> *"Begin at the beginning… and go on till you come to the end: then stop."*
>
> *Lewis Carroll*

Review: Ions in Solution

Early ideas of atoms and compounds, developed primarily through the reactions of solids and gases, did not include the concept of charge. Atoms and molecules were seen as neutral particles. However, as the study of chemistry progressed to include solutions, new models were needed because the old models could not explain electrical conductivity. Studies of the electrical conductivity of solutions, and other properties of solutions such as freezing point depression and osmotic pressure, showed an interesting dichotomy. Solutions of compounds like sugar did not increase the electrical conductivity of water, yet they had lower freezing points than pure water. Solutions of compounds such as sodium chloride greatly affected the electrical conductivity of water, and they also caused the freezing point of the solution to be reduced twice as much as was observed in sugar water solutions.

A new model that explained these observations was based on the concept that charged particles, which were called ions, formed in solutions. If compounds like sodium chloride broke apart into charged particles when in solution, the ions could carry electrical current. Substances such as sugar must not break into ions in solution because they did not conduct electricity. These studies of the characteristics of solutions led to a more complete and accurate understanding of chemistry at the particulate level.

Solvent and Solute

When a solid dissolves in a liquid to form a solution, the solid is called the *solute*, and the liquid is called the *solvent*. This is the only case that we will consider in this workshop. Note, these few terms are insufficient to describe solutions in general. They will be expanded upon in the workshop *Solutions*.

Mass of potassium chloride crystals

Solubility

Solubility is a measure of how much solute can dissolve in a given amount of solvent. A wide variety of units of concentration can be used for this purpose.

When describing how much of a given solute dissolves in water, the most common, "universal" solvent, the semi-quantitative terms: *soluble, slightly soluble*, and *insoluble*, can be used. These terms are applied quite loosely, and there tends to be substantial variation in the ranges of these categories and other descriptive terms. A more detailed treatment will be provided in a later workshop, *Solutions*. A table and a set of a few generalized rules follow that summarize the solubility characteristics of a number of compounds.

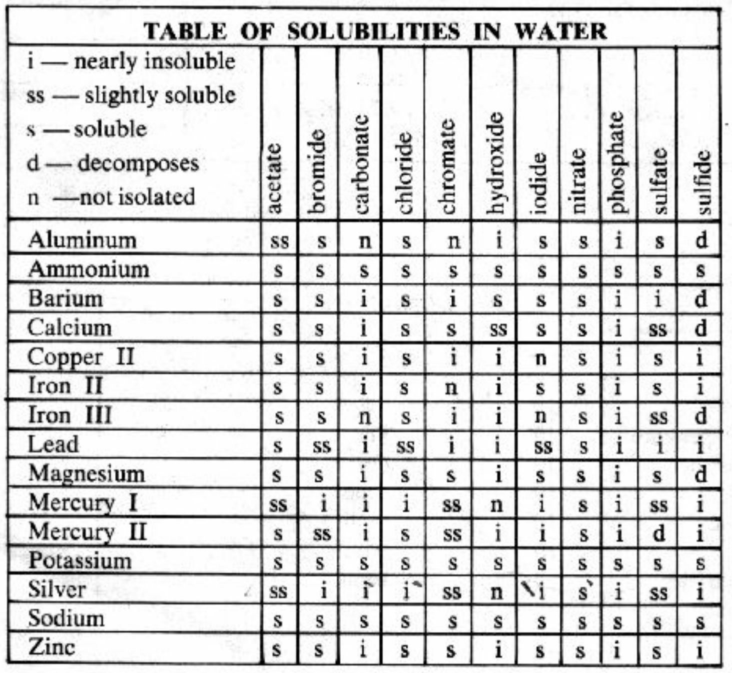

TABLE OF SOLUBILITIES IN WATER

i — nearly insoluble ss — slightly soluble s — soluble d — decomposes n — not isolated	acetate	bromide	carbonate	chloride	chromate	hydroxide	iodide	nitrate	phosphate	sulfate	sulfide
Aluminum	ss	s	n	s	n	i	s	s	i	s	d
Ammonium	s	s	s	s	s	s	s	s	s	s	s
Barium	s	s	i	s	i	s	s	s	i	i	d
Calcium	s	s	i	s	s	ss	s	s	i	ss	d
Copper II	s	s	i	s	i	i	n	s	i	s	i
Iron II	s	s	i	s	n	i	s	s	i	s	i
Iron III	s	s	n	s	i	i	n	s	i	ss	d
Lead	s	ss	i	ss	i	i	ss	s	i	i	i
Magnesium	s	s	i	s	s	i	s	s	i	s	d
Mercury I	ss	i	i	i	ss	n	i	s	i	ss	i
Mercury II	s	ss	i	s	ss	i	i	s	i	d	i
Potassium	s	s	s	s	s	s	s	s	s	s	s
Silver	ss	i	i	i	ss	n	i	s	i	ss	i
Sodium	s	s	s	s	s	s	s	s	s	s	s
Zinc	s	s	i	s	s	i	s	s	i	s	i

Simple Solubility Rules for Ionic Salts in Water

1. Most nitrate (NO_3^-) salts are soluble.
2. Most sodium, potassium, and ammonium (Na^+, K^+, NH_4^+) salts are soluble.
3. Most chloride (Cl^-) salts are soluble. Notable exceptions are $AgCl$, $PbCl_2$, and Hg_2Cl_2.
4. Most sulfate (SO_4^{2-}) salts are soluble. Combinations with sulfate ion which form insoluble compounds are: $SrSO_4$, $BaSO_4$, Hg_2SO_4, Ag_2SO_4, and $PbSO_4$.
5. Most hydroxide (OH^-) salts are only slightly soluble. The important soluble hydroxides are $NaOH$, KOH, and $Ca(OH)_2$.
6. Most sulfide, carbonate, and phosphate (S^{2-}, CO_3^{2-}, PO_4^{3-}) salts are only slightly soluble.

Electrolytes and Nonelectrolytes

An *electrolyte* is a compound whose aqueous solution contains ions. When NaCl dissolves in water, the compound dissociates into Na^+ and Cl^- ions. A good test to determine whether or not a compound is an electrolyte is to measure the ability of its water solution to conduct an electrical current. Consider a battery which has both a positive and a negative pole. If the poles are immersed in a solution via conductive metal electrodes, such as copper wires, the positively charged sodium ions in the solution will move toward the negative pole and the negatively charged chloride ions will move toward the positive pole. Such a solution has a high conductivity.

In contrast, if a neutral molecule such as sugar is in solution, it will not move toward either pole and the solution will be a non-conductor.

Strong and Weak Electrolytes

Electrolytes can be further classified as *strong* or *weak electrolytes*. Strong electrolytes are compounds like NaCl, which are nearly 100% dissociated in solution. This means that nearly every sodium chloride formula unit exists as sodium ions surrounded by water molecules and chloride ions surrounded by water molecules. We can represent this by the following equation:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

The Proton in Chemistry

Acids and bases form a special and very important class of electrolytes. Some acids, such as hydrochloric acid, HCl, almost completely dissociate in aqueous solution. They are strong electrolytes. These acids are similar to sodium chloride in that they exist as ions when in solution. Other acids such as acetic acid, CH_3COOH, dissociate only slightly when dissolved in water. These are classified as weak electrolytes. For example, at a certain concentration and temperature, only four of every one hundred acetic acid molecules will ionize in solution. We represent the ionization of weak electrolytes in solution with double arrows as shown below:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

In the case of a strong acid such as HCl, a single arrow is used in the reaction equation. This indicates that essentially all the HCl molecules dissociate.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Acids can be defined as substances that release hydrogen ions, $H^+(aq)$, in solution. The concentration of $H^+(aq)$ in solution is an important factor in a great number of chemical processes, including many of biological interest. Common acids that you may be familiar with include hydrochloric acid (sometimes called muriatic acid), which is used to control the acidity of swimming pools, sulfuric acid, found in automobile batteries, and phosphoric acid, which is widely used in colas for flavoring.

Now we will consider the chemical "opposite" of acids, which are compounds known as bases. A base is a compound that produces hydroxide ions, $OH^-(aq)$, in solution. As with acids, bases can be classified as either weak or strong. An example of a strong base is sodium hydroxide:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

Ammonia is a common weak base:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

When acids and bases react with each other, they form an ionic salt and water in what is called a neutralization reaction. Examples include:

$$NaOH(aq) + HCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(\ell)$$

$$Ba(OH)_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2\ H_2O(\ell)$$

The salt may be soluble in water, as is sodium chloride, or it may precipitate out as a solid, as does barium sulfate.

Molarity: Chemistry's Most Often Used Concentration Unit

Chemists for ease of application use a specialized mole-based system of concentration units to express the amount of solute in a solution. This system allows chemists to easily extend stoichiometric calculations to reactions that occur in solution.

Molarity is defined as the number of moles of solute per liter of solution and is given the symbol M:

$$M \equiv \frac{\text{moles of solute}}{\text{volume of solution in L}}$$

When chemists prepare solutions, they usually refer to the molarity of the compound dissolved in the solution, whether or not it exists as ions. For example, if sufficient water is added to dissolve 1.0 mole of NaCl and bring the total solution volume to 1.0 L, then the solution is called a 1.0 M NaCl solution. We know that there are no "NaCl" particles in the solution, but rather $Na^+(aq)$ and $Cl^-(aq)$ particles.

Chemical Analysis by Titration

Reactions in solution are useful for determining the amount of a particular chemical species present in a given aqueous sample. For example, swimming pool water is often analyzed for its acid content. One way to determine the amount of acid in a solution is to titrate the solution with a base of known concentration. To analyze a solution that contains the acid HCl, for example, you can add a *known concentration* of the base NaOH in small amounts until all of the acid is neutralized. By measuring the volume of NaOH solution needed to neutralize the HCl, the moles of NaOH added can be determined. Since the reaction of HCl and NaOH occurs in a 1:1 ratio, at the equivalence point of the titration, the moles of NaOH added must be equal to the moles of HCl in solution. The reaction equation is

$$\mathrm{HCl(aq)} + \mathrm{NaOH(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{H_2O}(\ell)$$

In every titration, we need a way to determine the point at which the reaction is complete. In the case of our example titration of NaOH into HCl, the net ionic equation is

$$\mathrm{H^+(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{H_2O}(\ell)$$

The equivalence point is reached when all of the $H^+(aq)$ ions in the HCl solution have reacted. The consumption of $H^+(aq)$ can be detected by employing a chemical dye known as an *indicator*. Indicators change color when the hydrogen ion concentration of a solution changes substantially. The color change signals the *endpoint* of the titration. A pH meter can also be used to measure the $H^+(aq)$ in solution and signal the endpoint.

As we noted earlier, we can apply stoichiometric calculations to reactions that occur in solution. The macroscopic–particulate conversion is made with the molarity concentration unit. Molarity allows us to convert from moles to liters and vice versa. Continuing to consider the titration of sodium hydroxide solution into hydrochloric acid: Assume that we want to know the concentration of a 25.0 mL (0.0250 L) sample of HCl. From the balanced chemical equation we know that 1 mole of HCl reacts with 1 mole of NaOH. If the titration required 17.9 mL (0.0179 L) of 0.122 M NaOH solution, the concentration of the HCl solution is calculated as follows:

$$0.0179\ \mathrm{L} \times \frac{0.122\ \mathrm{mol\ NaOH}}{\mathrm{L}} \times \frac{1\ \mathrm{mol\ HCl}}{1\ \mathrm{mol\ NaOH}} = 0.00218\ \mathrm{mol\ HCl}$$

$$\frac{0.00218\ \mathrm{mol\ HCl}}{0.0250\ \mathrm{L}} = 0.0872\,\frac{\mathrm{mol\ HCl}}{\mathrm{L}} = 0.0872\ \mathrm{M\ HCl}$$