Ionic and Covalent Bonding

Conductivity of Solutions of Ionic and Covalent Compounds

Purpose

• Use electrical conductivity as a way of discriminating between substances with ionic and covalent bonding.

• Compare the electrical conductivity of substances in the pure solid (or liquid) state and in solution.

• Measure the effects of solvent properties on the dissociation of substances with polar covalent bonding, such as HCl.

• Measure changes in conductivity that result from the reaction of ionic substances to form products that are weakly ionized or insoluble.

Pre-Lab Preparation

Ionic, polar covalent, and covalent bonding

When an active metal reacts with an active nonmetallic element, the nonmetal atom becomes negatively charged when one or more electrons transfer from the metal, which in turn becomes positively charged. In general, when atoms act cooperatively in this fashion, each element winds up with a closed-shell electron configuration, like the electronic configuration of the noble gases of Group VIII (18). For the reaction of a sodium atom and a chlorine atom, we can represent the changes in the valence shells of the atoms by electron-dot formulas; for example,

\[
\text{Na}^+ + \cdot\text{Cl}^- \longrightarrow \text{Na}^+ \cdot\text{Cl}^-;
\]

Such electrically charged atoms are called ions, and in the product Na\(^+\)Cl\(^-\), the Na\(^+\) ion has the same electron configuration as a neon atom, while the Cl\(^-\) ion has the electron configuration of argon. The bonding force between ions, due primarily to the attraction of unlike electric charges, is called an ionic bond.

However, when two elements of similar electronegative character react, they form electron pair bonds, mutually shared by both of the atomic nuclei. For example,

\[
\text{H} \cdot + \cdot\text{H} \longrightarrow \text{H} \cdot\text{H} \quad \text{or} \quad \text{H}_2
\]

\[
2\text{H} \cdot + \cdot\text{O}^- \longrightarrow \cdot\text{O}^-\cdot\text{H} \quad \text{or} \quad \text{H}_2\text{O}
\]

Such a bond is called a covalent bond. In the second example, the water molecule, the oxygen atom is more electronegative than hydrogen, so the O—H bond is slightly polar, or partially ionic, in character. We could describe the water molecule as having polar covalent bonding. Note that the two types of bonds found in Na\(^+\)Cl\(^-\) and molecular H\(_2\) are really two extremes of a continuum—the purely ionic bond at one extreme and the purely covalent bond at the other. In between are the polar covalent or partially ionic bonds.

Structure and bond type

Substances with covalently bonded atoms generally have discrete or separate molecules packed together in the crystal structure of the solid.\(^1\) If soluble in water or other suitable solvent, these substances dissolve to form a solution of electrically neutral molecules; the resulting solutions do not conduct an electric current. Examples of such nonelectrolytes are common table sugar (sucrose, C\(_{12}\)H\(_{22}\)O\(_{11}\)) and acetone (CH\(_3\)COCH\(_3\)).

Salts, as well as acids and bases, have either ionic bonds or bonds that are quite polar. In solid salts, the ions are packed together so that ions of positive charge are surrounded by ions of negative charge and vice versa. As a result, ions form the structural units of the crystal. When melted by heat, vacancies

\(^1\)Omitted from discussion here are substances called network solids, which form covalently bonded giant molecular networks such as silica (SiO\(_2\)) and carbon in the form of diamond, as well as metals and intermetallic compounds.
or holes are introduced into the rigid crystal structure, allowing the ions to move about so that the melted salt becomes fluid and a good electrical conductor. When these substances dissolve in water, the ions likewise separate as independently moving particles, and the solutions are electrical conductors.

So, in equations throughout this manual, we write the formulas of such substances in solution, or in the molten state, as separate ions. Examples of such electrolytes are sodium hydroxide (NaOH), which dissociates into Na\(^+\) and OH\(^-\) ions, and potassium sulfate (K\(_2\)SO\(_4\)), which dissociates into K\(^+\) and SO\(_4^{2-}\) ions in a 2:1 ratio.

**Strong acids and bases and many salts ionize completely in dilute aqueous solution.** (In fact, we may regard this as a definition of a strong acid or base—it is a substance that is completely dissociated into ions in solution.) In solutions of weak or less active acids and bases, a substantial fraction of the dissolved substance is present in molecular form. So although the total concentration may be high, the concentration of ions is low. Partial ionization (or dissociation) accounts for their lower conductivity. Solids that are only slightly soluble, even though they may be completely dissociated into ions in solution, have low electrical conductivity because of their limited solubility.

**The role of the solvent in dissociation reactions**

Most of the solution reactions we have studied have been in aqueous solution. However, it is important to remember that nonaqueous solvents are often used and that the dissociation of acids, bases, and salts depends very much on the properties of the solvent. For example, the dissociation of an acid involves the transfer of a proton from the acid to the solvent. Therefore, the extent of dissociation of an acid will depend on the intrinsic basicity of the solvent. Although acetic acid is only partially dissociated in water, it is completely dissociated in a more basic solvent, such as liquid ammonia.

\[
\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-.
\]

**PARTIAL REACTION**

\[
\text{HC}_2\text{H}_3\text{O}_2 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_3\text{O}_2^-.
\]

**COMPLETE REACTION**

The dielectric constant of the solvent and the solvation energy of ions in a solvent are also important. If two ions of opposite charge are placed in a vacuum, the force between them is given by Coulomb's law,

\[
\text{force} = \frac{kq_1 q_2}{r^2}
\]

where \(k\) is a constant, \(q_1\) and \(q_2\) are the charges on the ions, and \(r\) is the distance between the centers of the ions. When the two ions are immersed in a material medium, the force between them is reduced in inverse proportion to the dielectric constant, \(\varepsilon\), of the medium, as expressed in the equation

\[
\text{force} = \frac{kq_1 q_2}{e \varepsilon r^2}
\]

Therefore, the total energy expended in separating the ions will decrease as the dielectric constant increases. That means that a solvent with a large dielectric constant will tend to promote the dissociation of an ionic solute more than will a solvent with a small dielectric constant. The hydrocarbons (with \(\varepsilon < 5\)) do not promote the dissociation of ionic solutes. Water (with \(\varepsilon \approx 80\)) is a good solvent for ionic solutes.

Solvation energy is also an important factor. When an ionic solute dissociates in a solvent, the total energy of the reaction may be thought of as composed primarily of two terms: (1) the energy expended in the separation of the positive and negative ions of the crystal lattice (called the lattice energy), and (2) the solvation energy liberated by the association of the ions with solvent molecules. Solvation energy is the result of the interaction between the electric charges of the ions and the electric dipoles of the solvent molecules. When there is enough solvation energy to offset the energy expended in separating the positive and negative ions, the ionic solute will dissociate in the solvent.\(^2\) A polar solvent, therefore, will tend to promote the dissociation of an ionic solute.

**Ionic equations**

In describing a reaction in which ions are either the reactants or products, we often focus our attention on the essential changes, ignoring "spectator" ions that are not participating in the chemical reaction. We will call this abbreviated description the net ionic equation.

For example, the reaction of aqueous NaOH with aqueous HNO\(_3\) could be written in full as

\[
\text{Na}^+ + \text{OH}^- + \text{H}_3\text{O}^+ + \text{NO}_3^- \rightarrow \text{Na}^+ + \text{NO}_3^- + 2 \text{H}_2\text{O}
\]

\(^2\)A more careful examination of the factors that determine the solubility of a solute must include the effect of changes in the solvent structure that occur when ions are introduced, causing polar solvent molecules to cluster around the ions. The entropy change of the system is a measure of this effect, which can be strong enough that salts such as NaCl will dissolve even though the lattice energy is greater than the solvation energy.
which we will call the total ionic equation. Note that in this reaction, neither the Na\(^+\) nor the NO\(_3\)\(^-\) has reacted; both appear as separate particles on each side of the equation. When these spectator ions are omitted, the equation that expresses the essential change is the net ionic equation:

\[
\text{OH}^- (aq) + \text{H}_2\text{O}^+ (aq) \rightarrow 2 \text{H}_2\text{O}(l)
\]

(Note that the net ionic equation is still a balanced equation with respect to charge and the number of each kind of atom. The spectator ions that are not shown are also still contributing to the electrical conductivity of the solution.)

Typical ionic reactions are those in which ions unite to form a weakly ionized or insoluble substance. For example, if a weakly acidic substance such as ammonium chloride, NH\(_4\)Cl, reacts with a base such as sodium hydroxide, NaOH, the net change is expressed by

\[
\text{NH}_4^+ (aq) + \text{OH}^- (aq) \rightarrow \text{NH}_3 (aq) + \text{H}_2\text{O}(l)
\]

A typical example of ions uniting to form an insoluble substance is expressed by the equation

\[
\text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq) \rightarrow \text{CaCO}_3 (s)
\]

It makes no difference whether the Ca\(^{2+}\) is derived from calcium chloride, calcium nitrate, or any other soluble calcium salt. Carbonate ion, CO\(_3^{2-}\), could be obtained equally well from sodium carbonate, ammonium carbonate, or any soluble substantially ionized carbonate salt.

Often the net result of an ionic reaction is determined by a competition between two largely undisassociated substances. For example, carbonic acid, H\(_2\)CO\(_3\), is formed when a strong acid acts on a carbonate salt:

\[
\text{CaCO}_3 (s) + 2 \text{H}_2\text{O}^+ (aq) \rightarrow \\
\text{Ca}^{2+} (aq) + \text{H}_2\text{CO}_3 (aq) + 2 \text{H}_2\text{O}(l)
\]

Carbonic acid readily dehydrates to CO\(_2\) and water, so the net ionic reaction is

\[
\text{CaCO}_3 (s) + 2 \text{H}_2\text{O}^+ (aq) \rightarrow \\
\text{Ca}^{2+} (aq) + \text{CO}_2 (g) + 3 \text{H}_2\text{O}(l)
\]

Thus, this reaction is driven to the right by two factors: (1) the production of a very weakly dissociated substance, H\(_2\)O, and (2) the escape of volatile CO\(_2\) gas.

The experimental method: Electrical conductivity

In this experiment, we will measure the electrical conductivity of pure liquid substances and dissolved substances to determine whether there is any solvent-assisted ionic dissociation. We will also try to determine the net result of any reaction that may take place when solutions of ionic substances are mixed.

Solutions of ionic-type substances conduct electric current by the movement of their ions under the influence of an electric field. The faster the ion moves, the greater its ion mobility. At the solution–electrode interfaces, the circuit is completed by electron transfer reactions, because in metal wires the only charge carriers are electrons. For a given applied voltage, the amount of current depends on the concentration of ions and, to a lesser extent, on differences in individual ion mobilities. (Hydrogen ion has an unusually high mobility—five to eight times that of many other ions. To better understand why, see the Consider This discussion at the end of the experiment.) Figure 18-1 shows a simple apparatus for the comparison of electrical conductivities.

We will compare the electrical conductivities of a number of solutions and of the products formed after some chemical reactions, then use the data we obtain to interpret the character of the solutions and the course of any reactions. We will interpret these results in terms of the net ionic equations for the reactions.

### Experimental Procedure

**Special Supplies:** Conductivity apparatus. (Use a commercial conductivity meter or an apparatus constructed as described in the notes that follow and shown in Figure 18-1.)

**Chemicals:** Pure 17 M acetic acid; 6 M acetic acid; 0.1 M acetic acid; methanol (CH\(_3\)OH); 6 M HCl; 0.1 M HCl; toluene; anhydrous HCl in toluene produced by bubbling HCl gas through dry toluene (if gaseous HCl is not available, you may substitute a solution prepared by dissolving pure acetic acid in toluene to make a 1 M solution); 0.1 M HgCl\(_2\); 0.1 M NaOH; 0.1 M NH\(_3\); 0.1 M H\(_2\)SO\(_4\); 0.1 M Ba(OH)\(_2\); 0.1% thymol blue indicator solution; sucrose (s); NaCl(s); CaCO\(_3\)(s) (marble chips); zinc metal (mossy).

**NOTES TO INSTRUCTOR**

**Notes on the Construction and Use of the Conductivity Apparatus Shown in Figure 18-1**

1. Build the circuit in a small aluminum chassis box, with the power cord, fuse, and pilot light on the rear; the banana jacks on the side; and the push-button switch on top. Mount the chassis box on a

3With alternating current (AC), the net chemical reaction at the electrode surface is diminished; at high frequency, the chemical reaction is practically eliminated.
piece of \(\frac{3}{4}\) -in. plywood through which holes have been drilled to allow two pairs of 14-gauge copper wire electrodes (connected in parallel) to protrude about 15 cm. Space the wires about 1 cm apart. All but the bottom 5 cm of the copper wire should be insulated. Fasten a length of \(\frac{1}{2}\)-in.-OD aluminum rod on the underside of the plywood so that the apparatus can be supported by a clamp holder on a ring stand. Connect the aluminum chassis to the green ground lead of the three-wire power supply cord.

2. The voltage across the electrodes is about 6 V AC rms (18 V peak-to-peak) when the push-button switch is depressed, so be careful not to touch the electrodes while the switch is depressed. The 5-ohm, 5-watt resistor limits the current to a safe value if the electrodes are inadvertently shorted.

FIGURE 18-1 | An apparatus for comparing the electrical conductivities of various solutions.
1. Electrolytes and Nonelectrolytes

If you will be using the conductivity apparatus shown in Figure 18-1, read over the preceding notes describing how to use the apparatus. If you will use a commercial conductivity meter, follow your instructor’s directions. When you are confident that you understand how to use the conductivity meter, measure and record the conductivity of the following substances and/or their solutions in water. Determine whether they are largely, moderately, or poorly ionized, or whether they are essentially nonelectrolytes. (For an apparatus like that shown in Figure 18-1, a nonelectrolyte will give a very small current, less than a few microamperes. A completely dissociated strong electrolyte, such as 0.1 M HCl, will typically give a current of more than 100 mA.) Test the pure substance first; then add some water to it and retest. In each case, the magnitude of the current will be a measure of the conductivity of the solid or solution, indicating whether or not the substance contains ions that are free to move.

(a) To begin, test distilled (or deionized) water and tap water. What causes the difference in conductivity? Then test the following substances and their aqueous solutions: methanol (CH₃OH); glacial acetic acid (CH₃COOH); sucrose (table sugar, C₁₂H₂₂O₁₁); sodium chloride (NaCl); and dilute solutions only (not the pure substances) of 0.1 M HCl, 0.1 M NaOH, and 0.1 M HgCl₂. Be sure to dispose of the mercuric chloride, HgCl₂, in the waste container reserved for this purpose. Do not pour it down the drain—it is toxic.

(b) Observe the effect of the solvent on the ionization of HCl in toluene and in water. First test a little pure toluene (C₇H₈) in a thoroughly dry beaker, and then a solution of HCl in toluene. (Use the solution already on your reagent shelf, prepared by bubbling anhydrous HCl through dry toluene—do not add aqueous concentrated HCl to toluene.) Then add 5 mL of deionized water to this solution, mix it well, and repeat the test with the electrodes immersed farther into the lower aqueous layer. (If HCl in toluene is not available, you may substitute a 1 M acetic solution in toluene; the effect is less dramatic because acetic acid is not a strong acid in water like HCl.) Be sure to dispose of the toluene solutions in the waste container reserved for this purpose.

(c) Compare the chemical behavior of 6 M HCl and 6 M acetic acid with your conductivity data. Put three or four marble chips into each of two clean beakers. Add 6 M HCl to one beaker and 6 M acetic acid to the other. Compare the rate of evolution of CO₂ gas. Put one or two pieces of mossy zinc metal into another pair of beakers, add 6 M HCl and 6 M acetic acid, and compare the rates of evolution of hydrogen (H₂) gas. Record your observations and write balanced chemical reactions for each of the four reactions you observed.

2. Typical Ionic Reactions

You will experiment with some ionic reactions to determine the nature of their products. Through conductivity tests of the separate reactants and of the mixture after reaction, you will discover whether the acids, bases, and salts concerned are largely ionized (strong electrolytes) or only moderately ionized (weak electrolytes). For each reaction, write the total ionic equation and the...
net ionic equation that best describes the reaction taking place. This will require careful thinking on your part. Use the following procedures.

(a) 0.01 M HCl with 0.01 M NaOH. These solutions can be prepared by diluting 5 mL of each of the 0.1 M solutions to 50 mL. It is an advantage to use both pairs of electrodes connected in parallel (see Figure 18-1) by placing one pair of electrodes in 0.01 M HCl and simultaneously placing the other pair in an equal volume of 0.01 M NaOH contained in a separate beaker. Then mix the solutions, divide them into two equal portions, and again place the two solutions simultaneously in contact with the two electrode pairs. (This compensates for the dilution effect of mixing two solutions.) Why is the conductivity of the product solution lower than that of the reactant solutions?

(b) 0.1 M acetic acid, HCO2H, with 0.1 M NH3. As in part 2(a), test equal volumes of the separate solutions, mix them, divide the solution into two equal parts, then remeasure the conductivity. Record your measurements.

(c) 0.1 M H2SO4 with 0.1 M Ba(OH)2. Measure and record the conductivity of each solution by itself. Then add two or three drops of 0.1% thymol blue indicator solution to the sulfuric acid solution, and add 0.1 M Ba(OH)2 solution one drop at a time to the sulfuric acid solution, stirring continuously. The sulfuric acid will be exactly neutralized when the indicator changes from its pink form through its yellow (acid) form to its blue (basic) form. If you add too much Ba(OH)2, overshooting the end point, add 0.1 M H2SO4 drop by drop, stirring continuously, until the exact end point—shown by a sharp color change of the indicator—is reached. Now, measure and record the conductivity of this mixture. Write balanced ionic equations to describe the reactions that take place.

CONSIDER THIS

Solutions of strong bases like NaOH and strong acids like HCl have much higher conductivity than a solution of the same concentration of NaCl. By examining a number of examples of this, scientists have discovered that it is the hydronium ion (H3O+) and hydroxide ion (OH–) that are responsible for the higher conductivity.

Conductivity is related to the mobility of an ion (how fast it moves in solution under the influence of an electric field). In order to get from point A to point B in solution, most ions have to physically move from point A to point B, dragging along the cluster of water molecules that surrounds each ion. However, for hydronium ions, the whole hydronium ion does not need to move in order to transfer a positive charge from point A to point B. The way this works is shown in the following diagram:

Imagine that there is a hydronium ion at point A on the left end of a chain of water molecules. The water molecules are loosely associated by hydrogen bonding, as shown by the dotted lines representing the hydrogen bonds. The positive charge can be transferred from the hydronium ion at point A to the water molecule at point B by having three protons hop from one molecule to the next, as indicated by the three arrows. After transfer of the three protons, the water molecule at point B would be transformed into a hydronium ion (H3O+), so the charge associated with a hydronium ion would have moved from point A to point B without physical movement of the whole hydronium ion originally at point A. This rapid proton hopping (or proton transfer) process allows charge to move along much faster than physical movement of the whole ion, such as a Na+ or Cl– ion.

Now, you draw a similar diagram, starting with a hydroxide ion on the right at point B, that shows how the −1 charge associated with a hydroxide ion could move from point B to point A, by shifting protons left to right from one water molecule to the next. (Hydronium ions and hydroxide ions under the influence of the same electric field would move in opposite directions.)