

Subject: Physical Chemistry Lecturer: Shahd Ammar Hatem 1st term – Lect. Electrolytes

#### 1. Introduction

The science that deals with the relation between electricity and chemical change is called electrochemistry. Many chemical reactions that take place on their own release electrical energy, and some of these reactions are the basis for the batteries and fuel cells that provide electric power. Conversely, electric current also can bring about chemical reactions that do not occur on their own. The principal application of this process is to break down more complex compounds into simpler ones or to separate compounds into their elements. This is done in a process called electrolysis and in an apparatus called an electrolytic cell. The name electrolysis comes from Greek words that mean "loosening by electricity."

The use of electric current to produce a chemical change is a powerful aid to science and industry. In some cases, it is the only way to obtain metals from their ores quickly, cheaply, and free of impurities. Many gases, salts, and other products are also made this way. In a variation called electroplating, electrolysis can deposit films of metal from solution on objects with microscopic accuracy.

A typical electrolytic cell consists of two solid electrical conductors placed apart from each other into a container of liquid. The electrical conductors, which are often rods or plates of metal or graphite, are called electrodes. They are connected by wire to the terminals of a battery or another source of direct current. The electrode connected to the negative terminal is termed the cathode; the electrode connected to the positive terminal is the anode. The liquid in which the electrodes are immersed must be or must contain a substance that is electrically conducting. The electrically conducting substance is called an electrolyte. Certain liquids, such as molten sodium chloride (common salt heated above its melting point), are good conductors in themselves. Others, such as pure water, are poor conductors and must have an electrolyte dissolved in them. In many kinds of electrolytic cell with an electrolyte dissolved in water, it is the electrolyte that undergoes chemical change. Under proper conditions, however, water itself can also be electrolyzed,

during which it becomes chemically dissociated into its elements, hydrogen and oxygen.



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#### 2. How electrolytes dissolve

The most common electrolytic cells contain water with a dissolved electrolyte. Water's chemical neutrality allows it to dissolve acids, bases, and salts, which are the most familiar kinds of electrolytes. In addition, water's use as a solvent usually does not produce great heat or other violent reactions.

An electrolyte dissolves in water by dissociation—that is, the substance breaks down into its electrically charged constituent particles, called ions. Ions can transport electrical charge from place to place, and it is the presence of these ions in solution that makes water more electrically conductive. An ion having a negative (-) charge is called an anion because, in an electrolytic cell, anions are attracted to the positively charged anode. An ion having a positive (+) charge is called a cation; these particles migrate through the solution to the negatively charged cathode.

Water has the ability to dissociate electrolytes because the water molecule is electrically polar. It has positively and negatively charged portions, which attract and pull apart ions of opposite charge in the electrolyte. Sodium chloride (NaCl), for example, is dissociated into sodium cations (Na $^+$ ) and chloride anions (Cl $^-$ ). Sodium hydroxide (caustic soda; NaOH), a base, dissociates into sodium cations and hydroxyl anions (OH $^-$ ). In such acids as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), the hydrogen atoms form the cations (H $^+$ ), while the remainder forms an anion with a double negative charge (SO<sub>4</sub> $^-$ ).

Which substances will form ions and the type of ions that they form is determined by the tendency of their atoms to gain or lose electrons.

#### 3. Action at the electrolytes

The chemical changes in an electrolytic cell take place at the surfaces of the two electrodes. If it is an electrolyte undergoing the reaction, as cations of the substance reach the negatively charged cathode, they combine with one or more



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electrons supplied by the source of direct current. As a result, they lose part or all of their positive charge and become either new ions with a lower charge or neutral particles. This process is called reduction. At the same time, as anions arrive at the positively charged anode, they give up one or more electrons to the direct current source; they also become new ions or neutral particles. This process is called oxidation. The combined effect of the two processes is the transfer of electrons from the anions-through the wires and power source-to the cations. This overall process is a chemical reaction, specifically an oxidation-reduction reaction. The energy needed to make the reaction happen is supplied by the electric current. An example of such a reaction is the electrolysis of copper chloride (CuCl<sub>2</sub>) dissolved in water, which produces metallic copper at the cathode and chlorine gas at the anode:

In a molten electrolyte, melting frees the ions from their solid crystal structure so that they are able to move around in the liquid without having to be in a solution. When molten sodium chloride is electrolyzed, sodium cations migrate to the cathode, combine with electrons, become reduced, and form sodium metal; chloride anions migrate to the anode, give up electrons, become oxidized, and form chlorine gas.

In the electrolysis of water, the supplied electrical energy overcomes the strength of the bonds holding the hydrogen atoms to the oxygen atoms, causing ionization. At the anode, the oxygen in the water molecules gives up electrons and becomes oxygen gas, while the hydrogen is left in the solution in the form of positively charged ions. At the cathode, the hydrogen ions combine with electrons and become neutral hydrogen gas. The entire process can be summarized in the following reaction:



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#### 4. Uses of electrolysis

Electrolysis is used extensively in industry to extract or purify metals and prepare a variety of other substances. Sodium metal and chlorine gas, which have important commercial and scientific uses, are extracted in the electrolysis of molten sodium chloride. Both chlorine and sodium hydroxide are produced by the electrolysis of brine (a concentrated salt solution). Aluminum metal is extracted electrochemically from alumina that has been refined from bauxite ore. After copper metal is separated from its ores, it is purified in an electrolytic cell in which the anode is a bar of impure cast copper and the cathode is a bar of pure copper. During electrolysis, the copper anode dissolves in the electrolyte solution, and copper atoms are deposited, or plated out, on the cathode. The impurities are left behind either as ions in solution or as sludge at the bottom of the electrolytic cell.

The purification of copper also is an example of electroplating, another commercially important process. Electroplating is used to decorate metals and other materials, to form protective coatings against corrosion, and to deposit metals in precise locations and thicknesses for many industrial purposes. Many metals in addition to copper can be plated on a suitably prepared object, which forms the cathode in the electrolytic cell, or plating tank. Decorative gold and silver coatings, for example, are plated on jewelry and tableware. Zinc that is electroplated on steel objects protects the steel from rusting. Chromium and nickel plating is used both to embellish and to protect the underlying material.

#### 5. Classifying Electrolytes

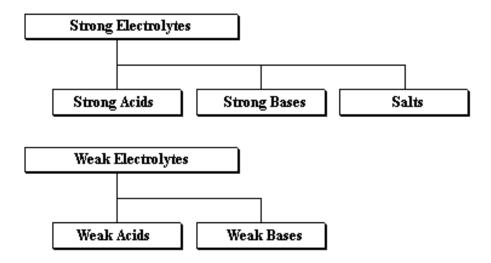
Electrolytes are substances which, when dissolved in water, break up into cations (plus-charged ions) and anions (minus-charged ions). We say they ionize. Strong electrolytes ionize completely (100%), while weak electrolytes ionize only partially (usually on the order of 1–10%). That is, the principal species in solution for strong electrolytes are ions, while the principal specie in solution for weak electrolytes is the un-ionized compound itself. Strong electrolytes fall into three categories: strong acids, strong bases, and salts. (Salts are sometimes also called

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ionic compounds, but really strong bases are ionic compounds as well.) The weak electrolytes include weak acids and weak bases.



Examples of strong and weak electrolytes are given below:

Strong Electrolytes strong acids HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub>,

and H<sub>2</sub>SO<sub>4</sub>

strong bases NaOH, KOH, LiOH, Ba(OH)<sub>2</sub>, and

 $Ca(OH)_2$ 

salts NaCl, KBr, MgCl<sub>2</sub>, and many, many

more

Weak Electrolytes weak acids HF, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (acetic acid),

H<sub>2</sub>CO<sub>3</sub> (carbonic acid),

H<sub>3</sub>PO<sub>4</sub> (phosphoric acid), and many

more

weak bases NH<sub>3</sub> (ammonia), C<sub>5</sub>H<sub>5</sub>N (pyridine), and

several more, all containing "N"



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#### **Six Steps for Categorizing Electrolytes**

So how do we categorize compounds based on their formula? One practical method is outlined below:

Step 1 Is it one of the seven strong acids?

Step 2 Is it of the form Metal(OH)<sub>n</sub>? Then it's a strong base.

Step 3 Is it of the form  $Metal(X)_n$ ? Then it's a salt.

Step 4 Does it's formula start with 'H'? It's *probably* a weak acid.

Step 5 Does it have a nitrogen atom? It may be a weak base.

Step 6 None of those? Call it a nonelectrolyte.

Note that there are ambiguities here starting in Step 4. That's just the way it is. To determine whether a substance is a weak acid or weak base you have to know more than the molecular formula, especially for compounds containing carbon. (A *structural* formula, which shows the detailed connections of atoms is often necessary.)