

1-1 THE EQUILIBRIUM STATE

When substances are mixed and undergo a chemical change, we say that a chemical reaction has occurred. Relatively few reactions proceed in such a way that the reactants are completely consumed and only a unique product remains. Those reactions that proceed nearly to completion are useful because they provide a basis for quantitative chemical analysis, but even those reactions which are sufficiently complete to be used for analysis are not complete in any rigorous sense. The products may react with each other, the opposition of the forward and reverse reactions resulting in equilibrium, with measurable amounts of the original reactants present. Such a situation constitutes a source of error in quantitative analysis which can be corrected for.

This book is concerned with equilibrium in reactions that occur between ions in aqueous solutions. There are several reasons for restricting ourselves to this apparently narrow field. First, most of the substances studied in inorganic and analytical chemistry exist as ions in solution. Second, reactions between ions are often very rapid and can reach a state of equilibrium almost as fast as the reactants can be mixed. Ionic reactions at equilibrium have thus been extensively studied, and a large body of experimental data is available. Third, simple but powerful theoretical principles governing reactions at equilibrium are known. By applying these principles, we can make quantitative theoretical predictions about the results of chemical experiments, including the numerical estimation of many quantities which would be extremely difficult to measure directly, but which may be of importance for many applications of inorganic and analytical chemistry.

When is a system at equilibrium? The investigator of an equilibrium system is first faced with the problem of whether the system he is studying is truly at equilibrium. There is a very simple test for true equilibrium: The reaction is allowed to proceed in the forward direction until nothing more appears to happen, and the chemical composition of the system is determined. Then the same reaction is allowed to proceed in the reverse direction until nothing more appears to happen. If the composition of

the system is the same regardless of the direction from which it was approached, then a true equilibrium exists.

It may happen that two substances are mixed but fail to react under ordinary conditions. It may happen that a different composition is reached from the forward and reverse directions. Such reactions do not proceed to a true equilibrium. Many reactions studied in organic chemistry proceed to one set of products under one condition and to a different set of products under slightly different conditions. In most cases the products of such reactions do not reach true equilibrium with the reactants. Rather, the reaction proceeds to one set of products because the rate of the reaction forming these products is somewhat faster than the rate of the reaction forming some other products. There may be hundreds of possible paths that the reaction could take if all the products could be detected, and this makes life very complicated for the chemist studying such reactions. Slow reactions with many possible paths are characteristic of the chemistry of covalent bonds.

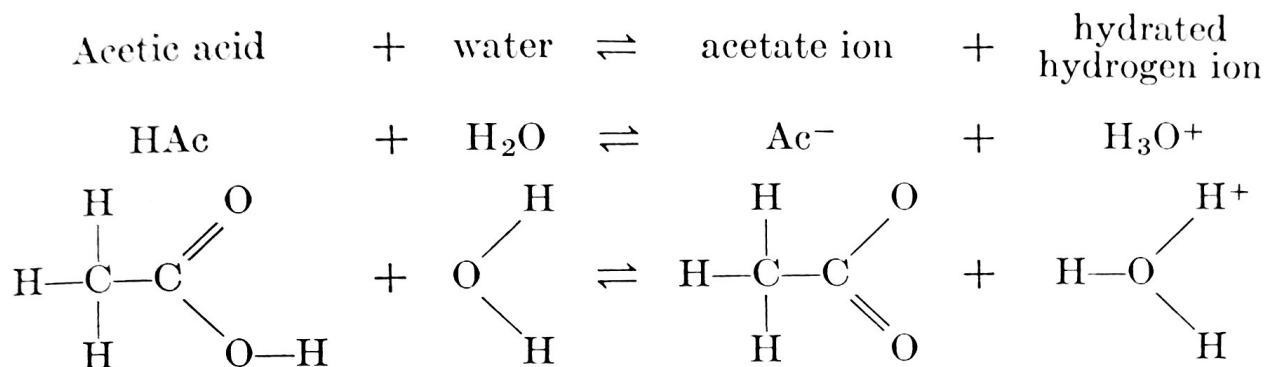
In contrast, it has been possible in many cases of reactions involving ions in solution to reduce to simple mathematical statements the laws governing the concentrations of all the various ions and molecules in an equilibrium mixture. This means that so long as we are sure that we are dealing with a true equilibrium mixture, we can calculate theoretically the concentrations of all the species present in solution.

Equilibrium as a balance of opposing reactions. Compared to the mathematics involved in many branches of physics and chemistry, the calculations here are not difficult. Although the large number of species present in some solutions makes the equations look formidable, in actual fact, only a little advanced algebra and some ingenuity are necessary. It is to be hoped that these requirements are not beyond the reach of most students of chemistry.

A simple and straightforward picture of a chemical equilibrium is that of the balance of opposing reactions. In approaching equilibrium, the reactants combine to give products, but the products themselves can combine to give the original reactants. Eventually, a balance is reached at equilibrium, where the rate at which the forward reaction proceeds is just balanced by the rate at which the backward reaction proceeds. Equilibrium is a dynamic balance, and changes in the concentrations of substances or the temperature of the solution will shift the position of equilibrium by altering the relative rates of forward and reverse reactions.

For the sake of concreteness, let us consider a particularly well-studied reaction, the dissociation of acetic acid into its ions. When acetic acid (CH_3COOH , abbreviated HAc) is dissolved in water, it releases a hydrogen ion which combines with a nearby water molecule to give a hydrated

hydrogen ion (H_3O^+),* leaving an acetate ion (CH_3COO^- , abbreviated Ac^-). This dissociation does not occur completely, because at the same time that molecules of acetic acid are breaking apart, acetate ions and hydrogen ions are recombining. At equilibrium these two processes exactly balance each other, and the concentrations of acetic acid, acetate ion, and hydrogen ion are independent of the time. Equilibrium is represented by a double arrow in the equation for the reaction:



The hydrogen ion is also written merely H^+ when we do not desire to emphasize the fact that it is hydrated (see Section 4-1).

The dissociation of acetic acid takes place extremely rapidly, being essentially at equilibrium only a few microseconds† after a molecule of acetic acid is introduced into the solution. Measuring the rate of approach to equilibrium is very difficult when a reaction occurs so rapidly, and even though the equilibrium of acetic acid had been thoroughly studied before 1900, it was not until a few years ago that Eigen was able to measure the rate of dissociation of acetic acid and the rate of association of acetate and hydrogen ions. The application of an intense electric field to the solution causes the acetic acid to dissociate to a slightly greater extent than at equilibrium, and the *relaxation* of the system to equilibrium was measured by following on an oscilloscope the conductivity of the solution, which depends on the extent to which the acid is dissociated (see Section 2-3).

Consider a hypothetical experiment, the results of which can be calculated from the above measurements: 100 micromoles‡ of acetic acid are mixed instantaneously with one liter of pure water. The concentrations of reactant, acetic acid, and product, acetate ion, are plotted in

* Also called *hydronium* or *oxonium* ion by analogy with ammonium ion NH_4^+ .

† One microsecond is one-millionth or 10^{-6} of a second.

‡ In this book the term *mole* is used to represent Avogadro's number (6.0235×10^{23}) of particles of any chemical species. That is, one gram-atom, one gram-molecule, one gram-ion, and one gram-formula-weight are all referred to as one mole. A micromole is 10^{-6} mole.

4 Introduction

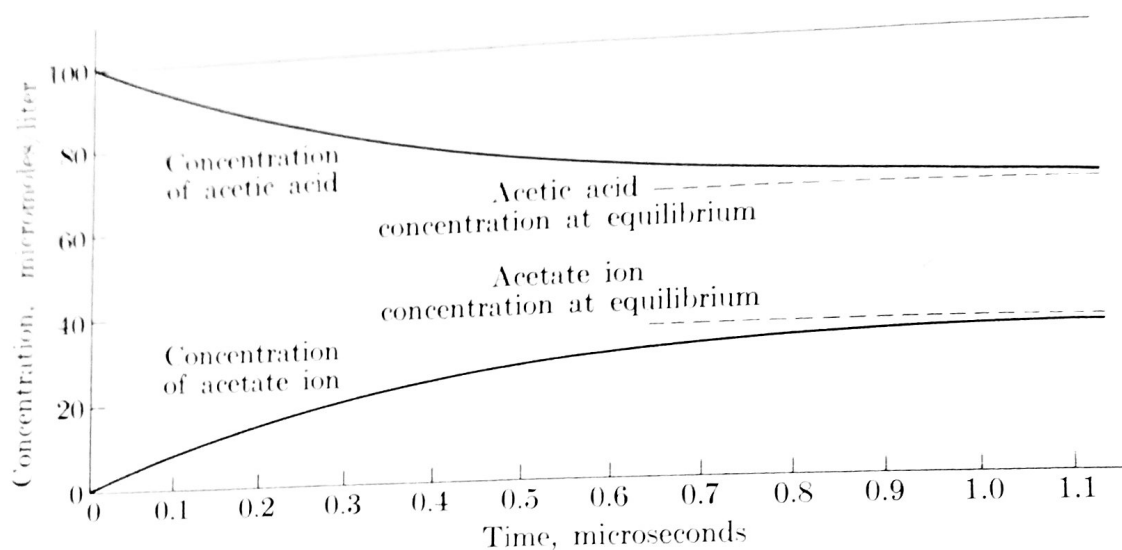


FIG. 1-1. Variation of the concentrations of undissociated acetic acid and acetate ion with time when the initial concentration of acetic acid is 1.00×10^{-4} mole/liter, and the initial concentration of acetate ion is zero. Note that equilibrium is reached in approximately one microsecond.

Fig. 1-1 as a function of time after the instantaneous mixing. The concentration of acetic acid decreases rapidly at first, and then more slowly, until after several microseconds its concentration becomes constant at 66 micromoles/liter. At the same time the concentration of acetate ions rises to its maximum value of 34 micromoles/liter. These final values are the equilibrium concentrations present in 10^{-4} molar acetic acid in water, and they will not change unless some substance is added or the temperature is changed.

Figure 1-2 shows the approach to equilibrium from the reverse direction. Here the hypothetical experiment requires that 100 micromoles of sodium acetate and 100 micromoles of hydrochloric acid be instantaneously mixed with one liter of water. (The sodium and chloride ions do not enter into the reaction, but are there merely to keep the charges balanced in the reacting substances.) The acetate ion concentration decreases from its initial value of 100 micromoles/liter, rapidly at first, then more slowly, until it reaches a stable value at 34 micromoles/liter. At the same time the acetic acid concentration increases to a maximum value of 66 micromoles/liter. Equilibrium is reached in several microseconds, and the concentrations are the same as were obtained from the forward reaction.

Note that the total concentration of acetate groups, which is equal to the sum of acetic acid and acetate ion concentrations, remains constant at 100 micromoles/liter regardless of the extent to which the reaction occurs or the direction from which equilibrium is approached. This is a direct result of the fact that the acetate group (CH_3COO) remains intact

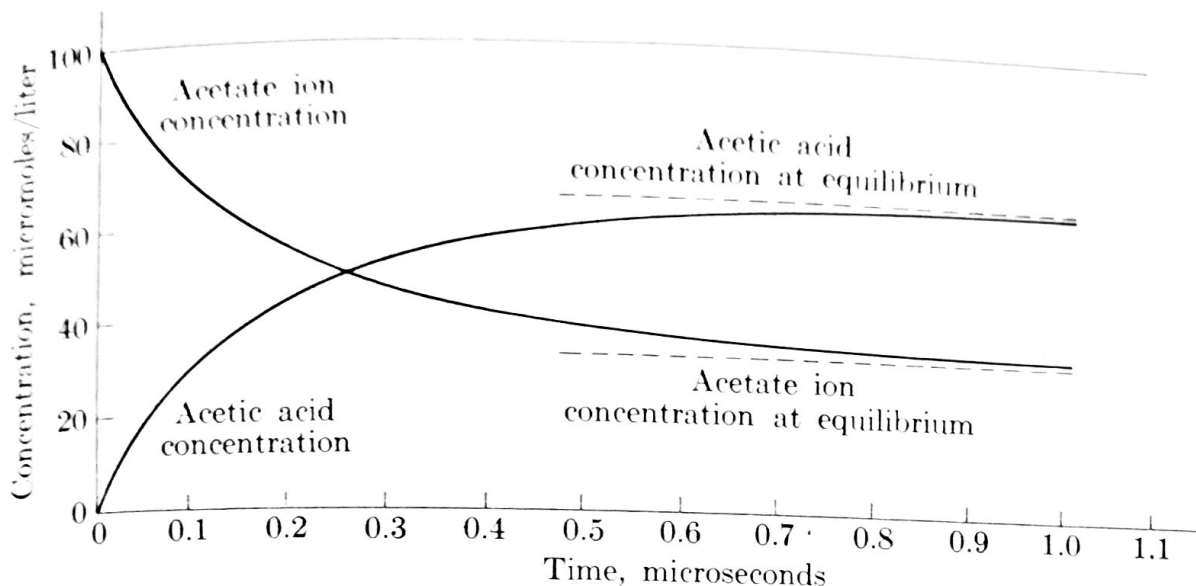
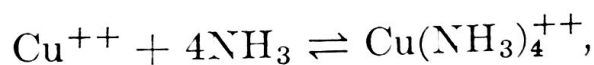


FIG. 1-2. Variation of the concentrations of undissociated acetic acid and acetate ion with time when the initial concentrations of acetate ion and hydrogen ion are 1.00×10^{-4} mole/liter, and the initial concentration of undissociated acetic acid is zero. Note that the same equilibrium values are reached as in Fig. 1-1, and that the time required to reach equilibrium is the same in both cases.

throughout the reaction. Physicists would say that acetate groups are "conserved," in the same sense as mass, momentum, and energy are conserved.

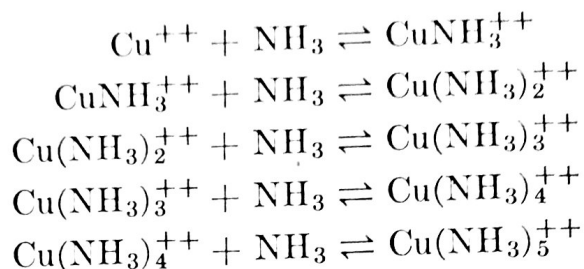
Simultaneous equilibria. The idea of equilibrium arising from two opposing reactions is a very fundamental one, but it is often incorrectly applied. Rigorously, the idea can be applied only to reactions, such as the dissociation of acetic acid, which take place in a single step without the formation of any intermediate species. Many common reactions are quite complicated when considered in detail and may involve several intermediate species. To consider such reactions as reaching equilibrium from the opposition of only two reactions is incorrect, and to understand fully the quantitative effects of changing conditions on the equilibrium, all the intermediate species must be taken into account.

For example, when a solution of copper sulfate is mixed with concentrated ammonia, it changes to a deep blue-violet color. The overall reaction is often given as



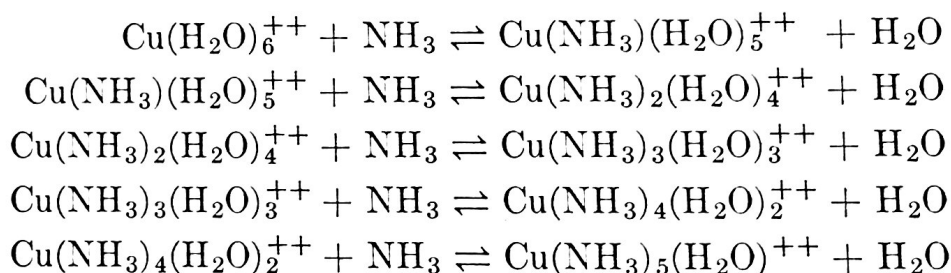
since most of the copper in the blue-violet solution is found to have four molecules of ammonia attached to it. More careful and detailed measurements of this reaction, in solutions of varying ammonia concentrations, show that four other species are present which contain copper and various

numbers of molecules of ammonia. The reaction can thus be represented as the five steps,



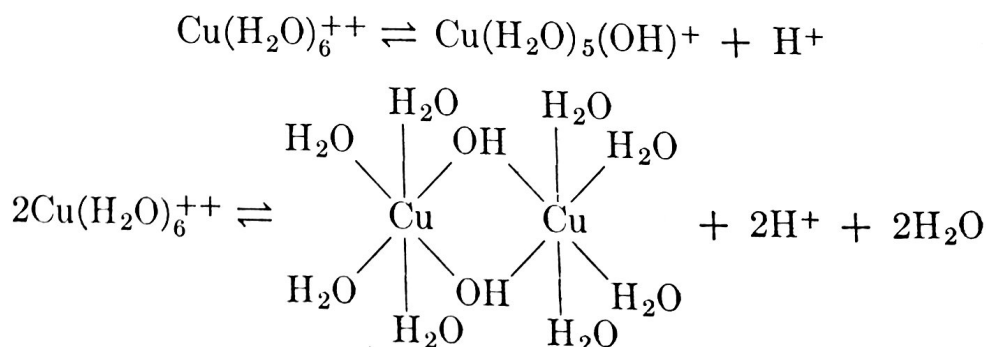
In salts such as $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$, the tetrammine copper ion $\text{Cu}(\text{NH}_3)_4^{++}$ is present in the crystal lattice, but in solution some of these ions lose ammonia molecules, while others may gain one, and all the possible species containing copper are present to some extent.

X-ray diffraction measurements on crystals of hydrated copper salts such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ show that in these, four water molecules are firmly bound to the copper ion. In solution, however, spectroscopic studies have indicated that two additional water molecules are bound to the copper ion at a somewhat greater distance. The reaction of copper ion with ammonia would thus be better represented as the replacement of water molecules by ammonia:



A species with six ammonia molecules would be expected to exist, but it has not been detected in equilibrium studies. Even at the highest concentrations of ammonia that it is possible to obtain in aqueous solutions, $\text{Cu}(\text{NH}_3)_6^{++}$ is present in undetectably small concentrations.

Water molecules attached to copper ions can lose hydrogen ions in solution to form ions like CuOH^+ and $\text{Cu}_2(\text{OH})_2^{++}$, which also exist in equilibrium with the copper ammine complexes:



The extra water molecules are usually not written in the formulas for the ions. Ammonia can take on a hydrogen ion to give the ammonium ion,



(see Section 5-3) and water itself dissociates to give a hydrogen and hydroxyl ion,



A complete picture of the reaction of copper ion with ammonia, therefore, involves knowledge of many different equilibria.

It must be emphasized that all the treatments discussed in this book apply to solutions more dilute than about 0.1 mole/liter. In concentrated solutions, specific interactions between ions become very important, and the general laws which apply to dilute solutions break down. Even with this limitation, however, a great many systems of practical importance can be treated in detail, using the general concepts and methods discussed in later chapters.

1-2 THE EQUILIBRIUM CONSTANT

The basic principle on which the quantitative study of equilibrium systems is based is the existence of the equilibrium constant. Guldberg and Waage in their statement of the "Law of Mass Action" (1865) realized that equilibrium was subject to quantitative laws. The correct formulation of the laws governing equilibrium was made by Van't Hoff in 1877, and generalized to various systems during the next thirty years by many workers, the most notable being Van't Hoff, Ostwald, Arrhenius, Nernst, and Gibbs.

Let us consider again the dissociation of acetic acid. The equilibrium concentrations of undissociated acid, hydrogen ion, and acetate ions measured under various conditions, including varying the concentration of the acid in pure water, adding hydrochloric acid, or adding sodium acetate, are given in Table 1-1. The concentration equilibrium constant for the dissociation of acetic acid is defined by the equation:

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAe}]}, \quad (1)$$

where brackets indicate concentrations in moles/liter. The concentration constant K_a can be seen from Table 1-1 to vary only slightly with the values of the various concentrations; K_a depends on the temperature of the solution (see Section 2-4), but not on the pressure of the atmosphere to any detectable extent.

TABLE 1-1
EQUILIBRIUM CONSTANT FOR THE DISSOCIATION OF ACETIC ACID
(All concentrations moles per liter)

<i>Acetic acid in water:</i>				
Analytical concentration*	[HAc]	[Ac ⁻]	[H ⁺]	K_a
1.00×10^{-5}	2.9×10^{-6}	7.1×10^{-6}	7.1×10^{-6}	1.74×10^{-5}
1.00×10^{-4}	6.6×10^{-5}	3.4×10^{-5}	3.4×10^{-5}	1.75×10^{-5}
1.00×10^{-3}	8.73×10^{-4}	1.27×10^{-4}	1.27×10^{-4}	1.85×10^{-5}
1.00×10^{-2}	9.65×10^{-3}	4.5×10^{-4}	4.5×10^{-4}	2.10×10^{-5}
<i>Acetic acid-sodium acetate mixtures (total concentration 1.00×10^{-3}):</i>				
	[HAc]	[Ac ⁻]	[H ⁺]	K_a
	9.0×10^{-4}	1.0×10^{-4}	1.7×10^{-4}	1.89×10^{-5}
	7.0×10^{-4}	3.0×10^{-4}	4.4×10^{-5}	1.89×10^{-5}
	5.0×10^{-4}	5.0×10^{-4}	1.8×10^{-5}	1.80×10^{-5}
	4.0×10^{-4}	6.0×10^{-4}	1.3×10^{-5}	1.95×10^{-5}
<i>Acetic acid-hydrochloric acid mixtures (total concentration 1.00×10^{-3}):</i>				
	[HAc]	[Ac ⁻]	[H ⁺]	K_a
	9.0×10^{-4}	1.7×10^{-4}	1.0×10^{-4}	1.89×10^{-5}
	7.0×10^{-4}	4.4×10^{-5}	3.0×10^{-4}	1.89×10^{-5}
	5.0×10^{-4}	1.8×10^{-5}	5.0×10^{-4}	1.80×10^{-5}
	3.0×10^{-4}	8.0×10^{-6}	7.0×10^{-4}	1.86×10^{-5}
	1.0×10^{-4}	2.0×10^{-6}	9.0×10^{-4}	1.80×10^{-5}

Note: Direct measurement of all the concentrations is not experimentally feasible. In practice the hydrogen ion concentration is measured potentiometrically, and the concentrations of the other ions are calculated from the known amounts of material put in. These data were adapted from the experimental results of Harned and Murphy, *J. Am. Chem. Soc.* **53**, 8 (1931), but have been greatly simplified. See Section 2-2.

* The analytical concentration is the total number of moles of a substance dissolved in a liter of solution. In 10^{-4} molar acetic acid, the analytical concentration C_{HA} of acetic acid is 1.00×10^{-4} mole/liter, whereas the actual concentration [HAc] is only 0.67×10^{-4} mole/liter, the rest being present as acetate and hydrogen ions. See Fig. 1-1.

Note that the total amount of solution does not enter into the equilibrium-constant expression. Only the ratio of the number of ions of a given kind to the total number of solvent molecules, that is, the *concentration* of the ions, is important in determining the equilibrium composition of the solution.

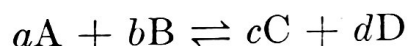
From the first group of data in Table 1-1, K_a can be seen to increase as the concentration of acetic acid increases. This results primarily from the electrostatic interaction of the ions, as distinct from their chemical interaction. As long as the total concentration of ions in the solution is below about 10^{-3} mole/liter, K_a , as given by Eq. (1), varies by only about $\pm 5\%$. If a more accurate relation is required, or if more concentrated solutions are to be considered, the concentrations in Eq. (1) must be replaced by *activities*, which contain corrections for the interionic forces:

$$K_a^0 = \frac{\{H^+\} \{Ac^-\}}{\{HAc\}}, \quad (2)$$

where the braces distinguish activity from concentration. The activity equilibrium constant K_a^0 is obtained by extrapolating the concentration equilibrium constant K_a to zero concentration, and has the value $K_a^0 = (1.75 \pm 0.02) \times 10^{-5}$ at 25°C . The relation between activity and concentration is discussed briefly in Section 2-4 and in more detail in Chapter 12. For a first approximation, the activity is usually replaced by the concentration in moles per liter.

1-3 FORMS FOR THE EQUILIBRIUM CONSTANT EXPRESSION

A general statement of the equilibrium law may be made as follows. For a reaction of the form



where A, B, C, and D are chemical species and a , b , c , and d are the numerical coefficients required to balance the equation, the following relation will be obeyed at equilibrium:

$$K^0 = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}, \quad (1)$$

where the braces indicate the *activity* of the species within the braces. The activity is interpreted as follows:

Ions and molecules in dilute solution. Activity is approximately equal to concentration in moles per liter. (See Section 2-4 and Chapter 12.)

The solvent in a dilute solution. Activity is equal to the mole fraction of solvent and is approximately unity.

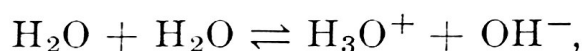
Pure solids or liquids in equilibrium with the solution. Activity is exactly unity.

Gases in equilibrium with the solution. Activity is partial pressure of the gas in atmospheres.*

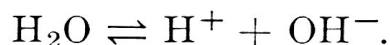
Mixtures of liquids. Activity of a given component is approximately equal to its mole fraction.

The equilibrium constant K^0 depends only on the temperature and not on the pressure or the composition of the system. The equilibrium law as stated above may be considered to be experimentally derived for purposes of calculations, although it can be theoretically derived using chemical thermodynamics. We shall consider below some important examples of the equilibrium law as applied to ionic solutions.

Ion product of water. A very important equilibrium in aqueous solutions is the dissociation of water to give hydrogen and hydroxyl ions:



which is conventionally written



In terms of activities, the equilibrium constant relation is

$$K^0 = \frac{\{\text{H}^+\} \{\text{OH}^-\}}{\{\text{H}_2\text{O}\}}. \quad (2)$$

The activities of the ions are approximately equal to their concentrations, and the activity of the solvent water is approximately unity. It is customary to use an approximate equilibrium constant relation,

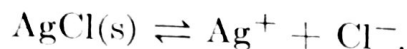
$$K_w = [\text{H}^+][\text{OH}^-], \quad (3)$$

where K_w is called the *ion-product of water*.

In very concentrated solutions, or if some other solvent such as alcohol is introduced, the activity of water is no longer unity, and the exact Eq. (2) must be used instead, with the activity of water set equal to its mole fraction, a number less than unity. Thus the concentrations of hydrogen and hydroxyl ions in an alcohol-water mixture will be less than in pure water under the same conditions.

* For gas reactions at high pressure, the activity is not precisely equal to the partial pressure, but nonideality corrections are usually small.

Solubility product. Another equilibrium constant which is mathematically similar to the ion product of water is the solubility product of a salt. If an ionic salt is present in excess in equilibrium with its saturated solution, the concentrations of the ions will be governed by the equilibrium law. For example, consider the salt, silver chloride:



The (s) following the formula of a compound indicates that it is present as a pure solid, and hence its activity is exactly unity. The equilibrium expression is:

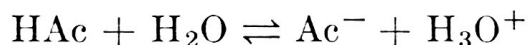
$$K_{s0}^0 = \{\text{Ag}^+\} \{\text{Cl}^-\}.$$

Replacing activities by concentrations, we have, approximately,

$$K_{s0} = [\text{Ag}^+][\text{Cl}^-];$$

K_{s0} is called the *solubility product constant* for the salt. The concentrations of the ions can be used for approximate calculations, but for accurate calculations at concentrations greater than 10^{-3} mole/liter, activities must be used.

Ionization constant of a weak acid. In our discussion of acetic acid, we have already given an example of a weak acid ionization. The reaction



is conventionally written



and gives the equilibrium expression

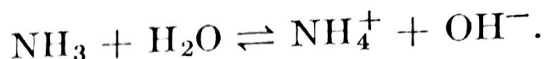
$$K_a^0 = \frac{\{\text{H}^+\} \{\text{Ac}^-\}}{\{\text{HAc}\}}.$$

In dilute solutions, the activities can be replaced by concentrations to give

$$[\text{H}^+][\text{Ac}^-] = K_a[\text{HAc}].$$

The terms *ionization constant* and *dissociation constant* are usually used interchangeably, but in some situations it becomes desirable to distinguish between ionization (formation of ions) and dissociation (separation into parts).

Ionization constant of a weak base. A weak base such as ammonia can react to some extent with water, forming an ammonium ion and a hydroxyl ion:

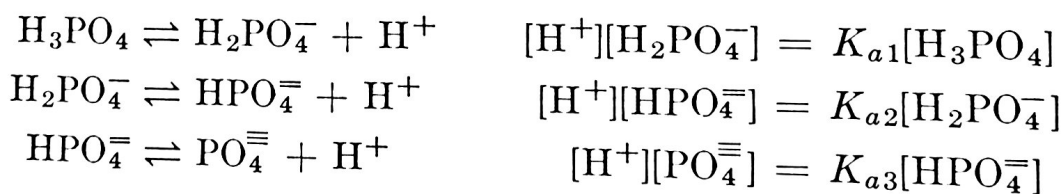


The equilibrium-constant expression for this reaction in dilute solution is approximately

$$[\text{NH}_4^+][\text{OH}^-] = K_b[\text{NH}_3],$$

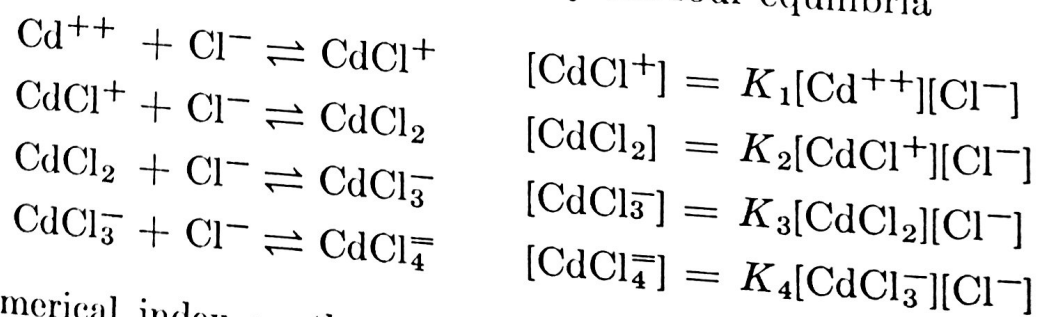
since the activities of the ions and ammonia are approximately equal to their concentrations, and the activity of water as solvent is approximately unity. Sometimes K_b is called the *basic dissociation constant* of ammonia with aqueous ammonia written as NH_4OH . (See Section 5-3.)

Stepwise ionization constants of polyprotic acids. When an acid can lose more than one hydrogen ion, several equilibria are involved and several independent equilibrium-constant expressions exist. For phosphoric acid, three successive dissociations take place, and three independent equilibrium constants are required to describe the experimental data:



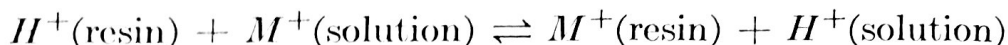
The numerical index on the equilibrium constant gives the charge on the ion that is formed in the reaction. Here, as before, activities have been replaced by concentrations.

Stepwise formation constants for complexes. Similar to the polyprotic acid equilibria are the equilibria for the formation of complex ions. These are usually written in the reverse direction, as formation rather than dissociation constants. For example, the formation of the four cadmium chloride complexes may be represented by the four equilibria



The numerical index on the equilibrium constant gives the number of chloride ions in the complex formed in the reaction. Activities have been replaced by concentrations.

the solution. Thus a cation-exchange resin can lose hydrogen ions to the solution and gain metal ions from the solution, the equilibrium



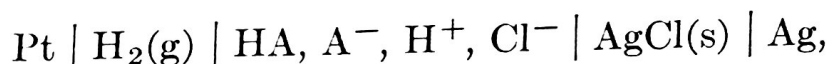
being established. For a given type of resin, the ratio of the activity of a given ion on the resin to the activity of the same ion in solution is a constant, called the partition coefficient (by analogy with solvent extraction).

With a cation-exchange resin, only positively charged species from the solution will exchange with the resin, and with an anion-exchange resin, only negatively charged species from the solution will exchange. Ion-exchange experiments have therefore been used primarily to determine whether the principal complexes in solution are positively or negatively charged.

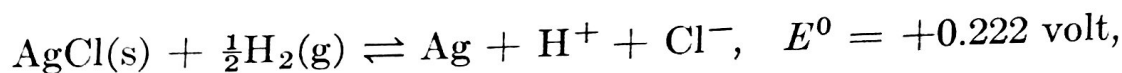
The calculation of equilibrium constants from ion-exchange data involves fitting the data to a theoretical curve calculated from the known partition coefficients. The partition coefficient of an ion depends primarily on its charge, and only slightly on the nature of the ion. Thus ion-exchange methods are suitable for studying the equilibrium between a series of complexes such as Pb^{++} , $PbCl^+$, $PbCl_2$, $PbCl_3^-$, and $PbCl_4^{--}$, where the charges vary widely. However, ion exchange is unsuitable for studying a series of complexes with an uncharged ligand, such as Ag^+ , $AgNH_3^+$, and $Ag(NH_3)^+$, since the partition coefficients of all these ions will be nearly the same, and almost no effect of ammonia concentration will be observed.

2-2 POTENTIOMETRIC METHODS

The most widely applicable methods for determining equilibrium constants depend upon the fact that the potential of a reversible electrochemical cell is directly related to the activity of the ions involved in the cell reaction by the Nernst equation (Eq. 2, Section 1-5). For example, the potential of the cell used by Harned and his associates to determine the dissociation constants of weak acids (Fig. 2-5),



depends on the activities of hydrogen and chloride ions in the electrolyte solution. The overall cell reaction is



and according to the Nernst equation, the potential of the cell is

$$E = +0.222 - 0.05915 \log \{H^+\} \{Cl^-\}.$$

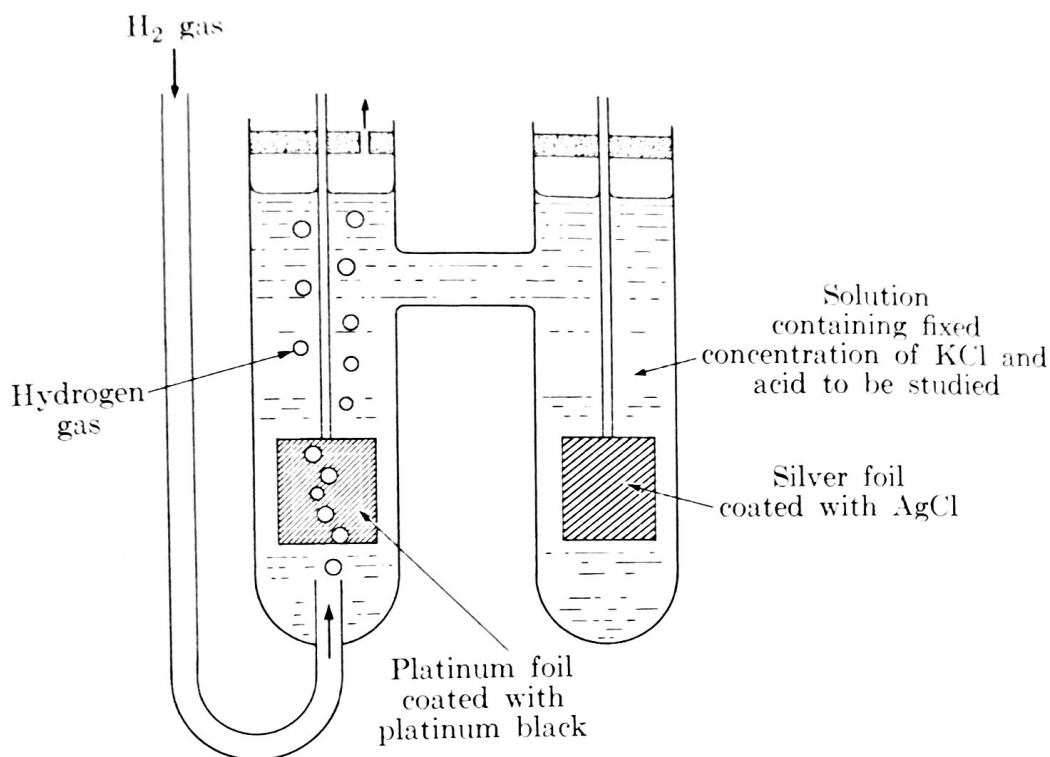


FIG. 2-5. Cell used by Harned and coworkers to measure the dissociation constant of a weak acid.

If the activity of chloride ion is held constant by using a fixed concentration of potassium chloride in the electrolyte, and the hydrogen ion results from the dissociation of a weak acid, then changing the amounts of weak acid and its salt present will vary $\{H^+\}$ according to the equilibrium constant

$$\{H^+\} \{A^-\} = K_a \{HA\}$$

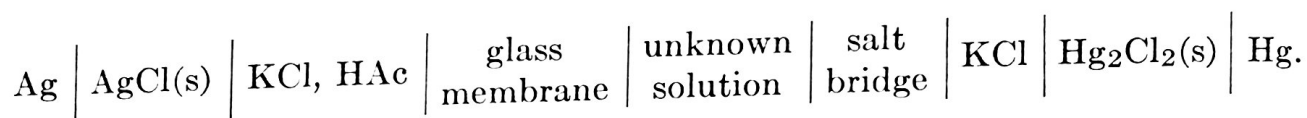
and hence vary the potential of the cell.

The potential of such a cell measures the activity of hydrogen ion in the electrolyte resulting from the dissociation of the weak acid. The concentrations of HA and A^- can be determined from the known amounts of acid and salt put into the solution, and with suitable corrections, the equilibrium constant can be determined. In this cell the hydrogen gas electrode is reversible to hydrogen ions and acts as a "meter" measuring the activity of hydrogen ion in the solution. It is called the *indicator electrode*. Since the concentration of chloride ion is fixed, the potential of the silver-silver chloride electrode does not vary, and it is called the *reference electrode*.

The general technique of measuring equilibrium constants potentiometrically is to set up an electrochemical cell which has an indicator electrode reversible to one of the ions to be studied, and a reference electrode of fixed potential. Usually it is not possible to set up such a cell without a liquid junction, and so the principal uncertainty in most investigations

arises from the liquid-junction potential between the reference electrode and the solution being studied. The cell of Fig. 2-5 is important because it does *not* have a liquid junction.

The glass electrode. One of the handiest and most widely used indicator electrodes is the glass electrode, which is reversible to hydrogen ions. Although the hydrogen gas electrode is the primary standard for the electrode potential scale, it is easily upset by the presence of oxidizing agents or heavy metal ions in the solution. Because the potential of a glass electrode arises by the transfer of hydrogen ions through a thin glass membrane and not by an oxidation process, the glass electrode is insensitive to metal ions, oxidizing agents, etc., and can be used to measure hydrogen ion concentrations in nearly any system. The glass electrode forms the basis of the commercial "pH meters," which have found wide application. The entire cell is set up as shown in Fig. 2-6, the two electrode systems being enclosed in separate tubes:



The potential of the calomel ($\text{Hg-Hg}_2\text{Cl}_2$) half-cell is fixed by the concentration of KCl in the right-hand electrode; the potential of the silver chloride electrode is fixed by the concentration of KCl in the left-hand electrode; and the hydrogen ion concentration inside the glass membrane (to its left) is fixed by the concentration of acetic acid. The only variable left is the hydrogen ion concentration in the unknown solution. The potential of this cell has been found experimentally to vary over a wide

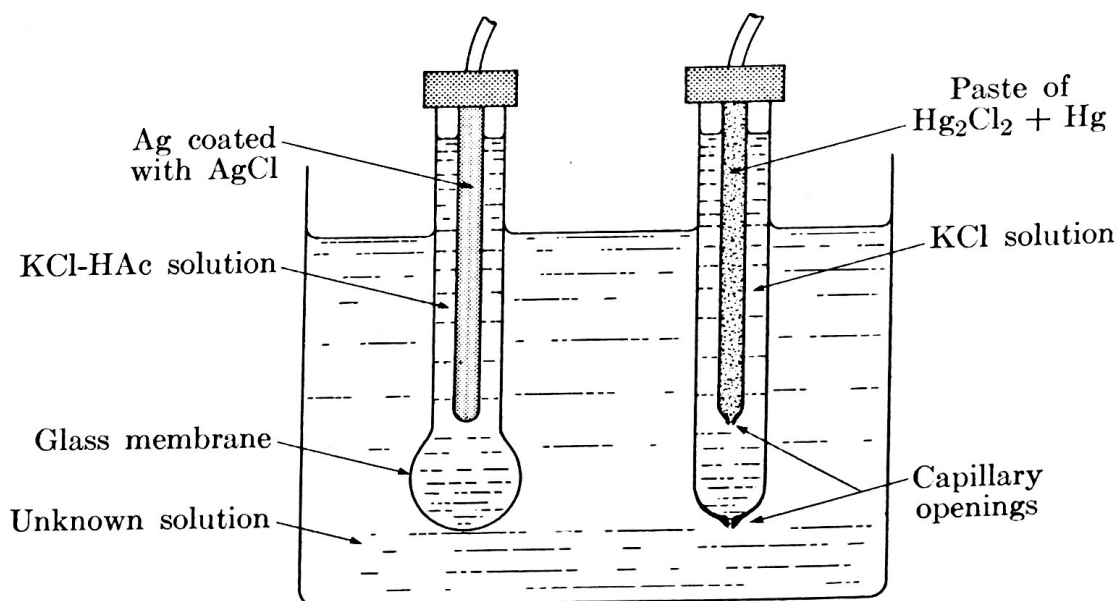


FIG. 2-6. Apparatus for measuring pH with a glass electrode.

range of hydrogen ion concentrations according to the relation

$$E = E^0 + 0.059 \log [H^+],$$

where E^0 depends not only on the standard potentials of the silver chloride and calomel electrodes, but also on an *asymmetry potential* which is characteristic of each particular glass membrane, and which varies somewhat with the previous history of the membrane. This means that the glass electrode is not an *absolute* measure of the hydrogen ion concentration, as the hydrogen gas electrode is, but must be calibrated at regular intervals against a buffer solution of known hydrogen ion concentration.

Other electrodes. If it is desired to investigate equilibria involving metal ions, the indicator electrode can sometimes be made of the metal itself. For example, the solubility products of silver salts can be measured by using a silver wire as an indicator electrode in a solution containing a known concentration of the anion, and saturated with the silver salt. The reference electrode is connected to the solution by a salt bridge. (Compare with Example 5, Section 1-5, where the solubility product of silver chloride is determined in a cell using a silver and a silver chloride electrode.)

Anions can be detected by means of a solution saturated with a metal salt of the anion and an electrode of the metal. A silver chloride electrode can thus be used to measure the activity of chloride ion in the cell shown in Fig. 2-5. Hydroxyl ions can be detected with a glass electrode, since the product of hydrogen and hydroxyl ion activities is fixed by the self-dissociation equilibrium of water.

The several equilibrium constants involved in the dissociation of polyprotic acids or the formation of complex ions can be measured by potentiometric methods. By titrating one reacting species with the other in the presence of an indicator electrode reversible to one of the species, it is possible to obtain the concentration of that species under a number of conditions. A plot of the experimental data is then fitted by a theoretical curve, the best fit determining the values of the various equilibrium constants. (See Section 9-3.)

2-3 CONDUCTIVITY METHODS

The ease with which an ionic solution conducts electricity depends upon the concentration of ions present in the solution, and to a lesser extent upon the nature of the ions. If one of the species in an equilibrium is an undissociated molecule or a slightly soluble salt, the conductivity of the solution will be a measure of the total number of ions in solution, and in a sufficiently simple system, measurement of the conductivity can give all the equilibrium concentrations.

From 1865 to 1910, Kohlrausch, Ostwald, and Arrhenius used this technique to determine the ion-product of water, the dissociation constants of weak acids and bases, and the solubility products of salts. Many of these measurements were surprisingly accurate, and have been verified by modern studies using much more sophisticated techniques.

Equivalent conductance. An important parameter in discussing the conductivity of solutions is the *equivalent conductance*, Λ , defined as follows: In a cell where the electrodes are 1 cm square and 1 cm apart, the specific conductance κ (reciprocal of the resistance, units ohm^{-1}) of a salt solution of concentration C moles/liter is given approximately by the relation

$$\kappa = \frac{\Lambda z C}{1000},$$

where z is the total number of positive charges on the ions from one formula unit of the salt. The concentration of the solution is zC *equivalents*/liter. The proportionality factor Λ is called the equivalent conductance of the solution, and has units $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{equivalent}^{-1}$. The factor of 1000 appears in the equation to convert from liters to cubic centimeters.

In the period from 1869 to 1880 Kohlrausch and his coworkers measured very carefully the conductances of a large variety of solutions, and discovered that they fell naturally into two classes. The first type, *strong* electrolytes, had an equivalent conductance that varied only slightly with

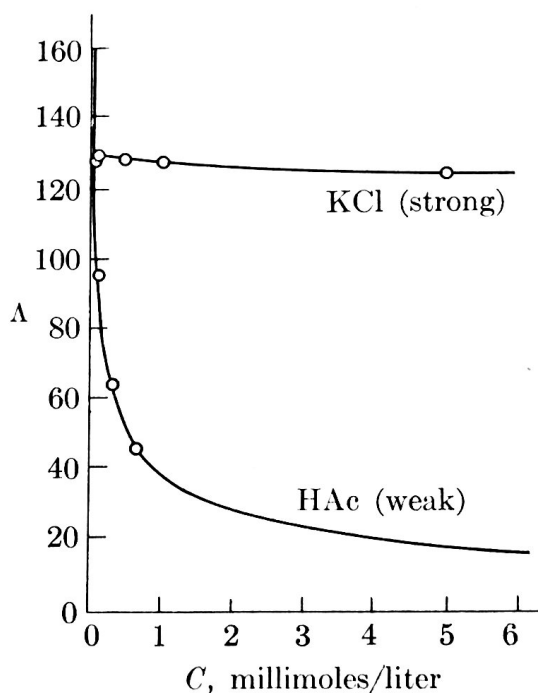


FIG. 2-7. Equivalent conductance as a function of concentration for a weak electrolyte (acetic acid) and a strong electrolyte (potassium chloride). Circles are experimental points. (Data from Nernst, *Theoretical Chemistry*. New York: Macmillan, 1923.)

the concentration of the solution. Salts such as sodium chloride, potassium nitrate, and sodium acetate; acids such as hydrochloric and nitric; and bases such as sodium and potassium hydroxide all fell into the class of strong electrolytes. The other type, *weak* electrolytes, had an equivalent conductance that varied markedly with the concentration of the solution. Acetic and hydrofluoric acids were typical weak electrolytes. Some of the experimental results are shown in Fig. 2-7. Note that for KCl, a strong electrolyte, the equivalent conductance is almost independent of the concentration of the solution. The curve through the data is the extrapolation curve

$$\Lambda = \Lambda_0 - A\sqrt{C} = 130.2 - 79\sqrt{C},$$

where C is the concentration in moles/liter, A is an empirical constant, and $\Lambda_0 = 130.2$ is the extrapolated value of the equivalent conductance at infinite dilution.

On the other hand, the equivalent conductance of the weak electrolyte acetic acid is very small at high concentrations and very large at low concentrations. This effect results from the dissociation of molecular acetic acid into acetate ions and hydrogen ions being governed by a chemical equilibrium.

Kohlrausch's law of independent migration. For strong electrolytes, the extrapolated value Λ_0 of the equivalent conductance at infinite dilution (intercept at $\Lambda = 130.2$ of the KCl curve in Fig. 2-7) can be considered to be the sum of independent contributions of the two ions. This is Kohlrausch's law of *independent migration* of ions. Kohlrausch showed that Λ_0 for one strong electrolyte could be very closely approximated by combining the values for three other strong electrolytes. For sodium nitrate, the measured value of Λ_0 is 105.33, and the calculated value is

$$\begin{aligned} \text{NaCl} + \text{KNO}_3 - \text{KCl} &= \text{NaNO}_3 \\ \Lambda_0 &= 108.99 + 126.50 - 130.10 = 105.39 \end{aligned}$$

assuming that the salts consist of ions that migrate independently.

Ostwald's dilution law. Ostwald used this law to estimate the equivalent conductance of acetic acid at infinite dilution. Sodium acetate is a strong electrolyte, and its equivalent conductance at infinite dilution can easily be found, by extrapolation, to be 87.4. If this is combined with values for hydrochloric acid and sodium chloride,

$$\begin{aligned} \text{NaAc} + \text{HCl} - \text{NaCl} &= \text{HAc} \\ \Lambda_0 &= 87.4 + 379.4 - 109.0 = 357.8 \end{aligned}$$

a value of $\Lambda_0 = 357.8$ can be obtained for acetic acid. The ratio of the

conductance of acetic acid at a measured concentration to this estimated value when it is completely dissociated is taken to be the degree of dissociation of the acid:

$$\alpha = \frac{[\text{Ac}^-]}{C} = \frac{\Lambda}{\Lambda_0}.$$

Knowing the concentration of acid C and the measured equivalent conductance Λ , one easily obtains the concentration of acetate ions:

$$[\text{Ac}^-] = C \frac{\Lambda}{\Lambda_0}.$$

If only pure acetic acid and water are present in the solution, one hydrogen ion is formed for each acetate ion:

$$[\text{H}^+] = [\text{Ac}^-] = \alpha C.$$

The concentration of undissociated acid is obtained by difference:

$$[\text{HAc}] = C - [\text{Ac}^-] = (1 - \alpha)C.$$

The values obtained experimentally were found to obey the equilibrium relation:

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{\alpha^2 C}{1 - \alpha} = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)} = 1.78 \times 10^{-5}.$$

This is Ostwald's dilution law. The solid curve for acetic acid in Fig. 2-7 was calculated by means of this equation.

Solubility from conductance measurements. Similarly, for pure water, the concentrations of hydrogen ions and hydroxyl ions must be equal. By measuring the specific conductance ($0.043 \times 10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$) of the purest water obtainable, Kohlrausch obtained the ion product of water: $K_w = 1.17 \times 10^{-14}$ at 25°C .

A saturated solution of pure barium sulfate in this ultrapure water had a specific conductance $2.785 \times 10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. Subtracting the conductance of the pure water, and making use of the equivalent conductances of other barium and sulfate salts to estimate the equivalent conductance of barium sulfate at infinite dilution, Kohlrausch was able to calculate the concentration of barium and sulfate ions in the saturated solution to be

$$0.957 \times 10^{-5} \text{ mole/liter.}$$

The solubility product of barium sulfate was thus

$$K_{s0} = [\text{Ba}^{++}][\text{SO}_4^{--}] = 0.917 \times 10^{-10},$$

which is in agreement with measurements based on solubility measured directly.

Ion-pair formation. Conductivity measurements can be used to study the formation of ion pairs in concentrated solutions. Electrostatic interactions between ions of opposite sign cause them to group together and to move more slowly under the influence of the electric field. By using more sophisticated theories of conductance in which the viscous drag of the water molecules is accounted for, it is possible to measure the equilibrium constant for ion-pair formation.

2-4 NONIDEALITY, TEMPERATURE, AND SOLVENT EFFECTS

According to the solubility-product law, the solubility of a salt should be unaffected by the addition of a salt having no ions in common with it. This is not in fact the case. Figure 2-8 shows the solubility of silver iodate in solutions containing added potassium iodate and potassium nitrate. As is predicted by the solubility-product law, the solubility of the salt in potassium iodate solutions decreases to a great extent as the concentration of potassium iodate is increased. However, the solubility of silver iodate in solutions of potassium nitrate is seen to *increase*, not remain constant, as the concentration of potassium nitrate is increased. This increase is a result of the interionic forces resulting from the addition of extraneous ions to the solution, even though no chemical reaction occurs between the ions of potassium nitrate and those of silver iodate.

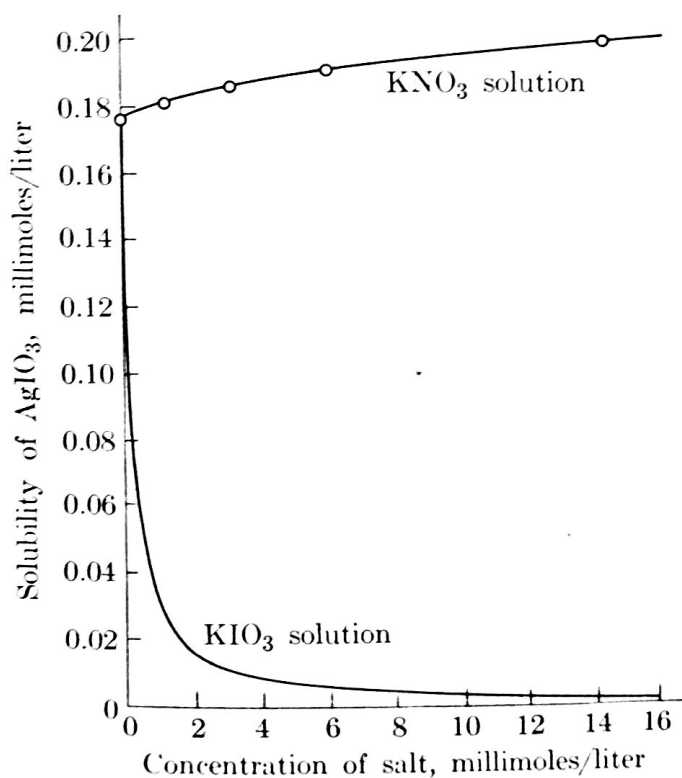


FIG. 2-8. Effect of added salt on the solubility of AgIO₃. The circles are experimental points obtained in potassium nitrate solutions. The curve for potassium iodate solutions was calculated from the solubility product of silver iodate. [Data from Kolthoff and Lingane, *J. Phys. Chem.* **42**, 133 (1938).]

Activity coefficients. In accordance with these observations, the solubility-product law can be written

$$K_{s,0} = \{Ag^+\} \{IO_3^-\} = [Ag^+][IO_3^-]\gamma_+\gamma_-, \quad (1)$$

where the activity of the silver ion is set equal to its concentration times an *activity coefficient* γ_+ , and the activity of the iodate ion is written as the product of its concentration and an activity coefficient γ_- . In very dilute solutions, the activity approaches the concentration, and the activity coefficients become unity.*

Experimentally, we can determine only the product $\gamma_+\gamma_-$ since we cannot isolate individual ions, but must always deal with electrically neutral solutions. Therefore, the activity coefficients of salt solutions are given as the geometric mean

$$\gamma_{\pm} = \sqrt{\gamma_+\gamma_-}.$$

This mean activity coefficient is found to depend on the total *ionic strength* I of the solution, defined to be

$$I = \frac{1}{2} \sum_i C_i z_i^2; \quad (2)$$

that is, the concentration C_i of each ion (i) is multiplied by the square of its charge z_i , all the terms for the various ions in solution are added together, and half the resultant is the ionic strength. For a simple salt like KNO_3 , the ionic strength is equal to its concentration:

$$I = \frac{1}{2}([K^+] \cdot 1^2 + [NO_3^-] \cdot [-1]^2),$$

$$I = [K^+] = [NO_3^-] = C.$$

For the mixture of potassium nitrate and silver iodate, the ionic strength is the sum of the concentrations of the two salts:

$$I = \frac{1}{2}([K^+] + [NO_3^-] + [Ag^+] + [IO_3^-]),$$

$$I = C_{KNO_3} + C_{AgIO_3}.$$

Thus by adding various amounts of potassium nitrate to saturated silver iodate solutions, the ionic strength of the solution is varied at will.

* The symbol f is sometimes used to distinguish activity coefficients based on concentration in moles per liter from activity coefficients based on weight-molality (moles per kilogram of water) which are given the symbol γ . Except in very concentrated solutions, these are nearly equal.

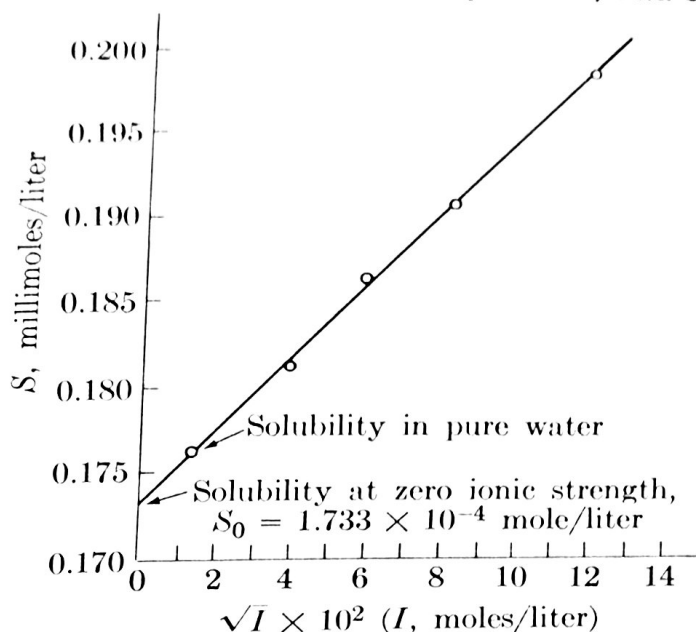


FIG. 2-9. Extrapolation of solubility to zero ionic strength. The circles are the same experimental points that were plotted in Fig. 2-8.

Activity coefficients from solubility. The activity coefficient γ_{\pm} can be calculated as follows: The measured solubilities are extrapolated (Fig. 2-9) to zero ionic strength, where $\gamma_{\pm} = 1$, giving a value of

$$S_0 = 1.733 \times 10^{-4} \text{ mole/liter}$$

for the solubility at zero ionic strength. The thermodynamic (activity) solubility product is calculated from this solubility to be

$$K_{s_0}^0 = S_0^2 = 3.00 \times 10^{-8} \text{ mole}^2/\text{liter}^2.$$

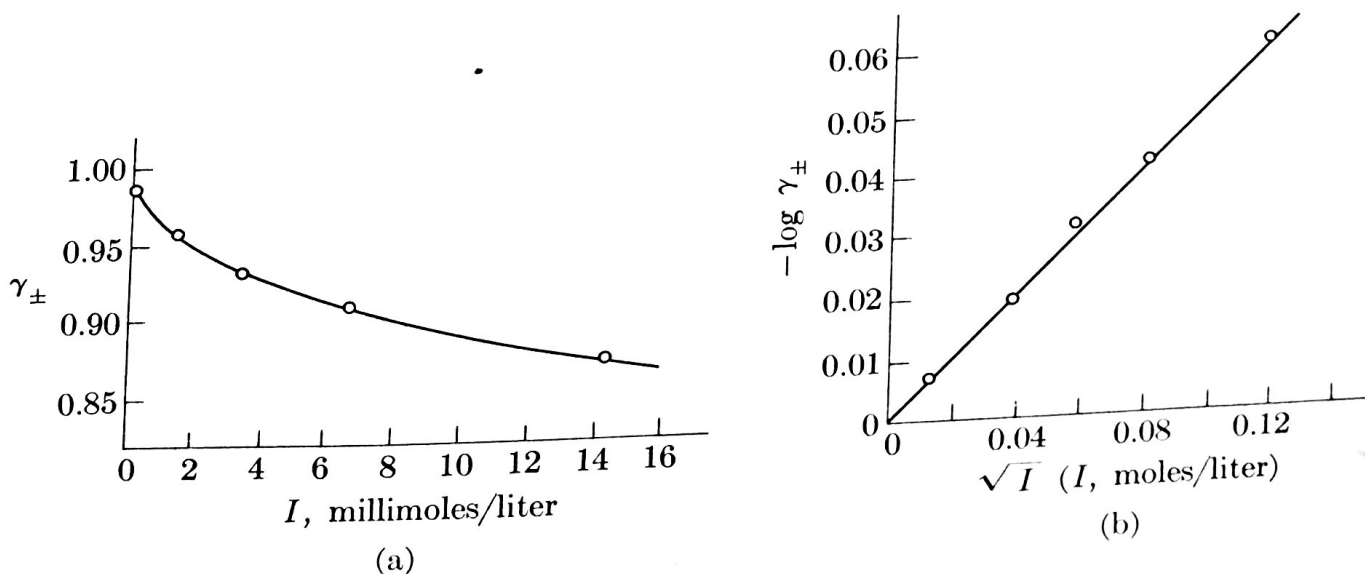


FIG. 2-10. (a) Variation of activity coefficient for silver iodate in potassium nitrate solutions. The circles are the same experimental points that were plotted in Fig. 2-8. (b) Fit of experimental activity-coefficient values (circles) to the Debye-Hückel limiting law: $-\log \gamma_{\pm} = \frac{1}{2}\sqrt{I}$.

Then the mean activity coefficient is calculated at each concentration from the measured solubility S by means of relation (1):

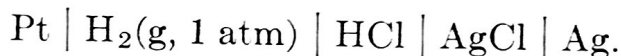
$$\gamma_{\pm}^2 = \gamma_+ \gamma_- = \frac{K_{s0}^0}{[\text{Ag}^+][\text{IO}_3^-]} = \frac{K_{s0}^0}{S^2}. \quad (3)$$

These activity coefficients are plotted in Fig. 2-10 as a function of the ionic strength. The measured values of γ_{\pm} are fitted quite closely by the equation

$$\log_{10} \gamma_{\pm} = -\frac{1}{2}\sqrt{I}, \quad (4)$$

which is the line drawn through the data in Fig. 2-10(b). This form is theoretically predicted by the Debye-Hückel theory (Section 12-2) with a coefficient of 0.509 at 25°C, instead of exactly one-half.

Measurement of standard potential by extrapolation. In the same way that the solubility of a salt can be extrapolated to zero ionic strength to get the activity equilibrium constant, the potential of a cell can be extrapolated to infinite dilution to obtain the standard potential. Consider the cell shown in Fig. 2-5, when the electrolyte is pure hydrochloric acid:



For this cell, the Nernst equation has the form

$$E = E^0 - 0.05915 \log \{ \text{H}^+ \} \{ \text{Cl}^- \}.$$

Since in pure hydrochloric acid,

$$[\text{H}^+] = [\text{Cl}^-] = C_{\text{HCl}},$$

we may rewrite this equation as follows:

$$E + 0.1183 \log C_{\text{HCl}} = E^0 - 0.1183 \log \gamma_{\pm}. \quad (5)$$

The left-hand side of Eq. (5) contains only measurable quantities; C_{HCl} is known from the amount of HCl put in the solution; E is the measured potential of the cell at this concentration.

If the electrolyte behaved ideally, the right-hand side of the equation should be a constant, equal to the standard potential. In fact, as can be seen from Fig. 2-11, the quantity on the left-hand side of Eq. (5) varies slightly with the concentration of HCl. Extrapolation to infinite dilution (zero concentration), as we did for the solubility product in Fig. 2-9, gives the standard potential E^0 , since by definition, $\gamma_{\pm} = 1$ at infinite dilution.

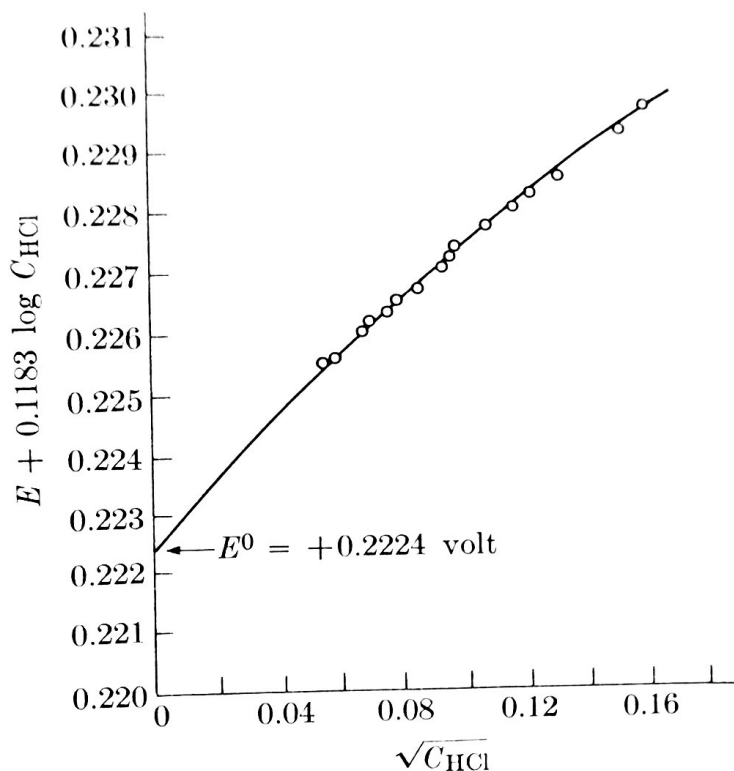


FIG. 2-11. Extrapolation of cell potential to infinite dilution in order to obtain the standard potential of the silver-silver chloride electrode. [Data from Harned and Ehlers, *J. Am. Chem. Soc.* **54**, 1350 (1932)].

The value obtained,

$$E^0 = +0.2224 \text{ volt,}$$

is the standard electrode potential of the silver-silver chloride electrode as well as the standard potential of this cell.

Potentiometric measurement of activity coefficients. This same cell can be used to determine values of γ_{\pm} for HCl, once E^0 has been determined. Using the known value of E^0 and the measured value of E in a solution of a given concentration C_{HCl} , one can calculate the activity coefficient from (5):

$$\log \gamma_{\pm} = \frac{E^0 - E}{0.1183} - \log C_{\text{HCl}}.$$

Extremely accurate measurements have been made of the activity coefficient of HCl in water and in mixtures of water with other solvents, in order to test the various theories of electrolyte behavior. Figure 2-12 is a plot of the values obtained for the mean activity coefficient of hydrochloric acid in water at 25°C by Harned and Ehlers in 1933. Note that the limiting law of Debye and Hückel (Eq. 4) is approximately true in dilute solutions, but that in more concentrated solutions the activity coefficient increases and actually exceeds unity in very concentrated solu-

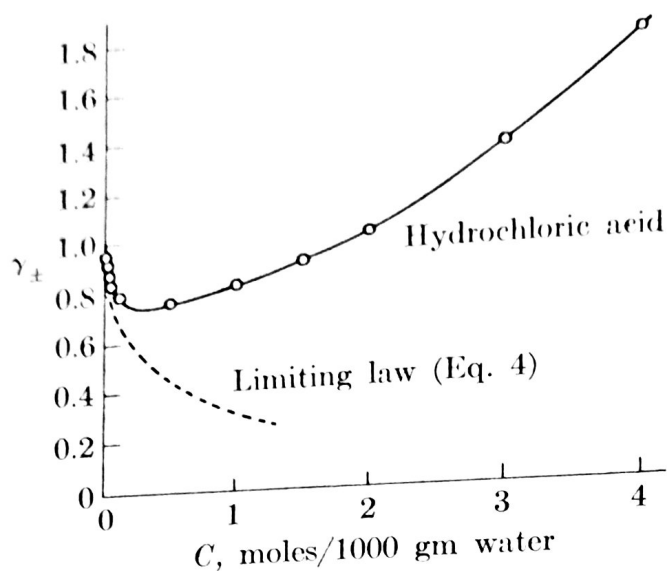


FIG. 2-12. Activity coefficient of hydrochloric acid in concentrated solutions. Note that the limiting law is not obeyed. (Data from Harned and Owen, *Physical Chemistry of Electrolyte Solutions*. New York: Reinhold, 1958, p. 716.)

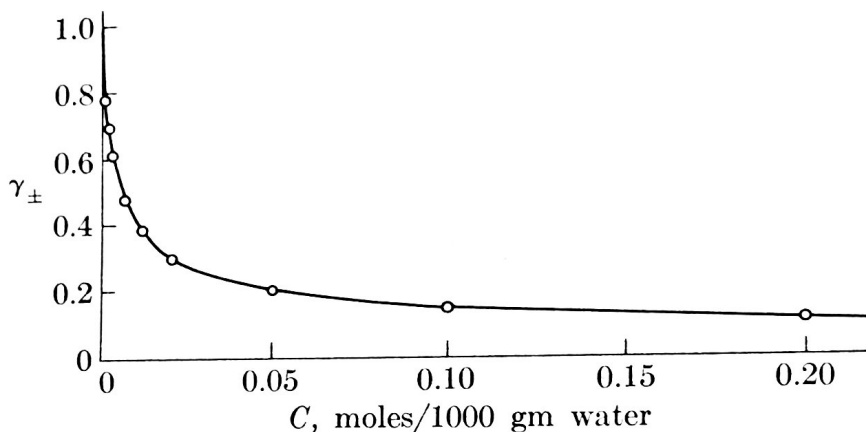


FIG. 2-13. Activity coefficient of zinc sulfate. Note that the values are much smaller than for hydrochloric acid. (Data from Harned and Owen, *op. cit.*, p. 564.)

tions. Theoretical relations taking into account the sizes of the ions are able to predict this dependence on concentration (see Section 12-2).

For polyvalent ions, the activity coefficients are smaller as well as more strongly dependent on concentration, most likely due to ion-pair formation (see Section 12-1). The measured mean activity coefficient of zinc sulfate is shown in Fig. 2-13.

Temperature dependence of equilibrium constant. Although most studies of ionic solutions have been made near room temperature (25°C), it is interesting to note the effect of temperature on these equilibria. The solubility products of most salts increase steadily with temperature. This is consistent with the observation that the dissociation of most crystals

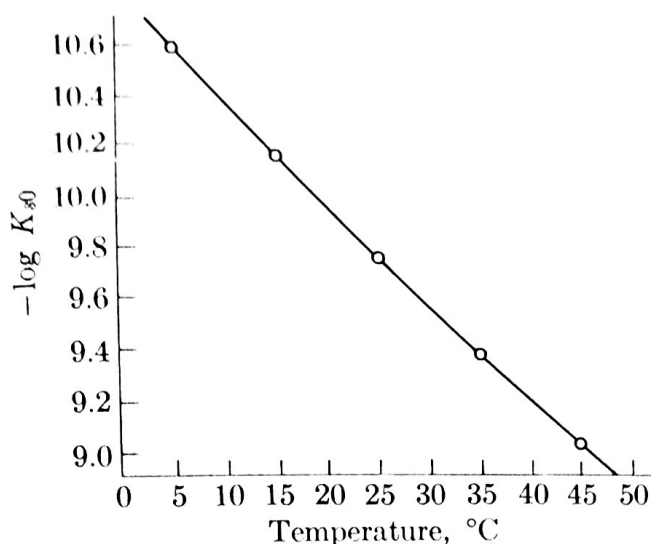


FIG. 2-14. Temperature dependence of the solubility product of silver chloride. [Data from Owen and Brinkley, *J. Am. Chem. Soc.* **60**, 2229, 2233 (1938).]

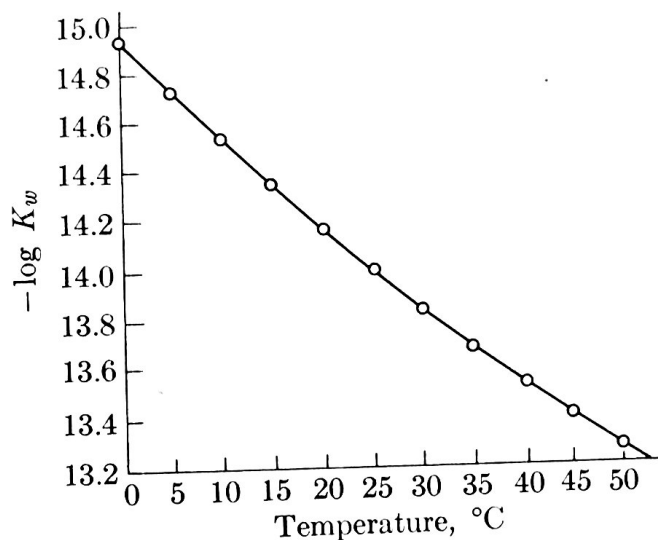


FIG. 2-15. Temperature dependence of the ion product of water. (Data from Harned and Owen, *op. cit.*, p. 638.)

into hydrated ions requires considerable energy, and thus the solution process is *endothermic* (requires heat). The temperature dependence of the solubility product of silver chloride is shown in Fig. 2-14. A plot of $-\log K_{s0}$ as a function of temperature is almost linear and very easily interpolated.

The temperature dependence of the ion product of water behaves similarly (Fig. 2-15), since the dissociation of water to its ions also is an endothermic process.

The temperature dependence of the ionization constants of weak acids is not so simple, since many of them go through a transition from exothermic to endothermic near room temperature. This is reflected in a

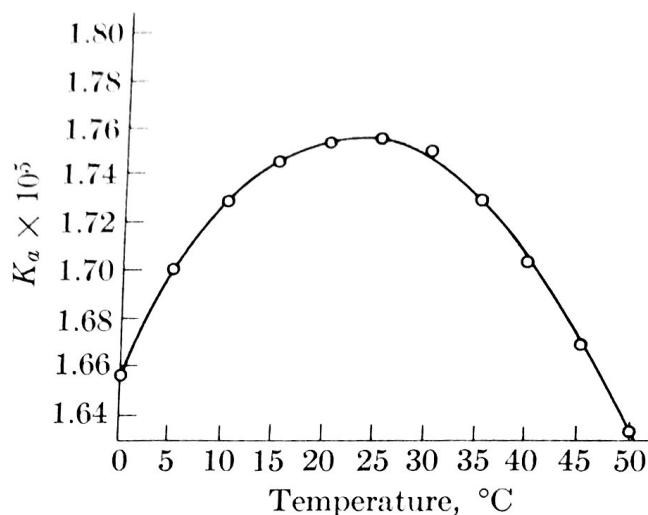


FIG. 2-16. Temperature dependence of the ionization constant of acetic acid. (Data from Harned and Owen, *op. cit.*, p. 755.)

maximum in the temperature dependence of K_a . Figure 2-16 is a plot of K_a for acetic acid as a function of temperature. Note that the maximum occurs very close to 25°C.

It is possible to predict the temperature dependence of an equilibrium constant if sufficient thermodynamic data are available, but in practical cases, graphical extrapolation and interpolation of K in the region around 25°C can be done accurately enough for most purposes from only a few experimental points, or by analogy with similar compounds.

Nonaqueous solutions. The addition of other solvents, such as alcohol, to water may affect the equilibria in a solution in two ways. First, the activity of water itself will be reduced by the presence of the foreign solvent, and second, the activity coefficients of the various ions will be changed because the dielectric constant of the medium in which they move will have changed. Such solutions may be of practical interest, since the solubility of many salts is much less in mixed aqueous-alcohol solutions than it is in pure water. Such solutions are also of theoretical interest since they provide a controlled way of varying the dielectric constant of the solvent in order to test the theories of ionic interaction.

Reactions in completely nonaqueous solutions are becoming more and more important in analytical methods, since titrations of very weak acids and bases, which are impossible to carry out in water because its dissociation produces too great a concentration of hydrogen or hydroxyl ion, become very simple in organic solvents such as ethylene glycol, methyl isobutyl ketone, or ethanol, which dissociate hardly at all. Equilibria in nonaqueous solutions will be considered briefly in Section 12-4, when we discuss Hammett's acidity function, but generally speaking, nonaqueous solutions are outside the scope of this book.

Contents

1. INTRODUCTION

1-1 The equilibrium state	1
1-2 The equilibrium constant	7
1-3 Forms for the equilibrium constant expression	9
1-4 Free energy and the equilibrium constant	15
1-5 Electrode potentials	19

2. MEASUREMENT OF EQUILIBRIUM CONSTANTS

2-1 Direct analysis	34
2-2 Potentiometric methods	40
2-3 Conductivity methods	43
2-4 Nonideality, temperature, and solvent effects	47
2-5 Precision and accuracy of equilibrium data	55

3. MATHEMATICAL METHODS USED IN EQUILIBRIUM CALCULATIONS

3-1 Introduction	61
3-2 Mass balances	63
3-3 Charge balances	66
3-4 Solving simultaneous equations	69
3-5 Approximations on the equations	71
3-6 Solving quadratic equations	75
3-7 Solving polynomial equations of higher degree	79
3-8 Logarithmic functions	85

4. STRONG ACIDS AND BASES

4-1 The ionization of water	90
4-2 Calculation of pH in solutions of strong acids and bases	93
4-3 Titration of strong acids and strong bases	100
4-4 Titration error	105

5. WEAK MONOPROTIC ACIDS AND BASES

5-1 Ionization of a weak acid	112
5-2 Graphical representations	120
5-3 Ionization of a weak base	128
5-4 Generalized acids and bases	134
5-5 Mixture of a strong and weak acid	138

Ionic Equilibrium

A Mathematical Approach

To the memory of
WILLIAM MOFFITT
1925–1958

*A giant among theoretical chemists
cut down before his prime*

Ionic Equilibrium

A Mathematical Approach

JAMES NEWTON BUTLER

*Senior Scientist in Chemical Physics at
TYCO Laboratories Inc., Waltham, Mass.*

*Formerly Department of Chemistry
University of British Columbia
Vancouver, B.C.*



ADDISON-WESLEY PUBLISHING COMPANY

Reading, Massachusetts

Menlo Park, California · London · Amsterdam · Don Mills, Ontario · Sydney

Copyright © 1964

ADDISON-WESLEY PUBLISHING COMPANY, INC.

Printed in the United States of America

ALL RIGHTS RESERVED. THIS BOOK, OR PARTS
THEREOF, MAY NOT BE REPRODUCED IN ANY FORM
WITHOUT WRITTEN PERMISSION OF THE PUBLISHER.

Library of Congress Catalog Card No. 63-14686

ISBN 0-201-00730-4
GHIJKLMNOP-CO-798765