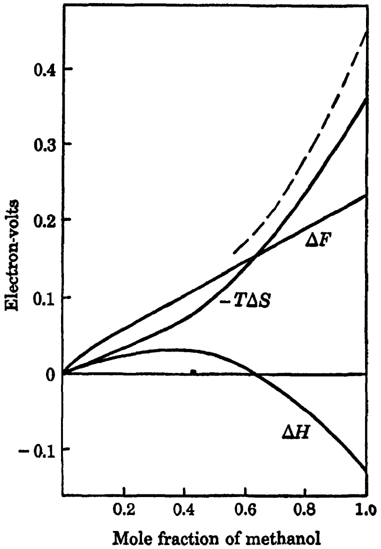

Fig 64. ΔF, $-T\,\Delta S$, and ΔH for the transfer of the ion pair ($Na^+ + Cl^-$) from water to methanol-water mixtures.

At the value of x_{meth} near 0.6, where ΔH is zero, the values of ΔF and $-T\,\Delta S$ must obviously be the same. The curves for ΔF and $-T\,\Delta S$ must intersect at this point, as shown in Fig. 64. In this diagram the values of ΔH for NaCl are reproduced from Fig. 63 but are expressed in electron-volts, and the values of ΔF from Fig. 61, while the values of $-T\,\Delta S$ are obtained from $(\Delta F - \Delta H)$. In the right-hand half of the diagram the magnitude of $-T\,\Delta S$ is greater than that of ΔF, in accordance with electrostatic theory; compare (24). As pointed out in Sec. 98, although the molecular dipoles in methanol are less numerous than in water, they lose more entropy; in fact they lose so much more entropy that the term $-T\,\Delta S$ is predominant in producing the e.m.f. of the cells (198) placed back to back.

The corresponding curve for the $-T\,\Delta S$ of KCl, instead of lying below the curve for NaCl, as would be expected from simple electrostatic theory for an ion with a larger radius, rises considerably higher, as shown by the broken line at the top of Fig. 64. In Sec. 114 we suggested that this excess is due to the fact that, while the K^+ ion produces order when dissolved in methanol, it does not do so when dissolved in water; as a result there is an unusually large loss of entropy on transferring this ion from water to methanol.

117. The Heat of Solution of HCl. Figure 63 includes values of the heat of solution of HCl in methanol-water mixtures over the range from pure water to pure methanol. As in the case of NaCl, it will be seen that, for a value of x_{meth} in the neighborhood of 0.6, the heat of solution has the same value as in pure water; in other words, the heat of transferring the ions from pure water to this mixed solvent is zero. In the left-hand half the ΔH for this transfer is again positive, while in the right-hand half it is again negative.

Unfortunately no measurements were made with HCl in the range between 64 per cent methanol and pure methanol. According to the discussions of Secs. 36 and 115 this should be the most interesting range, for consider what happens when HCl goes into solution. When HCl dissolves in pure methanol, we obtain Cl^- negative ions and $(CH_3OH_2)^+$ positive ions. On the other hand, when HCl dissolves in methanol containing a little water, we obtain apparently Cl^- negative ions and mostly $(H_3O)^+$ positive ions, and the heat of solution for this process may be quite different. More heat will, in fact, be evolved, if the binding energy of the added proton is greater in $(H_3O)^+$ than in $(CH_3OH_2)^+$. Although in Fig. 63 it is possible to complete the curve by drawing a smooth curve through the few experimental points (as shown by the broken line), it is very doubtful whether we should be right in attempting to do this.

118. Proton Transfer Equilibrium from Measurements of E.M.F. We shall conclude this chapter by describing the use of a cell containing a hydrogen electrode, to measure the equilibrium constants for proton transfers from the molecules of a weak acid in aqueous solution. As already mentioned in Sec. 110, the cell used for this purpose contained five solute species, in addition to the molecular hydrogen with which the solution in the hydrogen half-cell was saturated. If the weak acid is denoted by HA, these ionic species were $(H_3O)^+$, A^-, Na^+, Cl^-, and the Ag^+ in the Ag/AgCl half-cell. Only two of these ions, however, took part in the reaction of the cell, namely, the hydrogen ions and the chloride ions. The cell may be written

$$H_2(\mathrm{Pt}) \left| \begin{matrix} \mathrm{HA} \\ \mathrm{NaA} \\ \mathrm{NaCl} \end{matrix} \right\} \begin{matrix} \text{in aqueous} \\ \text{solution} \end{matrix} \Bigg| \; \mathrm{AgCl/Ag}$$

As pointed out in Sec. 110, when the cell has been calibrated by a series of solutions of HCl, it may be used to determine the activity of the hydrogen ions provided by a known concentration of a weak acid HA.

Since the Cl^- ions and the H^+ ions are the only ions that take part in the cell reaction, the e.m.f. of the cell is given by

$$\mathcal{E} = \mathcal{E}_0 - \frac{kT}{e} \ln (\gamma_{H^+} m_{H^+} \gamma_{Cl} \, m_{Cl^-}) \tag{205}$$

The dissociation constant of the acid HA is given by

$$K = \frac{\gamma_{H^+} m_{H^+} \gamma_{A^-} m_{A^-}}{\gamma_{HA} m_{HA}} \tag{206}$$

Substituting in (205) for m, and rearranging the terms, we obtain

$$\ln K + \ln \frac{\gamma_{H^+} \gamma_{Cl^-} \gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} = \frac{e}{kT} (\mathcal{E}_0 - \mathcal{E}) - \ln \frac{m_{HA} m_{Cl^-}}{m_{A^-}} \tag{207}$$

In (206) and in (207) m_{HA} denotes the amount of the acid which remains undissociated. By assuming a preliminary value for K this may be estimated; thus all the quantities on the right-hand side of (207) are known. The values of the activity coefficients that occur on the left-hand side depend on the ionic strength of the solution; in a mixture of uni-univalent solutes, such as we are dealing with here, the ionic strength is equal to the total concentration of all species of positive ions, or of negative ions. Plotting the value of the right-hand side of (207) against the ionic strength, and extrapolating to the extremely dilute range, neither the numerator nor the denominator of $\frac{\gamma_{H^+} \gamma_{Cl^-} \gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$ differs appreciably from unity; so the left-hand side of (207) is the required value of $\ln K$.

In the case of acetic acid in aqueous solution at 25° this extrapolation was shown in Fig. 33 in Sec. 63.

Problem

Write out the derivation of equation (202) from (201).

CHAPTER 14

Proton Transfers in Various Solvents. The Autoprotolysis of Methanol. Formic Acid as Solvent. The Sulfate Ion. Autoprotolysis of Formic Acid. The Urea Molecule. Sulfuric Acid and Liquid Ammonia as Solvents.

119. Proton Transfers in Various Solvents. As soon as sufficient data are available, it will be possible to construct accurate charts, similar to Figs. 36 and 40, showing the occupied and vacant proton levels in non-aqueous solvents. Let us first consider proton transfers between *solute* particles—that is to say, where no solvent particle is involved. Considering various species of solute particles in a certain solvent, we may ask to what extent the intervals between proton levels will differ from the corresponding intervals found in water at 25°C (throughout this discussion the word *interval* will mean the interval between two proton levels in a diagram similar to Fig. 36). In attempting to answer this question, the division of proton transfers into classes I, II, III, and IV introduced in Sec. 66 will clearly be relevant when the electric susceptibility, or dielectric constant, of the non-aqueous solvent differs markedly from that of water. For this classification of Sec. 66 was based upon the presence of electrostatic energy, whose magnitude makes the proton transfer relatively sensitive or insensitive to a change of environment. Since proton transfers of class I are least sensitive, we must expect that, for such a proton transfer, the interval on the new diagram will differ least from the interval drawn in Fig. 36 for aqueous solution. On going from class I to classes II, III, and IV, the difference should become progressively greater. In a solvent of lower dielectric constant, more work must be done to separate charges; this means a wider interval for such a proton transfer. But in the level diagram, there will evidently be no *uniform* widening of the intervals.

Let us discuss next some proton transfers involving a molecule of the solvent. Consider, for example, the proton transfer

$$(NH_4)^+ + CH_3OH \rightarrow NH_3 + (CH_3OH_2)^+ \qquad (208)$$

carried out in methanol solution. Here we merely replace one positive ion by another; and *as far as the electrostatic energy is concerned,* we do not expect J to differ much from the value of J for the proton transfer

$$(NH_4)^+ + H_2O \rightarrow NH_3 + (H_3O)^+$$

in aqueous solution, though it is true, of course, that the values of J may differ owing to a difference in J_{non}—that is to say, owing to a difference between the binding energies of the proton in the solvent molecule.

TABLE 37. EQUILIBRIUM CONSTANTS IN METHANOL[a]

	Temp., °C	$-\log K$
$\dfrac{[NH_4^+][CH_3O^-]}{[NH_3]}$	18	5 92
$\dfrac{[NH_3][CH_3COOH]}{[NH_4^+][CH_3COO^-]}$	18	1 48
$\dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$	18	9 65
	25	9 65
	37	9 66
$[CH_3OH_2^+][CH_3O^-]$	18	16 96
	25	16 66
	37	16 15

[a] N. Bjerrum, A. Unmack, and L. Zechmeister, *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.,* **5**, No. 11 (1925).

For comparison consider the proton transfer

$$NH_3 + CH_3OH \rightarrow (NH_4)^+ + (CH_3O)^- \tag{209}$$

carried out in methanol solution. Here we expect the value of J_{el} to be larger than the value of J_{el} for the proton transfer

$$NH_3 + H_2O \rightarrow (NH_4)^+ + (OH)^-$$

in aqueous solution. At the same time there may be a difference between the values of J_{non}.

In connection with Fig. 36, consider an aqueous solution containing $(NH_4)^+$ ions and $(CH_3COO)^-$ ions; and suppose that we raise a proton from the occupied level of a $(NH_4)^+$ ion to the vacant level of a $(CH_3COO)^-$ ion. In this process both the ionic fields disappear. But the relative position of the levels in Fig. 36 shows that, in spite of the electrostatic energy released in the recombination of the positive and negative charges, an amount of work equal to more than 0.26 electron-volt must be done, to raise the proton, owing to the large value of J_{non}.

For comparison, consider now the same ions in methanol solution. Each ionic field will contain more electrostatic energy than the corresponding ionic field in aqueous solution. Suppose that again we raise a proton from the occupied level of a $(NH_4)^+$ ion to the vacant level of a $(CH_3COO)^-$ ion. In this process the amount of electrostatic energy released will be greater than in water. If then the value of J_{non} is roughly the same as before, the total amount of work required to transfer the proton will be *smaller* than in water. Hence, in the chart of the proton levels in methanol, we expect that the interval between these two proton levels will be narrower than in Fig. 36.

This prediction can be tested by examining the data given in Table 37 for the equilibrium

$$(NH_4)^+ + (CH_3COO)^- \rightleftarrows NH_3 + CH_3COOH \qquad (210)$$

in methanol solution. From Table 37 it will be seen that the value of $-\log K$ is only 1.48, which, as we shall see, means that the equilibrium lies much farther to the right than in aqueous solution; it implies a much smaller value of J. In Table 12 at 20°C we had

$$J = 0.6464 - 0.3781 = 0.2683 \text{ electron-volt}$$

In methanol solution at 18°C we find

$$\begin{aligned} J = -kT \ln K_x &= -kT \ln K \\ &= 0.0591 \times 1.48 = 0.088 \text{ electron-volt} \end{aligned}$$

As expected, this is smaller than the value in aqueous solution. Although in both solvents a positive amount of work is required to transfer the proton, the amount in methanol is smaller, owing to the greater amount of electrostatic energy released in the disappearance of the ionic fields.

120. The Autoprotolysis of Methanol. The table gives the value $\log K = -16.6$ for the autoprotolysis constant at 25°C. From this value we find

$$\begin{aligned} J &= -kT \ln K + 2kT \ln M \\ &= 0.591(16.66 + 2.99) = 1.16 \text{ electron-volts} \end{aligned}$$

The interval is thus a little wider than in the case of water; this is shown in Fig. 65.

Using (204), let us attempt to predict the degree of dissociation of nitric acid in methanol solution. According to (204) the occupied proton level of $(H_3O)^+$ in methanol lies about 0.12 electron-volt below the level of $(CH_3OH_2)^+$, while in Fig. 40 the proton level of HNO_3 in aqueous solution lies about 0.05 electron-volt below the level of $(H_3O)^+$. If we add together these quantities, we obtain $(0.12 + 0.05) = 0.17$. In addition, we must take into account the fact that the environment of the ions is different. From the simple electrostatic point of view we should say that, when the positive and the negative ions are created (by proton transfer) in methanol, more electrostatic energy must be put into the ionic fields than for the corresponding ionic fields in water. Thus we may expect that the dissociation constant K for nitric acid will have a value corresponding to a value of J *greater* than $+0.17$ electron-volt. Such a value would be sufficient to reduce nitric acid to quite a weak acid in methanol, although it is classed as a strong acid in water. This is found to be the case; from measurements of electrical conductivity the value of K for nitric acid is 6.4×10^{-4}, from which we estimate

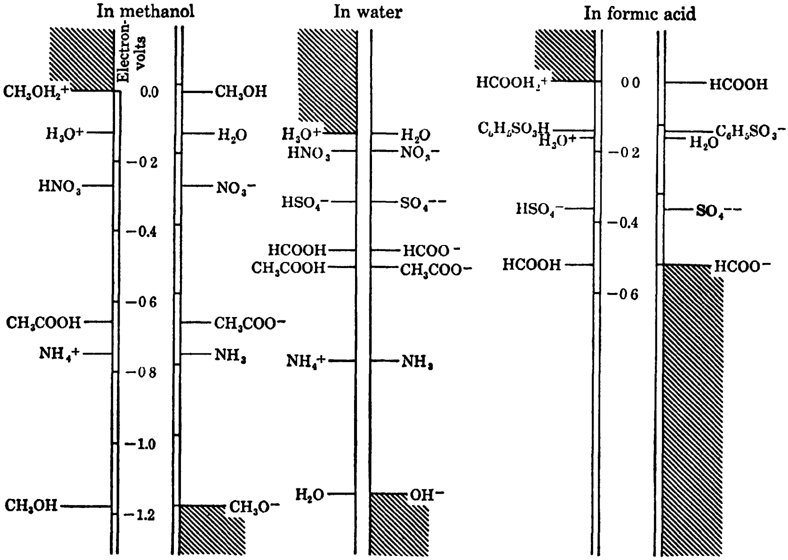

FIG. 65

$$J = -kT \ln K_x = 10.8\, kT = 0.27 \text{ electron-volt}$$

This is 0.22 electron-volt greater than the value of J for nitric acid in water. The relative positions of the proton levels in methanol, using this value, is shown in Fig. 65.

TABLE 38. AUTOPROTOLYSIS OF PURE SOLVENTS AT 25°C

Solvent	M	$-\log K$	J, electron-volts	References for $\log K$
Water	55.5	14.0	1.04	
Methanol	31.1	16.7	1.18	a
Ethanol	21.6	19.1	1.3	b
Formic acid	21.6	6.2	0.52	c
Sulfuric acid	10.2	3.1	0.3	d
Ammonia:				
−33°	58.6	22?	1.5?	e
−50°		33?	2.2?	f

[a] Bjerrum, Unmack, and Zechmeister, *Kgl. Danske Videnskab. Selskab. Mat-fys Medd.*, **5**, No. 11 (1925).

[b] Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).

[c] L. P. Hammett and N. Dietz, *J. Am. Chem. Soc.*, **52**, 4795 (1930); L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 4239 (1932).

[d] L. P. Hammett, *Chem. Rev.*, **13**, 62 (1933).

[e] L. P. Hammett, "Physical Organic Chemistry," p. 256, McGraw-Hill, 1940.

[f] V. A. Pleskov and A. M. Monoszon, *Acta Physicochim. U.R.S.S.*, **1**, 725 (1935); W. C. Fernelius and G. B. Bowman, *Chem. Rev.*, **26**, 5 (1940).

121. Formic Acid as Solvent. In Tables 9 and 12 data were given for the proton transfer

$$HCOOH + H_2O \rightarrow (HCOO)^- + (H_3O)^+ \qquad (211)$$

carried out in aqueous solution. In this process the solute particle HCOOH on the left-hand side is replaced by the two solute particles on the right-hand side; that is to say, in (211) we have $\Delta q = +1$. If now we take pure formic acid as solvent and dissolve in it a small quantity of water as solute, the thermal agitation will again throw up protons from HCOOH molecules to the vacant proton level in a certain number of H_2O solute particles, to form $(H_3O)^+$ ions. In this process the solute particle H_2O on the left-hand side of (211) is replaced by the two solute particles on the right-hand side; and again in (211) we have $\Delta q = +1$.

The macroscopic dielectric constant of liquid formic acid at 25° has the value 64, not much lower than that of water. Hence, from the simple electrostatic point of view, we should expect J_{env} for the proton transfer (211) carried out in formic acid solution, to have a value somewhat greater, but not much greater, than when the same proton transfer is carried out in water as solvent. In Table 12 we found that, in aqueous solution, the value of $(J_{non} + J_{env})$ rises from 0.3197 at 20°C to 0.3425 at 40°C. Measurements in formic acid at 25°C yielded for the equilibrium of (211) the value $-kT \log K = 4.76$. Since for formic acid the number of moles in the b.q.s. is $M = \frac{1000}{46}$, we find

$$\begin{aligned} J &= -kT \ln K + kT \ln \tfrac{1000}{46} \\ &= 0.059(4.76 + 1.34) = 0.36 \text{ electron-volt} \end{aligned}$$

If then we construct a tentative diagram for the proton levels in formic acid solution, the gap between the vacant level of $(HCOO)^-$ and the occupied level of H_2O will be a little wider than in Fig. 36. This has been shown in Fig. 65.

122. The Sulfate Ion. In Fig. 36 we see that the vacant level of the $(SO_4)^=$ ion in aqueous solution lies only 0.13 electron-volt above the occupied level of HCOOH. If the interval has a comparable value when sulfate ions are present in formic acid as solvent, the thermal agitation should transfer a large number of protons from solvent HCOOH molecules to the $(SO_4)^=$ ions. This was found to be the case when Na_2SO_4 was dissolved in pure formic acid. Such a transfer of protons from molecules of a solvent to the anions of a salt is analogous to the hydrolysis of the salt in aqueous solution and is known as "solvolysis," as mentioned in Sec. 76. In a 0.101-molal solution of Na_2SO_4 in formic acid the degree of the solvolysis was found to be 35 per cent.[1]

123. Autoprotolysis of Formic Acid. The self-dissociation of pure formic acid yields, in addition to the formate ion, the positive ion $(HCOOH_2)^+$, according to

$$HCOOH + HCOOH \rightarrow (HCOO)^- + (HCOOH_2)^+ \qquad (212)$$

In Table 38 the autoprotolysis constant of formic acid is given by $-\log K = 6.2$. For the proton transfer (212) we thus obtain

$$\begin{aligned} J &= -kT \ln K + 2kT \ln \tfrac{1000}{46} \\ &= 0.059(6.2 + 2.67) \\ &= 0.52 \text{ electron-volt} \end{aligned}$$

This value, which is only about half as large as the corresponding quantity for water or methanol, has been used in constructing Fig. 65 for the proton levels in formic acid.

Furthermore, since in Sec. 121 we found the value $J = 0.36$ electron-volt for the proton transfer (211), this gives the occupied proton level of the $(HCOOH_2)^+$ ion a position at $(0.52 - 0.36) = 0.16$ electron-volt above that of the $(H_3O)^+$ ion in formic acid as solvent. This is shown in Fig. 65, where, for comparison, a diagram for proton levels in aqueous solution has been included, the level of the $(H_3O)^+$ ion in aqueous solution being drawn opposite to the level of the same ion in formic acid solution. This choice is quite arbitrary, but was made in order to show more clearly that we may expect that one or more acids that are strong

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[1] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 4244 (1932).

acids in aqueous solution will be incompletely dissociated in formic acid solution.

In the dilute solution of an acid that is a strong acid, in any solvent the transfer of the proton leaves a vacant proton level in the anion. As mentioned in Sec. 69, we should like to know, for each acid, the energy of this vacant level, for inclusion in Fig. 36; for there may be a wide difference in this respect, between the familiar strong acids HCl, H_2SO_4, $HClO_4$, and so on. But no method of obtaining direct information on this question has been widely accepted as reliable. If we adopt the point of view that the binding energy of the proton in any neutral molecule is very nearly independent of the solvent in which it is dissolved, it should be possible to arrange the strong acids in an order of strength that would be the same in all solvents, except insofar as the order is upset by the considerations of Sec. 99. From a study of acids in nonaqueous solvents, the following order—of increasing strength—has been adopted:[1] nitric, hydrochloric, benzene-sulfonic, sulfuric, perchloric.

Although benzene-sulfonic acid, $C_6H_5SO_3H$, is a strong acid in aqueous solution, it is not completely dissociated in formic acid solution. In a 0.1-molal solution the degree of dissociation was estimated at 60 per cent.[2] This is comparable with the dissociation of HIO_3 in aqueous solution and is compatible with $J = 0.14$ electron-volt for the formation of $(HCOOH_2)^+$. Using this value the level has been included in Fig. 65.

It is found that HCl is likewise incompletely dissociated in formic acid solution. There do not appear to be any accurate data on the degree of dissociation; so we do not know whether it is necessary to place the proton level of HCl below that of $(H_3O)^+$ in formic acid solution.

124. The Urea Molecule. In Fig. 40 the vacant level of the CON_2H_4 molecule lies 0.085 electron-volt below the vacant level of the H_2O molecule. If, when dissolved in formic acid, the vacant level of CON_2H_4 lies in a similar position relative to the vacant level of the H_2O molecule in this solvent, it is clear that the tendency for protons to be transferred from the solvent, according to

$$CON_2H_4 + HCOOH \rightarrow (CON_2H_5)^+ + (HCOO)^- \qquad (213)$$

will be much greater than for the corresponding process (146) in water; this is found to be the case.[3]

125. Sulfuric Acid and Liquid Ammonia as Solvents. The proton transfer that takes place in pure sulfuric acid is believed to be

$$H_2SO_4 + H_2SO_4 \rightarrow (HSO_4)^- + (H_3SO_4)^+ \qquad (214)$$

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[1] L. P. Hammett, "Physical Organic Chemistry," p. 261, McGraw-Hill, 1940.

[2] Hammett and Deyrup, *loc. cit.*

[3] L. P. Hammett and N. Dietz, *J. Am. Chem. Soc.*, **52**, 4806 (1930).

In Table 38 the autoprotolysis constant of sulfuric acid is given by $-\log K = 3.1$, from which we calculate

$$\begin{aligned} J &= -kT \ln K + 2kT \ln \tfrac{1000}{98} \\ &= 0.059(3.1 + 2.02) = 0.30 \text{ electron-volt} \end{aligned}$$

This represents an interval narrower than that of any of the other solvents included in Table 38.

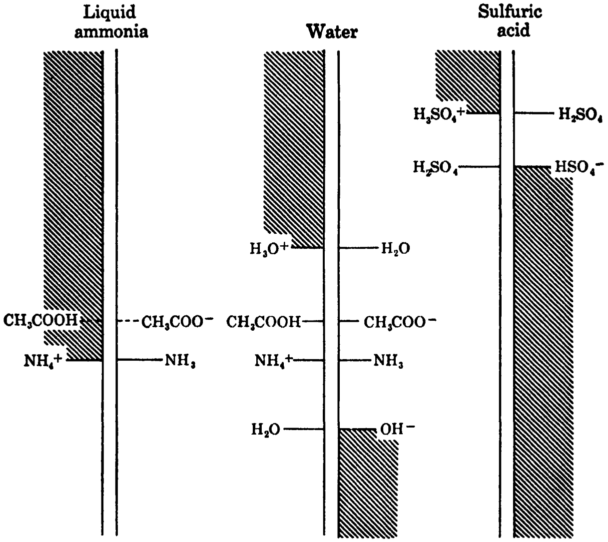

FIG. 66

On the other hand, for liquid ammonia at −33°C, we find a value of J greater than that of all the other solvents. A tentative scheme for the proton levels in these two solvents is sketched in Fig. 66, in comparison with the scheme of levels in water.

If the occupied proton level of the CH_3COOH molecule dissolved in liquid ammonia lies above the vacant level of NH_3, as it does in aqueous solution, acetic acid should be a strong acid in liquid ammonia. This is found to be the case; the carboxylic acids are strong acids in this solvent, the protons being transferred to NH_3 to form $(NH_4)^+$.

CHAPTER 15

Proton Transfers in More Concentrated Solutions. Measurements with Indicators. The Proton Levels of Indicator Molecules in Dilute Solution. Indicators in More Concentrated Solutions.

126. Proton Transfers in More Concentrated Solutions. In discussing ions in solution, one of our major interests has been the ionic environment and the problem of disentangling characteristic and intrinsic ionic properties from the effects that result from a change of environment. We have discussed the change of temperature, and more than once we have examined the effect of changing from one solvent to another. In this chapter we shall consider a change of environment of another kind.

In a very dilute solution the number of solvent dipoles per unit volume is nearly the same as in pure solvent. On the other hand, if we go to more concentrated solutions, this is no longer so, and we must say that the environment of any ion suffers a progressive change. In this chapter we shall describe experiments that have been made on proton transfers at high concentrations. In each case, our purpose will be to distinguish, as far as possible, between the binding energy of the proton (a quantity that depends on the quantization of the molecule or molecular ion containing the proton) and the energies that depend on the environment. This will certainly be much more difficult than in dilute solutions; so we shall prefer to discuss the type of proton transfers that are least sensitive to a change of environment. Now from Chapter 7 we know that the proton transfers that are least sensitive to the environment are those of class I, where one species of positive ion is merely replaced by another, or where one species of negative ion is merely replaced by another.

There are, in fact, two reasons why we should prefer to discuss proton transfers of class I. In concentrated solutions the average electrostatic forces between the ions will be intense. Only in proton transfers of class I does the number of positive and negative charges in the solution remain unaltered when the proton is transferred; only here do we find the possibility that the contribution from the interionic forces will remain almost unchanged in a proton transfer. At the same time, although the number of solvent dipoles per cubic centimeter is smaller in a concentrated solution than in pure solvent, we may expect that this will be relatively unimportant in proton transfers of class I.

In Chapter 4 we saw that in the common solvents the permanent dipole moment of each molecule is due to the presence of one or more protons within the electron cloud. It was pointed out that, if we consider any acid in liquid form (such as $HClO_4$ or H_2SO_4), each molecule necessarily contains a proton; as a result, these are polar liquids, and when an electrolyte is dissolved in one of these liquids, an ionic solution is formed. From this point of view, a mixture of one of these acids in water is a mixture of two solvents. If we were to mix 1 mole of H_2SO_4, for example, with 1 mole of water, we might be inclined to regard the resulting ionic solution as a concentrated solution of H_2SO_4 in water; but when we mix a smaller quantity of water with a larger quantity of H_2SO_4, this point of view becomes somewhat strained. As described below, proton transfers have been studied over the whole range of composition from dilute aqueous solutions of H_2SO_4 up to 100 per cent H_2SO_4.[1] These measurements, and the others described in this chapter, were made by the spectrophotometric method, which has already been mentioned in Secs. 74 and 80.

In Chapter 7 we found it convenient to distinguish between proton transfers involving a solvent molecule and those involving only solute particles; but this difference will lose its significance when the distinction between solvent and solute begins to break down. We recall that in Sec. 54 the mole fraction of the solvent did not differ appreciably from unity and could be omitted from (72). In investigating concentrated solutions, however, there is no question of extrapolating to infinite dilution; the mole fraction of the solvent will differ from unity and will have to be retained in all formulas. At the same time each of the mole fractions will need to be multiplied by its activity coefficient.

127. Measurements with Indicators. The proton transfers studied were of the type

$$(H_3O)^+ + B \rightarrow H_2O + (BH)^+ \qquad (215)$$

where B is a solute molecule at a very low concentration, chosen because either B itself or $(BH)^+$ has an intense absorption band in the visible spectrum—in other words, is an "indicator." In order to use the expressions of Chapter 7 as a starting point, let us begin by such a proton transfer in the dilute aqueous solution of a strong acid. If [B], $[BH^+]$, $[H_3O^+]$, and $[H_2O]$ denote the mole fractions of the four species in (215), the expression (132) may be written in the form

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[1] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

$$\frac{[BH^+]}{[B]} = \frac{[H_3O^+]}{[H_2O]} e^{-J/kt} \tag{216}$$

A measurement of the optical absorption of the solution at a suitable wavelength tells us how much of the solute B has been converted to $(BH)^+$ and how much remains in the neutral form B. This measurement gives accurate results over a certain range of concentration of acid. This range includes the concentration that makes $(BH)^+$ equal to B, and extends unequally on either side. The reason for this asymmetry may be understood as follows. Suppose that it is the ion $(BH)^+$ that is responsible for the absorption spectrum, and consider a concentration of acid to make $[BH^+]/[B]$ equal to 9; that is to say, 90 per cent in the form $(BH)^+$ and 10 per cent remaining in the form B. Now, no matter how much the acidity of the solution is increased, one cannot obtain more than 100 per cent in the form $(BH)^+$; consequently, in this range of concentration the method becomes very insensitive. On the other hand, when we go to lower concentrations of acid, the method becomes insensitive only when the total absorption of the solution falls too low for accurate measurement. A similar limitation applies, *mutatis mutandis*, to the case where it is the form B that is responsible for the absorption spectrum. A list of the solutes used is given in Table 39. The pattern of the experiments to be described depends on the fact that each of these indicators can be used only over that range of acidity to which it is appropriate, this range being determined by the energy of the vacant proton level in the B molecule, relative to the occupied level of the $(H_3O)^+$ ion.

128. The Proton Levels of Indicator Molecules in Dilute Solution. Let us now ask where the vacant proton level must lie, in order that an indicator molecule shall be suitable for use in a very dilute acid solution —where the ratio $[H_3O^+]/[H_2O]$ will be very small compared with unity. According to (216) in order that $[BH^+]/[B]$ shall be near unity, obviously J must have a large negative value; in other words, the vacant proton level of the molecule B must lie considerably below the occupied proton level of $(H_3O)^+$; otherwise, an insufficient crop of $(BH)^+$ ions will be obtained.

As an example, take the molecule aminoazobenzene, one of the solutes listed in Table 39. When colorimetric measurements were made at room temperature on very dilute aqueous solutions of HCl, containing a trace of this substance, it was found that neutral molecules and $(BH)^+$ ions were present in *equal* numbers when the concentration of the HCl was 0.0016 molal.[1] At this low concentration the activity coefficient of the HCl is very near unity, and we may use (216) to find how far the vacant proton level provided by the aminoazobenzene molecule in aque-

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[1] L. P. Hammett and M. A. Paul, *J. Am. Chem. Soc.*, **56**, 827 (1934).

ous solution lies below the occupied proton level of the $(H_3O)^+$ ion. Setting the left-hand side of (216) equal to unity, and taking the logarithm, we obtain

$$\ln (1.0) = 0 = \ln \frac{[H_3O^+]}{[H_2O]^-} - \frac{J}{kT} \tag{217}$$

whence

$$\begin{aligned} J &= kT \ln \frac{0.0016}{55.5} \\ &= -10.4kT \\ &= -0.268 \text{ electron-volt} \end{aligned}$$

The vacant proton level lies 0.268 electron-volt below the occupied level of $(H_3O)^+$. Referring to Table 12 we see that this level lies at about the same depth as the vacant level of the chloraniline molecule.

Consider now two solute species B_1 and B_3, between which no direct experimental comparison by the colorimetric method is possible, because their useful concentration ranges just fail to overlap. We can find an intermediate indicator solute B_2, whose useful range partly overlaps that of B_1 and partly overlaps that of B_3. Using B_2, a relation between B_1 and B_3 may thus be established indirectly. In dilute solution this relation will be a simple one. We do not know enough about concentrated solutions to be in a position to say whether a similar relation should be expected. In the experiments to be described, the first aim was to obtain an answer to this question.

For the proton transfer from $(H_3O)^+$ to B_1 let the J value be denoted by J_1; and likewise in a solution containing B_2, let the value be J_2. If the ratio $[H_3O^+]/[H_2O]$ is denoted by y_{H^+}, we obtain from (216),

$$kT \ln \frac{[B_1H^+]}{[B_1]} = kT \ln y_{H^+} - J_1 \tag{218}$$

$$kT \ln \frac{[B_2H^+]}{[B_2]} = kT \ln y_{H^+} - J_2 \tag{219}$$

If, having in mind two dilute solutions containing the same concentration of hydrogen ions, we subtract (219) from (218), the value of the right-hand side is clearly just $(J_2 - J_1)$, which is equal to the difference between the binding energies of the additional proton added to the molecules B_2 and B_1.

It will be recalled that in the equation (216), from which this result has been derived, the disparity between the cratic term and the complete communal term had been neglected, and only the cratic term included. The question then arises as to the degree of applicability of the result to solutions whose concentrations are more than ten times greater than that to which (217) referred.

It was pointed out in Sec. 126 that in any proton transfer of class I the number of negative ions remains unchanged and the number of positive ions remains unchanged; and consequently there is the possibility that the contribution from the interionic forces shall remain unchanged. Whether this is so or not can be decided only by experiment. Consider what result should be obtained if (218) and (219) are applicable. In this case, if experimental values of the left-hand side of (218) are plotted against $\ln y_{H^+}$ the points should lie on a straight line, whose slope is kT; and if experimental values of the left-hand side of (219), obtained at the same temperature T, are likewise plotted against $\ln y_{H^+}$, a parallel straight line should be obtained, displaced by the amount $(J_2 - J_1)$. That such parallel straight lines are obtained is shown in Fig. 67.

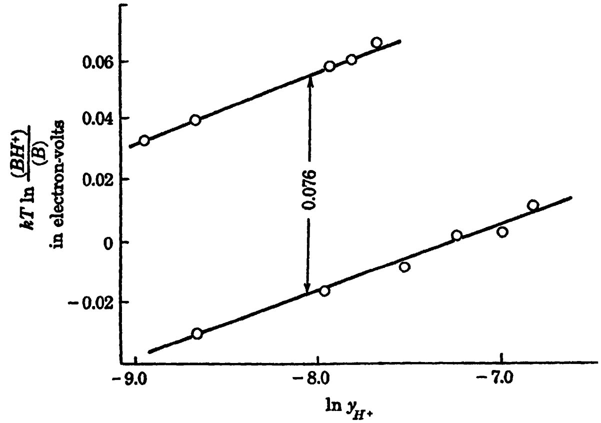

FIG. 67. Experimental results at 25°C for indicators 1 and 2 in Table 39.

The indicators numbered 1 and 2 at the bottom of Table 39 both have vacant proton levels low enough for use in dilute solution; the circles in Fig. 67 give the experimental results obtained in aqueous solutions of HCl. In each case the slope of the line does not differ from the theoretical slope of (218) by as much as 5 per cent. Reading off the constant vertical distance between the two curves (the length of the vertical arrow in Fig. 67), we find

$$(J_2 - J_1) = 0.076 \text{ electron-volt}$$

In Table 39 this value is recorded at the bottom of column 3. We have already found above that J_1 is equal to -0.268 electron-volt. We find then $J_2 = (-0.268 + 0.076) = -0.192$. This is the amount by which the vacant proton level lies below the occupied proton level of the $(H_3O)^+$ ion; the value is included in column 2 of Table 39.

TABLE 39

No.		Electron-volts	
17	2,4,6-Trinitroaniline	+0.447	
			0.063
16	Anthroquinone	+0.384	
			0.097
15	6-Brom-2,4-dinitroaniline	+0.287	
			0.023
14	*p*-Benzoyldiphenyl	+0.264	
			0.016
13	*α*-Benzoylnaphthalene	+0.248	
			0.019
12	Benzalacetophenone	+0.229	
			0.054
11	*N*,*N*-Dimethyl-2,4,6-trinitroaniline	+0.175	
			0.018
10	2,4-Dinitroaniline	+0.157	
			0.004
9	2,6-Dinitro-4-methylaniline	+0.153	
			0.057
8	*p*-Nitroazobenzene	+0.096	
			0.008
7	2,4-Dichlor-6-nitroaniline	+0.088	
			0.050
6	*p*-Nitrodiphenylamine	+0.038	
	H_2O.	0.0	0.090
5	*p*-Chlor-*o*-nitroaniline	−0.052	
			0.044
4	*o*-Nitroaniline	−0.096	
			0.071
3	*p*-Nitroaniline	−0.167	
			0.025
2	Benzene-azodiphenylamine	−0.192	
			0.076
1	Aminoazobenzene	−0.268	

129. Indicators in More Concentrated Solutions. The five acids that have been investigated are HCl, $HClO_4$, H_2SO_4, HNO_3, and HCOOH. When we go to more concentrated solutions, there are three questions to be asked: (1) When the behavior begins to deviate from (219) characteristic of dilute solution, what is the character of this deviation? (2) To what extent does this deviation depend on the particular acid that is being used to provide the protons? (3) When two indicators are studied over the same range of acid concentration, is their behavior similar, apart from the difference in the binding energy of the proton which we expect to be predominant?

When two indicators are studied at high concentration, we cannot expect to obtain two parallel straight lines, like those of Fig. 67. If, however, a curve is obtained for one indicator, we may hope that the experimental points for the other indicator will lie on a curve which is the same except that it is displaced vertically with respect to the other by an amount equal to $(J_m - J_n)$, the difference between the binding energies. Some experimental results are shown in Fig. 68 where the scale of ordinates is again in electron-volts, and the small circles show the experimental results for the substances numbered 4 and 5 near the bottom of Table 39. The range of concentrations of the aqueous solutions of HCl, covered by the abscissa, runs from 1 to 6 molal. It will be seen that the upper curve is merely the lower curve displaced upward by a certain amount, which in this case is equivalent to 0.044 electron-volt. This value is recorded in the last column of Table 39. The broken line in Fig. 68 reproduces from Fig. 67 the slope of the straight lines found in dilute solutions of HCl for the substances numbered 1 and 2 in Table 39. It will be seen that the slope of the curves is considerably steeper, indicating that, to produce a given additional transfer of protons from the $(H_3O)^+$ ions, a smaller increment in acid concentration is needed than in the more dilute solutions. This means that, in the continually changing environment, the occupied proton level of the $(H_3O)^+$ ion is

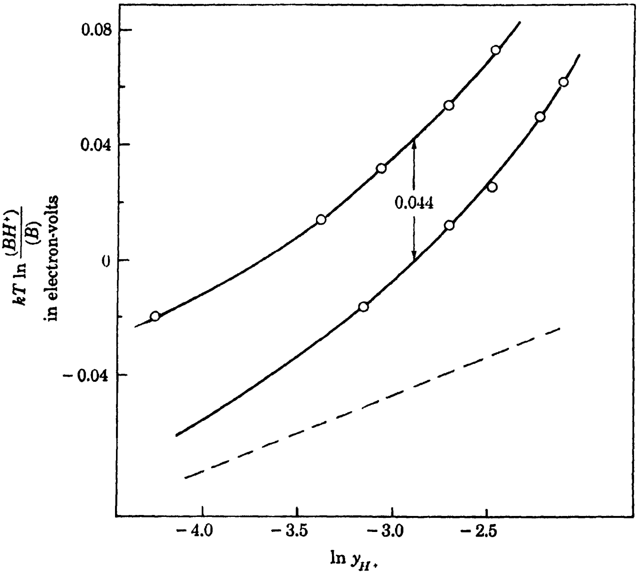

FIG. 68. Experimental results at 25°C for indicators 4 and 5 in Table 39.

being progressively raised relative to the vacant level of B, or the occupied level of $(BH)^+$.

Similar pairs of curves were obtained for indicators 4 and 5 in aqueous solutions of HNO_3, H_2SO_4, and $HClO_4$. In solutions of HNO_3 the curves were slightly less steep, but the vertical displacement between the two curves was nearly the same, being 0.045 electron-volt in HNO_3 solutions, and likewise 0.043 electron-volt in H_2SO_4 and $HClO_4$ solutions, as compared with 0.044 in the HCl solutions. In these solutions, at any rate, the binding energies of the protons appear to differ by the same amount within a few per cent.

In Sec. 128 it was found that the vacant proton level of indicator 2 lies at 0.192 electron-volt below the occupied level of $(H_3O)^+$ in dilute aqueous solution. Using the successive increments listed in the last column of Table 39, we find, counting upward, that the value for indicator 5 is -0.052, referred to the same zero of energy. Proceeding by the same stepwise method to No. 6 we find for the energy of the vacant proton level the positive value $+0.038$. This still refers to the occupied level of the $(H_3O)^+$ ion in dilute aqueous solution. It means that work equal to 0.038 electron-volt would be required to transfer a proton from the $(H_3O)^+$ ion in very dilute solution to the vacant level of No. 6 in the concentrated acid solution in which the measurements were made. A further amount of work would be required to transfer the proton from the occupied level of No. 6 to the vacant proton level of one of the H_2O molecules in the same concentrated solution. This is the situation because, as mentioned above, the changing environment has raised the proton level of the $(H_3O)^+$ ion relative to that of each of the indicator molecules.

With still further increase in concentration this process continues. In addition, we may mention that, although in the solutions discussed the H_2O molecules outnumber the $(H_3O)^+$ ions nearly ten to one, in the still more concentrated solutions the H_2O molecules become more and more sparse. For indicators 6 to 17 the same stepwise procedure was followed in mixtures of H_2SO_4 and water and yielded progressively higher proton levels. With the last indicator, No. 17, measurements were made in mixtures containing from 96 to 100 per cent of H_2SO_4. In the 100 per cent H_2SO_4 the proton transfer presumably was

$$H_2SO_4 + B \rightarrow (HSO_4)^- + (BH)^+$$

As shown in Table 39, by the successive increments, the value $+0.448$ was obtained for the position of the vacant proton level of this indicator.

Using these indicators, Hammett was able to define a scale of acidity over the whole range from dilute aqueous solution to 100 per cent H_2SO_4.[1]

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, 1940.

CHAPTER 16

The Orientation of Water Molecules Adjacent to an Ion. Order and Disorder in the Vicinity of Solute Particles. Coulomb Attraction and Repulsion between Ions. Activity Coefficients. The Distance of Closest Approach. Activity Coefficients of Various Solutes. Forces Superimposed on the Coulomb Forces.

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130. The Orientation of Water Molecules Adjacent to an Ion. Figure 19 shows an isolated group consisting of four tetrahedra ranged round a central tetrahedron. We notice that two of the four outer tetrahedra have a positively charged corner directed inward, while each of the other two has a negatively charged corner directed inward. This arrangement is one of low potential energy. Now let us suppose that we remove the central tetrahedron and replace it by a spherical conductor bearing a rather large electric charge (either positive or negative). If we suppose that we do this without disturbing the orientations of the other four tetrahedra, it is clear that a state of lower potential energy can be reached if each tetrahedron is free to rotate about its center. If the charge on the central sphere is positive, those two tetrahedra that already have their negative corners pointed toward it are well placed; but each of the other two will, with advantage, turn so as to point likewise a negative corner inward. Conversely, if the central sphere bears a negative charge the two tetrahedra that have a negative corner pointing inward will turn until all four have a positive corner pointing toward the sphere. We have been discussing an isolated group representing an isolated group of five water molecules; let us now go on to consider a similar group of water molecules that forms part of a larger ordered group.

In Chapter 3, in discussing water near its freezing point, we took the point of view that at any moment the liquid contains many groups of molecules that have a local order similar to that of ice. In Fig. 20 the molecules numbered 2, 3, 4, 5 are nearest neighbors of molecule 1, while molecules 6, 7, 8 are neighbors of 5, and consequently are next-nearest neighbors of 1. To be definite, let us identify the molecules 2, 3, 4, 5 with the outer tetrahedra of Fig. 19, and let us suppose that the protons of these molecules point in the directions indicated in Fig. 19--that is to say, molecules 4 and 5 have a proton pointing toward 1.

We may now emphasize the mutual control that is exercised between adjacent water molecules. The orientation of molecule 5, for example, is controlled by the orientations of 1, 6, 7, and 8; and we may say that, in turn, molecule 5 does its share in controlling the orientations of 1, 6, 7, and 8. We may add that, throughout the liquid, near its freezing point, any local ordered arrangement arising from this kind of mutual control is not easily upset by the thermal agitation present in the liquid.

Suppose now that we remove molecule 1 and replace it by an ion of roughly the same size (either positive or negative), doing this without disturbing any of the molecules in the vicinity; we mean that molecules numbered 6, 7, and 8, for example, still exercise the same degree of control over 5 as they did before. Only the interaction between 5 and 1 has now been replaced by the interaction between a water molecule and an ion. We have not yet decided what is the magnitude of the charge borne by the ion. In order to consider the possible interactions, it will be convenient here to discuss an imaginary experiment, in which the charge on this ion is made to vary continuously from a value near zero to a value greater than $+2e$. The purpose of this is as follows: so long as the charge on the ion is very small, the control that it exerts on any neighbor will certainly be smaller than the control exerted on this molecule by the other molecules that are in contact with it; the control exerted on 5, for example, by the ion will be less than that exerted on 5 by molecules 6, 7, and 8. Similarly, we can say that the control exerted by the ion on 2 will certainly be smaller than the control exerted on 2 by its neighbors acting together; and we can make the same remark with regard to the control exerted by the ion on 3 and 4. Considering the potential energy of the whole group, this means that the lowest potential energy is still possessed by the arrangement where two of the ion's nearest neighbors (2, 3, 4, and 5) have a proton pointing toward it, and the other two do not.

We can say that this certainly will be so, only because we are imagining that the (positive or negative) charge on the ion is small—that is, small compared with an electronic charge. Consider, however, what happens when we imagine the magnitude of the charge increases steadily toward the value $\pm 2e$. Sooner or later, these directions for the H_2O molecules will cease to be the preferred directions; sooner or later the situation will be reversed, and the state of lowest potential energy will be where each of the four water molecules in contact with the ion has a proton pointing toward it, if the ionic charge is negative; and vice versa, if it is positive. Before the preferred directions can have become reversed in this way, the (continuously increasing) ionic charge must have passed through a *critical* value for which there is no preferred direction for an adjacent molecule. Consider once more molecule 5, supposing that 6, 7, and 8 have not been disturbed; there must be a critical value of the ionic charge such that the potential energy of 5 has the same value, whether a proton remains pointing toward the ion or not.

The possible importance of such a situation is seen, if we consider the thermal agitation; for we may imagine that, when there is no longer a preferred direction for 4 and 5, the thermal agitation is likely to break up the whole local structure. This tentative argument, though crude in some respects, suggests one way in which an ionic charge could produce local disorder, and an increase in entropy.

The question immediately arises: what is the magnitude of this critical charge? We must answer that the value depends on the radius of the ion, for we are primarily concerned with the intensity of the ionic field to which the adjacent solvent molecules are subject. Above, where we proposed the removal of a water molecule and the substitution of an ion, we suggested an ion having roughly the same radius as a water molecule. For an ion of this size the magnitude of the critical charge appears to be *a little less than that of the electronic charge e itself;* for the ions Cs^+ and Br^- seem to be typical disorder-producing ions; they bear charges $+e$ and $-e$, and their radii are larger than that of a water molecule. The small ions Li^+ and Na^+ seem to be order-producing ions; we may suppose that in both cases the intensity of the ionic field is so great that the ion is able to set up and maintain an arrangement of local order somewhat more stable than that of pure water.

131. Order and Disorder in the Vicinity of Solute Particles. Returning to the question of order-disorder in the vicinity of a solute particle, we may now discuss another aspect of the problem. In Fig. 69*a* let each of the small circles represent a solute particle, and let each of the shaded areas represent that adjacent spherical portion of solvent where the degree of order differs from that of the pure solvent. Let us first suppose that both solute particles are of the same species; in the solvent surrounding each solute particle there has been a certain change in the free energy; when the solvent contains only the two distant solute particles, the value of the total change in the free energy is twice that for a single solute particle. This is true so long as the distance between the two solute particles is great. Let Fig. 69*b* depict the situation when the same solute particles are near together. If each particle is a disorder-producing particle, the pair of particles will now be surrounded by a common portion of disordered solvent.

Assuming for the moment that the solute particles are not electrically charged, we must now ask the question: Is it likely that the free energy of the whole system has the same value as it had when the solute particles were widely separated? The value of the free energy of the system may be lower, or it may be higher. If the free energy is lower when the particles are nearer together, this is equivalent to saying that these solute particles attract one another. If for another solute species the free energy is greater when the particles are nearer to each other, this is equivalent to saying that these particles repel one another. In the same way, instead of considering two solute particles of the same species, we may recognize the possibility of forces of attraction and repulsion between unlike particles, arising from the degree of order in the solvent adjacent to each.

We have considered electrically neutral particles only as a preparation for a discussion of ions. Here the above considerations must be examined in relation to the Coulomb forces. In Sec. 15 we discussed the amount of work required to increase the separation of a pair of ions from r to $(r + \delta r)$. In a vacuum, for charges $\pm e$ this would amount to $(e^2/r^2)\ \delta r$. But in water with $\epsilon = 80$ the amount of work would be just $\frac{1}{80}$ of this, because the free energy lost by the solvent during the process accounts for the remaining $\frac{79}{80}$. If this free energy loss is to be exactly $\frac{79}{80}$, it is clear that the behavior of the solvent dipoles in the ionic field must follow strictly the regime demanded by the electrostatic theory. In view of the various degrees of disorder in the co-spheres of different species of ions, we must ask the question: have we any right to expect Coulomb's law to be obeyed, except for large values of r? If the solute particles in Fig. 69 are electrically charged, it is clear how the argument must run. If the free energy associated with the order-disorder situation of Fig. 69b is greater when the particles are near together than when they are widely separated, a rather short-range repulsion will be superimposed on the usual Coulomb attraction or repulsion, as the case may be. In the converse case a rather short-range attraction will be superimposed on the usual Coulomb forces.

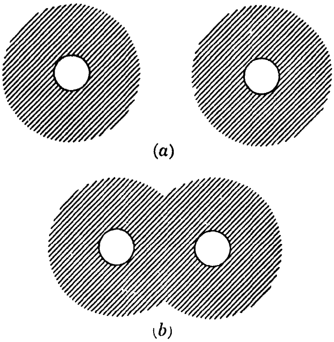

FIG. 69

In Fig. 69 we have been considering a pair of solute particles in pure solvent. We shall postpone further discussion of this question until later. In the meantime we shall review the Coulomb forces in very dilute ionic solutions as they are treated in the Debye-Hückel theory.

132. Coulomb Attraction and Repulsion between Ions. Consider the random Brownian motion of the positive and negative ions in any dilute solution. There is a tendency for ions of like sign to avoid one another owing to their mutual repulsion, while there is a converse tendency for ions of unlike sign, owing to their mutual attraction. We may make use of this fact in considering an aqueous solution of KCl, or any similar solution that contains exactly n singly charged positive ions of a certain species, and exactly n singly charged negative ions of a certain species. In this dilute solution let us fix our attention on one particular positive ion. The remainder of the solution contains $(n - 1)$ similar positive ions, and n negative ions. Thus the solution which surrounds the chosen positive ion bears an equal negative charge, because the $(n - 1)$ positive ions fail to neutralize the charge of the n negative ions. We wish to inquire how, on the average, this negative charge is distributed. We may say that the distribution would, on the average, be quite uniform, if it were not for the fact, mentioned above, that any positive ions which, in their Brownian motion, approach a positive ion, tend to avoid it, while any negative ions that approach a positive ion are, to some extent, attracted toward it.

Returning to the positive ion on which we have chosen to fix our attention, we may say that the solvent in the vicinity contains, on the average, rather more negative ions than positive; in other words, it contains on the average, a certain density of negative charge. This enables us to answer the question as to the distribution of the charge that is present in the solution because the $(n - 1)$ positive ions fail to neutralize the n negative ions. Nearly the whole of this compensating charge will be found within a rather small sphere surrounding the chosen ion. We may describe this by saying that the positive ion is surrounded by a cloud of negative charge, just as we say that in a hydrogen atom the proton is surrounded by an electronic cloud; in the solution, however, the negative charge will usually be spread through a much larger sphere. In neither case does the cloud of negative charge have a definite boundary, but the charge density falls off exponentially with distance from the center. In both cases the density must be such that integration leads to $-e$ as the value of the total charge. In this respect, however, there is one important difference; in the hydrogen atom the integration is taken from zero to infinity, whereas in solution the integration will be taken from a to infinity, where a is the "distance of closest approach" of the positive and negative ionic charges, which will be discussed later.

We may add now that, if initially we fix attention on a particular negative ion in this solution, we shall have the exact converse of the above. Each negative ion in the solution will be surrounded, on the average, by a cloud of positive charge decreasing exponentially with distance from the center in such a way that the total positive charge is $+e$.

We may recall that in the NaCl crystal structure each positive ion is surrounded by six negative ions, while each negative ion is surrounded by six positives; as a result the crystal can be broken up into its component ions only if work is done equal to the crystal energy. In a dilute solution we find a tendency toward a somewhat similar situation: each positive ion is surrounded by a cloud of negative charge, while at the same time each negative ion is surrounded by a cloud of positive charge; as a result, for the n ion pairs in the solution there is a quantity analogous to the lattice energy of a crystal. The cloud of negative charge surrounding each positive ion and the cloud of positive charge surrounding each positive ion are the well-known ionic atmospheres of the Debye-Hückel theory, from which the disparity and the activity coefficients of very dilute solutions may be calculated.

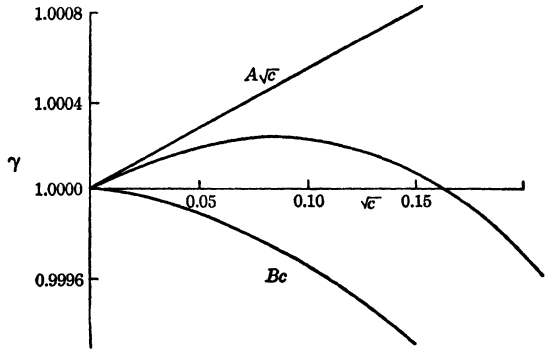

FIG. 70. Activity coefficient of lithium bromide in aqueous solution at 25°C.

133. Activity Coefficients. Turning now to the experimental data on activity coefficients, Fig. 70 shows the results for lithium bromide in aqueous solution at 25°C, plotted against the square root of the concentration.

If the set of experimental points plotted in Fig. 70 is compared with that of Fig. 51, it will be seen that the situation is very similar. Nor is this close resemblance accidental. It will be recalled that in equation (161) the term Bc represents the type of term that would be characteristic of a solute of any kind, and that the situation in Fig. 51 arises from the superposition, on this term, of another term arising from the ionic character of the solute. When the interionic effects had been eliminated, ourin terest turned, in Chapter 9, to a discussion of the B-coefficients characteristic of the various pairs of ions. In Fig. 70 we encounter a situation of the same kind arising from the superposition of interionic contribution upon the term Bc, where B is the activity B-coefficient characteristic of the solute. As in Fig. 51, the interionic effects are predominant at low concentrations; and for each solute the value of the B-coefficient will be derived from the experimental data by subtraction of the interionic term. For lithium bromide in aqueous solution at 25° the value of B is 0.130 (see Table 40).

134. The Distance of Closest Approach. According to quantum mechanics, when the electronic shells of two atoms or ions come into contact, their overlapping gives rise (as in Fig. 11) to an intense mutual repulsion, which varies exponentially with the distance. In any ionic crystal there must be a balance between the repulsive forces and the attractive forces that hold the ions together in the crystal. The value of the lattice spacing between the ions is determined by this balance. This is shown in Fig. 71 where the curves represent the potential energy as a function of the interionic distance. Curve a represents the potential energy of the attractive forces, while the exponential curve b represents the potential energy of the quantum mechanical repulsion. In each of the alkali halides the repulsive exponential curve is taken to be one that falls to half value in a distance of 0.24 angstrom.[1] On adding the ordinates of the two curves, we obtain curve c with a sharp minimum for a certain interionic distance. The position of this minimum gives the lattice spacing that will be adopted by the crystal. For every crystal of the NaCl type the attractive energy amounts to $-1.747e^2/r$ per ion pair, 1.747 being the Madelung constant for any crystal of this type.

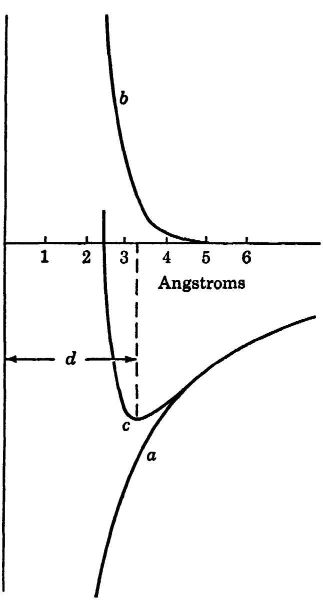

FIG. 71

Let us now consider a pair of ions in aqueous solution from such a crystal. In the Debye-Hückel theory it is assumed that in pure solvent, the mutual potential energy is $-e^2/\epsilon r$, where ϵ is the macroscopic dielectric constant of the solvent,[2] until the ions come into contact with each

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[1] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932); see also N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," p. 6, Cambridge, 1940.

[2] For Coulomb forces see also Note 3 of the Appendix.

other. In water at room temperature, we have then $-e^2/76r$, instead of $-1.747e^2/r$; that is to say, at every point the slope of the curve corresponding to curve *a* will be 132 times smaller.

Returning to Fig. 71, we can say that in the crystal the minimum occurs, of course, at the point where the slope of curve *b* is exactly equal and opposite to the slope of curve *a*. To find the "distance of closest approach" for the same pair of ions in aqueous solution, we have to make a similar construction. We may take the quantum-mechanical forces of repulsion to be independent, or almost independent, of the environment; and the following treatment will be sufficiently accurate for our purpose. Since in the NaCl crystal structure each ion has six ions of opposite sign in contact with it, the repulsive energy per ion pair in Fig. 71 receives contributions from six adjacent pairs. When we are dealing with an isolated ion pair, the ordinates of curve *b* in Fig. 71 must be divided by 6, while the ordinates of curve *a*, as we have seen, will be divided by 132. In aqueous solution the very weak attractive force will be unable to bring the ionic nuclei as close together as in the crystal. We see now how the required potential minimum will be related to the position of the potential minimum in Fig. 71: we have to look for the point on curve *b* where the slope is $\frac{132}{6}$ times less steep than before—that is to say, 22 times less steep. Since the slope of the exponential curve, as mentioned above, falls to half value in 0.24 angstrom, it will fall to $\frac{1}{16}$ of its value in four times this distance, that is, in 0.96 angstrom, and will fall to $\frac{1}{22}$ of its value in a little more than 1 angstrom.

In applying the Debye-Hückel theory to alkali halides in aqueous solution, we ought to expect that the use of the quantity $-e^2/\epsilon r$ for ions of opposite sign will necessarily be accompanied by a "distance of closest approach" that is in each case about 1 angstrom greater than in the corresponding crystal lattice. This fact seems to have escaped notice, and an additional assumption has been thought necessary to account for the observed fact that agreement between theory and experiment is obtained with a distance of closest approach that is, in most cases, greater than the crystal-lattice spacing; for example, "The formation of a sheath of water molecules around the ion will result in high values of *a*, compared with crystallographic radii."[1]

Values of the "distance of closest approach" derived from experimental values of the activity coefficients are given in column 2 of Table 40. It will be seen that for the lithium and sodium salts the value is greater than the crystal-lattice spacing (given in column 4) by rather more than 1 angstrom, as is expected. For the salts of cesium, rubidium, and potassium, on the other hand, the distance of closest approach

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[1] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," p. 385, Reinhold, 1943.

is too small; for the cesium salts it is even smaller than the lattice spacing in the crystal. The reason for this will be discussed in Sec. 136.

TABLE 40. ACTIVITY COEFFICIENTS IN WATER AT 25°[a]

Solute	*a*	*B*	Lattice spacing
LiI	5.05	0.165	3.00
LiBr	4.3	0.130	2.74
LiCl	4.25	0.121	2.57
NaI	4.2	0.100	3.23
NaBr	4.1	0.0687	2.97
NaCl	4.0	0.0521	2.81
KI ..	3.94	0.0462	3.53
KBr	3.84	0.0282	3.29
KCl.	3.8	0.0202	3.14
RbCl	3.6	0.010	3.29
RbBr	3.55	0.010	3.43
RbI	3.5	0.0085	3.66
CsCl	3.0	0.0	3.46
CsBr	2.93	0.0	3.61
CsI	2.87	0.0	3.85
	2.50	0.014	

[a] R. A. Robinson and H. S. Harned, *Chem. Rev.*, 28, 452 (1941).

135. Activity Coefficients of Various Solutes. When curves like that of Fig. 70 are drawn for the various uni-univalent solutes, the situation is, in one respect, simpler than in Fig. 51, and in another respect, more complicated. If in Fig. 51 we consider the slope of the curve, as the concentration of the solute tends to zero, this slope is given by the value of the coefficient A, which is different from each solute, as shown in Table 19. In plotting the logarithm of an activity coefficient, however, the limiting slope of the curve in any solvent at a given temperature has, as is well known, the same value for all uni-univalent electrolytes. In this respect the behavior of the activities is simpler than that of the viscosities. On the other hand, whereas the straight line $A\sqrt{c}$, drawn in Fig. 51, gives the whole interionic contribution to the viscosity, the straight line drawn in Fig. 70 gives *only* the limiting slope, the expression for $-\log f$ being

$$-\log f = \frac{A\sqrt{c}}{1 + C\sqrt{c}} - Bc$$

where the parameter C has a different value for each solute. As the concentration tends to zero, the value of the denominator tends to unity and the value of the first term tends to $A\sqrt{c}$, where A in aqueous solution has the value 0.506 for all uni-univalent electrolytes at 25°C.

In Fig. 70 the quantity $-\log f$ was plotted, instead of $+\log f$, in order that the relation of the diagram to Fig. 51 should be more clearly seen. It is more usual to plot $+\log f$, in which case the diagram is inverted, and the curve passes through a minimum—or else to plot simply the activity coefficient f or γ against the concentration. The curve for lithium bromide included in Fig. 72 represents the same experimental results as those already plotted in Fig. 70. It will be seen that the curves for the five bromides lie in the order Li, Na, K, Rb, Cs. On the other hand, in Fig. 73, it will be seen that, when the activity coefficients of the alkali hydroxides are plotted, the order is inverted. The curve for lithium lies at the bottom, while that for cesium lies at the top. The interionic forces are evidently very different from those present in solutions of the halides.

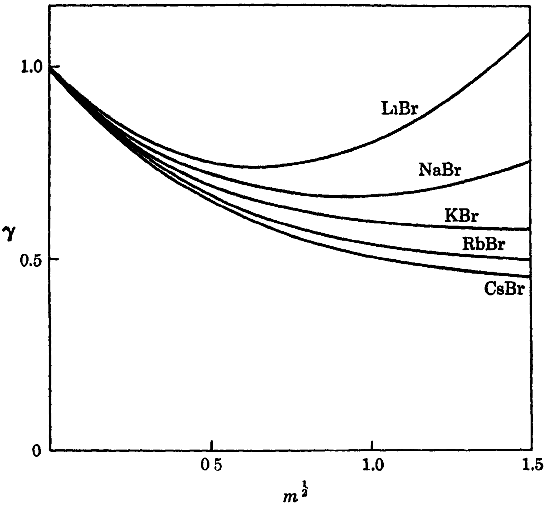


FIG. 72. Activity coefficients of alkali bromides in aqueous solution at 25°C.

Since we have reason to believe that the order-disorder situation in ionic co-spheres, overlapping and merging as in Fig. 69, could give rise to forces of attraction or repulsion, superimposed on the Coulomb forces, we may inquire whether the observed facts as to activity coefficients may be correlated with the known behavior of the ions as regards viscosity and entropy.

In Chapter 10 we found evidence that in aqueous solution the hydroxyl ion is a strong order-producing ion, as regards both viscosity and entropy, as shown by the point that was plotted in Fig. 54. In the uppermost curve of Fig. 73 we have, in the solution of CsOH, this hydroxyl ion accompanied by the order-destroying ion Cs^+. We see that, in the family of curves, as we go down through the ion K^+ to the order-producing ions Na^+ and Li^+, the activity coefficients become progressively smaller. The question is, are we right in discussing such a family of curves in terms of the order-disorder characteristics of the ions? In order to test this, we may invert the situation with respect to the signs of the ionic charges: instead of the order-producing negative ion $(OH)^-$ let us consider an order-producing positive ion, such as Li^+ (or Na^+). If this positive ion behaves toward negative ions in the same way that $(OH)^-$ behaves toward positive ions, we certainly expect to find a similar family of curves with the strongest order-destroying anion at the top; that is to say, in Fig. 72 we expect the curve for lithium iodide to lie above that for LiBr, and that for lithium chloride to lie below that for LiBr. This is found to be the case. (The activities of lithium fluoride do not seem to have been measured as a function of concentration.) Likewise the curves for the sodium salts lie in the order NaI, NaBr, NaCl, NaF; that is, we go down from ions of opposite character to the pair of order-producing ions, Na^+ and F^-.

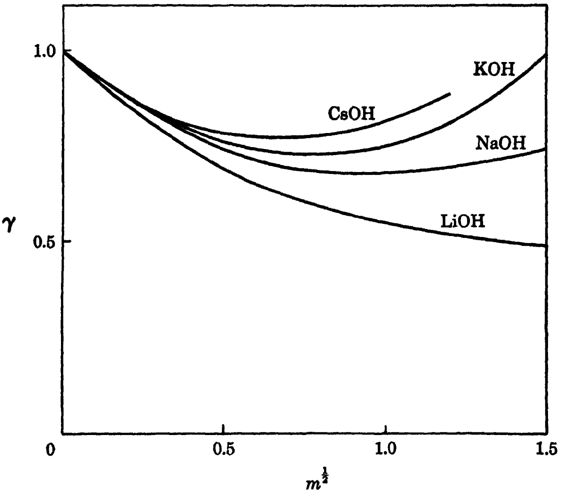


FIG. 73. Activity coefficients of alkali hydroxides in aqueous solution at 25°C.

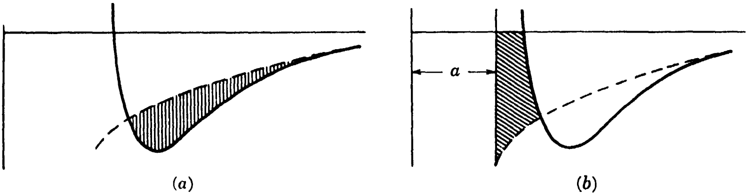
Turning next to the large molecular ions, there are extensive data for two which, fortunately, have very different order-disorder characteristics

—the nitrates and the acetates. It will be recalled that of all the ions in Fig. 53 the $(NO_3)^-$ ion has the lowest temperature coefficient of mobility, and at the same time has the largest negative value for the B-coefficient of viscosity. On the other hand, it was mentioned that potassium acetate has a rather large positive viscosity B-coefficient, in contrast to KCl, KBr, and KI; this B-coefficient is greater than that of acetic acid, and we regard the acetate ion as an order-producing ion. Thus, according to the above tentative scheme, we should expect the activity coefficients of the alkali acetates to give a family of curves similar to that of the hydroxides—that is to say, lying in the order Cs, K, Na, Li. The experimental curves are, in fact, found to lie in this order, in contrast to the nitrates, which lie in the same order as the halides, as expected.

Although the viscosity B-coefficients for the fluorides are not known, we see that the value for the ionic entropy of F^- listed in Table 45 is -2.3 ± 2, very different from the value $+13.5$ for Cl^-. The value for F^- is, in fact, very near the value -2.49 for $(OH)^-$. We have then the very interesting question, whether the activities of the fluorides will fall in line with the other halides. In structure the ion F^- certainly resembles Cl^- and the other halide ions; but according to the tentative scheme proposed above, we should perhaps focus attention on the solvent in the co-sphere of each ion. In this case we should expect to obtain for the fluorides a family of curves similar to that of the hydroxides, in contrast to that of the chlorides. The activities are known as a function of concentration for NaF and KF only. It is found that the curve for NaF lies *below* that of KF—that is to say, the order is the same as that of NaOH and KOH, in contrast to that of NaCl and KCl.

Systematizing these results, we see that both in Fig. 72 and in Fig. 73, if we follow the succession of curves from top to bottom, we go from ions of dissimilar character to ions of similar character: in Fig. 73 we go down to Li^+ and $(OH)^-$, both strong order-producing ions, while in Fig. 72 we go down to Cs^+ and Br^-, both strong order-destroying ions. If the same rule—*from dissimilar character downward to similar character*—is to be applied to the rubidium and cesium halides, the order I, Br, Cl, F, will clearly have to be reversed, in order that RbI and CsI shall be the lowest in each case. It has been known for several years that such an inversion exists. Table 40, compiled by Robinson and Harned, shows the order observed in the whole set of iodides, bromides, and chlorides. It will be seen that, for RbCl, RbBr, and RbI, and likewise for CsCl, CsBr, and RbI, the observed order is opposite to that found for the other alkali halides. Hitherto this inversion has been regarded as mysterious. But it falls in line with the facts depicted in Fig. 72, all of which suggest that we may be right in discussing these activity coefficients solely in terms of the order-disorder character of the ionic co-spheres, overlapping as in Fig. 69.

136. Forces Superimposed on the Coulomb Forces. The discussion has been based on the idea that, superimposed on the electrostatic forces between a pair of ions, there are rather short-range forces of other origin, which may be attractive or repulsive. Consider now what the situation will be if these forces cause the mutual potential energy to fall at short distances, below the value $-e^2/\epsilon r$ that is assumed in the Debye-Hückel theory. In Fig. 74 let the broken curve be a plot of $-e^2/\epsilon r$, while the full curve gives the actual potential energy between a certain pair of ions in solution. We must ask now, how agreement can be obtained with experiment, seeing that the shaded area in Fig. 74*a* has been left out of account. The answer is that, since the Debye-Hückel theory is committed to the use of $-e^2/\epsilon r$, the only way to compensate is by adding a piece, as shown by the other shaded area in Fig. 74*b*; that is to say, approximate agreement with experiment can be obtained by using a distance of closest approach that is somewhat smaller than the actual distance of closest approach.



(*a*) (*b*)

FIG. 74

In Table 40 the values for the cesium salts show that, if a zero value or a positive value of the activity *B*-coefficient is used, approximate agreement with experiment can be obtained only by introducing a value of *a* that is smaller than the lattice spacing in the crystal- an impossibly small value. Figure 74 indicates that this situation may have arisen because a mutual attraction between the Cs^+ ion and the halide ion is superimposed on their electrostatic attraction. We may tentatively look for the source of this additional attraction in the situation depicted in Fig. 69.

In Table 40 we notice that likewise for rubidium iodide the value adopted for the distance of closest approach is smaller than the lattice spacing in the crystal.

In contrast to the foregoing, consider now the case depicted in Fig. 75, where the presence of moderately short-range forces of repulsion causes the potential-energy curve to lie above the broken curve for $-e^2/\epsilon r$. In this case the use of the Coulomb value, to which the Debye-Hückel theory is committed, means too much attraction; and approximate compensation can be obtained only by cutting off a piece, as shown by the upper shaded area on the left; that is to say, approximate agreement with experiment can be obtained by using a value of *a* that is rather greater than the actual distance of closest approach. In this way one can perhaps account for the fact that the values of *a* given in Table 40 for the lithium salts are a little larger than is to be expected in water.

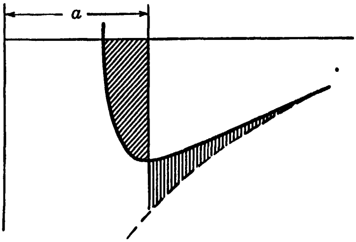


FIG. 75

APPENDIX

Note 1. The Free Energy Lost by a Polar Dielectric in an Electrostatic Field. Let Fig. 76 depict a permanent rigid dipole whose axis makes an angle Θ with a uniform field of intensity E. If μ is the dipole moment, the potential energy of the dipole in the field is $-E\mu \cos \Theta$. If the dipole is held in this fixed position, any increment dE in the intensity of the field will clearly mean a change in the potential energy of the dipole, equal to $-\mu \cos \Theta \, dE$.

Consider now a stage in the charging of a parallel-plate condenser, where the charges already on the plates produce a field E in the dielectric, and a polarization P. We may next imagine the further charging of the condenser to be carried out by a series of alternating steps: (*a*) holding every dipole in a fixed position, as above, we add charges $+dq$ and $-dq$ to the plates: (*b*) we now release the dipoles; since the intensity of the field has been increased, the dipoles will turn slightly in the field, toward a greater degree of alignment. This movement of the dipoles generates heat; but if this heat is allowed to escape from the dielectric, it will make no difference to the change of free energy in the isothermal process.

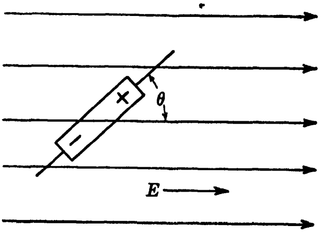


FIG. 76

In practice a polar molecule is not a rigid dipole but suffers some distortion in the field. In this case we shall assume that in the step (*a*) not only is the axis of every dipole held in a fixed position, but also the distortion of the molecule is held at a fixed value. During this step (*a*) the total polarization P of the dielectric will remain constant.

Now let X be the intensity of the field which the charges $\pm q$ would produce if there were a vacuum between the plates, and let dX be the increment that would be produced by the addition of the charges $\pm dq$. Then in the step (*a*) the increment in the intensity of the field is equal to dX, even when the dielectric is present, since in the dielectric nothing has been allowed to move. The free energy of the dielectric changes by the amount $-P \, dX$.

The electric susceptibility χ of the material is defined by $\chi = P/E$. Hence

$$-\int P \, dX = -\chi \int E \, dX$$

The expression (7) of Chapter 1 can now be derived at once, by making the following substitutions: the dielectric constant $\epsilon = 1 + 4\pi\chi$; and $E = X/\epsilon$.

Note 2. The Mutual Potential Energy of a Rigid Dipole of Moment μ and a Distant Charge q. Let the length of the dipole be $2l$. Since the moment μ of the dipole is equal to the magnitude of either of its charges multiplied by $2l$, the magnitude of either charge is $\mu/2l$. Let r be the distance between the distant charge q and the center of the dipole. In the position of Fig. 77 the distance between the charges of like sign is $(r + l)$ and their potential energy is clearly

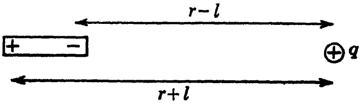


FIG. 77

$$\frac{q\mu/2l}{r + l}$$

Similarly the mutual potential energy of the unlike charges is

$$-\frac{q\mu/2l}{r - l}$$

The total mutual potential energy of the rigid dipole and the charge q is thus

$$\frac{q\mu}{2l}\left(\frac{1}{r + l} - \frac{1}{r - l}\right) = -\frac{\mu q}{r^2 - l^2}$$

When l^2 is very small compared with r^2, this does not differ appreciably from the value $-\mu q/r^2$, given in Sec. 25.

In the same way, one may go on to derive the mutual potential energy of two dipoles, given in (38).

Note 3. The Coulomb Attraction between Charges. It is well known that at any point lying at a great distance R from the center of a bar magnet the intensity of the magnetic field is proportional to the moment of the magnet—that is to say, is proportional to the magnitude of either pole, multiplied by the distance between the poles. Likewise, if we have two equal and opposite electric charges, as in Fig. 78b, and we consider the mid-point of the line joining them, the field in any element of volume dv lying at a great distance from this point is proportional to the magnitude of either charge, multiplied by the distance between the charges. If then we have charges $\pm e$, and we increase the distance between them, the intensity of the field at every distant point increases in proportion to their separation. If now the whole of space is occupied by a uniform polar dielectric, in this increasing field the local degree of alignment of the dipoles at every distant point will increase in proportion to the distance between the charges. This increment in the degree of alignment is accompanied by a loss of entropy (a greater degree of order). Now a loss of entropy means a gain of free energy, or work done. In fact, it follows from (27) that the total loss of entropy, obtained by integrating over all space, when the distance between the charges is increased from r_1 to r_2, will according to simple electrostatic theory be proportional to

$$\frac{q^2}{\epsilon}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

which is the work done to separate the charges against their mutual attraction.

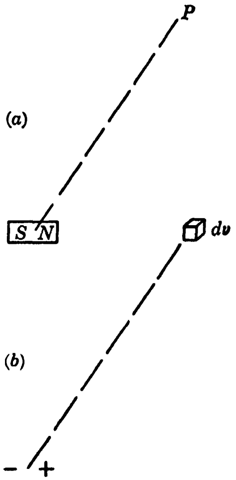


FIG. 78

Note 4. The Number of Dipoles per Unit Volume (Sec. 98). Between 25 and 100°C the value of $1/\epsilon$ for water rises from $\frac{1}{76}$ to $\frac{1}{55}$, while the increment in the value of $1/(\epsilon - 1)$ is nearly the same, namely, from $\frac{1}{75}$ to $\frac{1}{54}$. Similarly in any solvent whose dielectric constant is large compared with unity the temperature coefficients of $1/(\epsilon - 1)$ and of $1/\epsilon$ are nearly equal. In comparing the behavior of different solvents, let us consider now how the loss of entropy in an applied field will depend upon n, the number of dipoles per unit volume. Let us ask what will be the behavior if $(\epsilon - 1)$ is nearly proportional to n/T as it is in the case of a polar gas. In this case we have $1/(\epsilon - 1)$ nearly proportional to T/n; and since in a liquid n is almost independent of T, we have $\frac{d}{dT}\left(\frac{1}{\epsilon - 1}\right)$ nearly proportional to $1/n$. At the same time, if ϵ is large compared with unity, the temperature coefficient of $1/\epsilon$ will likewise be roughly proportional to $1/n$.

Let us return now to the sphere of Sec. 98, bearing a fixed charge q and immersed in one solvent or another. We know from (19) that the loss of entropy is proportional to $\frac{d}{dT}\left(\frac{1}{\epsilon}\right)$, which we have found, under the above reasonable assumptions, to be roughly proportional to $1/n$.

This means that, if the number of dipoles per unit volume has been diminished, the loss of entropy in the field of the charge q will actually be greater—roughly in proportion to $1/n$.

TABLE 41. PERMANENT DIPOLE MOMENTS OF MOLECULES IN A VACUUM

	$\mu \times 10^{18}$		$\mu \times 10^{18}$
Water	1.85	*n*-Propanol	1.66
Methanol	1.68	Isopropanol	1.7
Ethanol	1.70	*n*-Butanol	1.65
Ammonia	1.49	Isobutanol	1.7

TABLE 42. CRYSTALLOGRAPHIC RADII OF IONS IN ANGSTROMS[a]
And in parentheses the reciprocals of the radii

	Li^+ 0.78 (1.28)	Be^{++} 0.34 (2.94)
F^- 1.33 (0.75)	Na^+ 0.98 (1.02)	Mg^{++} 0.78 (1.28)
Cl^- 1.81 (0.55)	K^+ 1.33 (0.75)	Ca^{++} 1.06 (0.94)
Br^- 1.96 (0.51)	Rb^+ 1.49 (0.67)	Sr^{++} 1.27 (0.79)
I^- 2.20 (0.45)	Cs^+ 1.65 (0.60)	Ba^{++} 1.43 (0.70)

[a] V. M. Goldschmidt, *Chem. Ber.*, **60**, 1263 (1927).

TABLE 43. THE VISCOSITY OF WATER[a]

Temp., °C	η
0	0.017887
5	0.015155
10	0.013061
15	0.011046
20	0.010046
25	0.008941
30	0.008019

[a] N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold, 1940.

TABLE 44. ENTROPY OF IONIC CRYSTALS AT 25°C[a]

Ion	e.u.	Ion	e.u.
NaCl	17.3 ± 0.5	AgCl	23.0 ± 0.1
NaOH	13.8	AgBr	25.60 ± 0.1
$NaNO_3$	28.8 ± 0.1	AgI	27.1 ± 1.0
KCl	19.76 ± 0.1	$AgIO_3$	35.7 ± 1.0
KBr	22.6 ± 0.5	Ag_2SO_4	47.9 ± 0.3
KI	24.1 ± 0.5	TlCl	24.8 ± 1.0
$KClO_3$	34.2 ± 0.2	TlBr	26.8 ± 1.0
$KBrO_3$	35.7 ± 0.2	TlI	29.9 ± 1.0
KIO_3	36.2 ± 0.2	$TlNO_3$	38.4 ± 0.2
$KClO_4$	36.1 ± 0.4	Li_2CO_3	21.60 ± 0.05
KNO_3	31.8 ± 0.2	BaF_2	23.03 ± 0.1[b]
$KMnO_4$	41.04 ± 0.1		
$CsClO_4$	41.89 ± 0.2[b]		

[a] K. K. Kelley, *U.S. Bur. Mines Bull.* 394 (1936).

[b] K. S. Pitzer, W. V. Smith, and W. M. Latimer, *J. Am. Chem. Soc.*, **60**, 1826 (1938).

TABLE 45. CONVENTIONAL PARTIAL MOLAL ENTROPIES OF IONS IN WATER[a] AT 25°C
($H^+ = 0.0$)

Ion	e.u.	Ion	e.u.
Li^+	4.7 ± 1.0	OH^-	−2.49 ± 0.06
Na^+	14.0 ± 0.4	ClO^-	10.0 ± 2
K^+	24.2 ± 0.2	ClO_2^-	24.1 ± 0.5
Rb^+	28.7 ± 0.7	ClO_3^-	39.4 ± 0.5
Ag^+	17.54 ± 0.15	ClO_4^-	43.6 ± 0.5
NH_4^+	26.4 ± 0.5	BrO_3^-	38.5 ± 1.0
Tl^+	30.5 ± 0.4	IO_3^-	28.0 ± 1.0
Mg^{++}	−31.6 ± 3.0	HS^-	14.9 ± 1.0
Ca^{++}	−11.4 ± 0.3	HSO_3^-	32.6 ± 1.5
Sr^{++}	−7.3 ± 1.5	$SO_3^=$	3 ± 3
Ba^{++}	+2.3 ± 0.3	HSO_4^-	30.6 ± 2
Fe^{++}	−25.9 ± 1.0	$SO_4^=$	4.4 ± 1.0
Cu^{++}	−26.5 ± 1.0	NO_2^-	29.9 ± 1.0
Zn^{++}	−25.7 ± 1.0	NO_3^-	35.0 ± 0.2
Cd^{++}	−16.4 ± 1.5	$H_2PO_4^-$	28.0 ± 1.5
Hg_2^{++}	+17.7 ± 3.0	$HPO_4^=$	−2.3 ± 1.5
Sn^{++}	−4.9 ± 1.0	$PO_4^{\equiv}$	−45 ± 2
Pb^{++}	+3.9 ± 0.9	HCO_3^-	22.2 ± 0.8
Al^{+++}	−76 ± 10	$CO_3^=$	−13.0 ± 1.0
Fe^{+++}	−61 ± 5	$C_2O_4^=$	9.6 ± 1.0
Cl^-	13.5 ± 0.1	CN^-	25 ± 5.0
Br^-	19.7 ± 0.2	MnO_4^-	46.7 ± 0.4
I^-	25.3 ± 0.5	$CrO_4^=$	10.5 ± 1.0
F^-	−2.3 ± 2		

[a] W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.* **60**, 1829 (1938).

TABLE 46. PARTIAL MOLAL VOLUMES OF ION PAIRS AT INFINITE DILUTION IN WATER AT 25°C AND 1 ATMOSPHERE[a]
(See also Table 31)

	Cm³/mole		Cm³/mole
KF	6.6	$AgNO_3$	28.3
KOH	3.4	$CaCl_2$	18.5
NaOH..	−6.8	$SrCl_2$	18.0
LiOH.	−6.3	$BaCl_2$	23.9
KNO_3	38.0		

[a] B. B. Owen and R. S. Brinkley, *Chem. Rev.*, **29**, 461 (1942).

TABLE 47. CONSTANTS AND CONVERSION FACTORS

Avogadro's number = 6.023×10^{23} per mole
Electronic charge = 4.802×10^{-10} e.s.u.
Boltzmann's constant = 1.380×10^{-16} erg/deg
Molar gas constant = 1.987 cal/deg mole
25°C = 298.16°K
1 cal/mole = 4.336×10^{-5} electron-volt/kome
1 electron-volt/kome = 23,060 cal/mole
$\frac{e^2}{r}$ (for r equal to 1 angstrom) = 2.306×10^{-11} erg = 14.4 electron-volts
$\ln(10) = (\ln x)/\log x = 2.3026$

At 25°C

kT = 0.02569 electron-volt
$2.3026\ kT$ = 0.05916 electron-volt
RT = 592.5 cal.
$2.3026\ RT$ = 1364.3 cal.

NAME INDEX

SUBJECT INDEX