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

Solutions

To a chemist, a solution is nothing more than a homogeneous mixture. The defining phrase is comprised of two words, each of which has a very specific meaning in chemistry: Homogeneous, meaning that the sample has a uniform appearance and composition throughout, plus mixture, a sample that consists of two or more substances. If both of these definitions are met, a sample is a solution.

Solutions are frequently, both in the chemistry laboratory and in everyday life. In the laboratory, solutions are an excellent medium for promotion of chemical reactions and growing crystals. The particles are much closer together than in a gas, and they have more freedom of movement than in a solid. Outside of the laboratory, the process of life itself depends on solutions. The air we breathe and the oceans, lakes, and streams that cover most of our planet are examples of solutions.

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.

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 table and a set of a few generalized rules follow that summarize the solubility characteristics of a number of compounds.

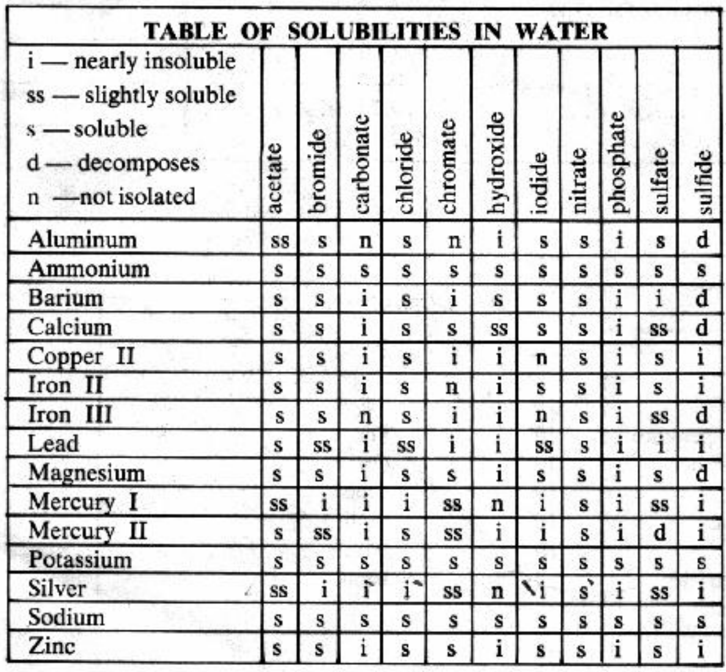


TABLE OF SOLUBILITIES IN WATER

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

http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Equilibria/Solubilty/Solubility_Rules

The following is a list of solubility rules for common ionic solids. If there are two rules that appear to contradict each other, the preceding rule takes precedence.

1. Salts containing Group I elements (Li^+, Na^+, K^+, Cs^+, Rb^+) are soluble . There are few exceptions to this rule. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^-, Br^-, or I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)_2^+$. Thus, $AgCl$, $PbBr_2$, and Hg_2Cl_2 are insoluble.
4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually all others are insoluble.
5. Most sulfate salts are soluble. Important exceptions to this rule include CaSO4, BaSO4, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble, including CdS, FeS, ZnS, and Ag_2S. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates ($CaCO_3$, $SrCO_3$, and $BaCO_3$) are insoluble, as are $FeCO_3$ and $PbCO_3$.
9. Chromates are frequently insoluble. Examples include $PbCrO_4$ and $BaCrO_4$.
10. Phosphates such as $Ca_3(PO_4)_2$ and Ag_3PO_4 are frequently insoluble.
11. Fluorides such as BaF_2, MgF_2, and PbF_2 are frequently insoluble.

Solutions are not limited to ionic and molecular solids being dissolved in water.

Terms, which relate to solutions, need to be expanded. In general, the component of the solution that is present in the greatest amount is called the *solvent*. The substance with the smaller amount in the solution is called the *solute*. These terms are not precise, however, and their usage varies among different specialties in chemistry. For example in water solutions, water is almost always referred to as the solvent no matter its relative amount. Also when a solid or a gas is dissolved in a liquid, the liquid is generally called the solvent.

It is often important to know a quantitative maximum amount of a solute that will dissolve in a given solvent at a specified temperature. This measure is known as the *solubility* of that solute. Reference sources often report solubilities in grams of solute per 100 grams of solvent. When a solution contains a solute amount less than the solubility limit, it is said to be *unsaturated*; if it is at the solubility limit, it is *saturated*. Under certain special conditions, a solution can contain more solute than it normal solubility limit, and in this case, it is called *supersaturated*.

The terms concentrated and dilute are often used to describe solutions. It is important to keep in mind that these terms are valid only in a relative sense. A *concentrated* solution has a relatively large amount of solute per given amount of solvent when compared with a *dilute* solution. The comparison is only valid for systems of the same solute and solvent.

When discussing solutions of liquids in liquids, the term *miscible* is used to describe two liquids that will dissolve in one another in all possible combinations. When liquids will not dissolve in one another, they are said to be *immiscible*. A chemist would say that oil and water are immiscible, whereas alcohol and water are miscible.

Solution Concentration Units

A number of different units are used to express the quantity of solute dissolved in a given amount of solvent.

Molarity: The Chemist's Favorite Concentration Unit

Chemists use a mole-based system of concentration units to measure 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:

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

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 aqueous solution, but rather $Na^+(aq)$ and $Cl^-(aq)$ particles.

Some other common units include percentage by mass, percentage by volume, (which relates to alcoholic proof), parts per million, parts per billion, and molality. The definition of each provides the basis for calculations with that unit.

$$\%\text{ by mass} = \frac{\text{mass solute}}{\text{mass solution}} \times 100$$

$$\%\text{ by volume} = \frac{\text{volume solute}}{\text{volume solution}} \times 100$$

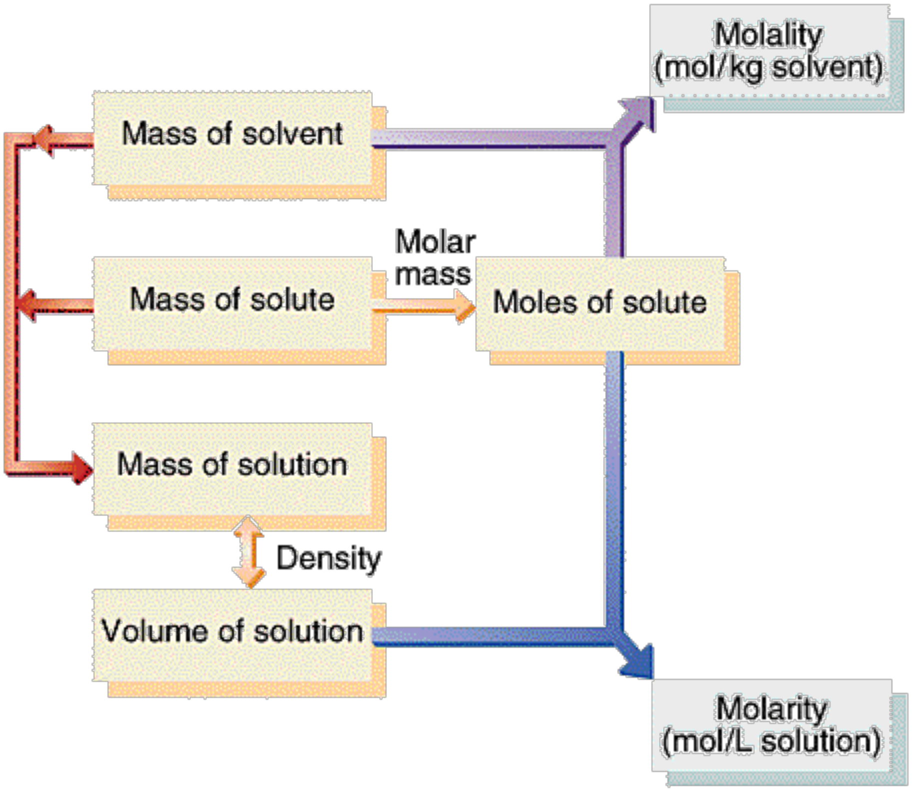
[Proof = % by volume x 2]

$$\text{parts per million} = \text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6$$

$$\text{parts per billion} = \text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9$$

$$\text{molality} = \text{m} = \frac{\text{moles solute}}{\text{kilograms solvent}}$$

The choice of concentration unit is largely a matter of application and convenience; other units beyond these may be encountered. There are some technical factors that must be considered. Percentage by mass, parts per million, parts per billion, and molality are applicable at any temperature. However, molarity and percent by volume must specify a temperature, since the volume varies with temperature.



Solution Formation

Consider the process by which table salt, sodium chloride, dissolves in water. Positively-charged sodium ions and the negatively-charged chloride ions are attracted to one another, this attraction is termed to be an *ionic bond*. When a solution forms, the ions must be separated from each other, and thus energy is required to separate the solute particles. A similar situation occurs with the solvent particles. The water molecules are clumped together in hydrogen-bonded groups. These groups must be "pulled apart" so that solute ions can fit between them. This process also requires an input of energy. Energy is released when the solute and solvent particles interact. The negative ends of water molecules surround positively-charged sodium ions and the positive ends of water molecules surround negatively-charged chloride ions and pull apart the respective ions.

Crystal Formation (Crystallization)

If solutes and solvent do not chemically react, solution formation can be reversed. It is possible to recover the solute by removing all or some of the solvent. This can be particularly useful in purifying solids through "recrystallization", where the solid has contaminants that are more soluble in the solvent than the wanted solid.

Another useful application is in growing "single" crystals from saturated and super-saturated solutions. Single crystals are the exact geometrical shape as the salt's unit cell. There are seven different types of unit cells found in nature.

http://webphysics.davidson.edu/alumni/MiLee/JLab/Crystallography_WWW/intro.htm

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 nonconductor.

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.

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

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

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

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

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, let's 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:

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

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