

Solubility Rules Help Avoid Water Treatment Pitfalls

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Knowledge of solubility behavior of water contaminants can help predict proper treatment system application and avoid pitfalls in operation and maintenance of treatment equipment.

Water treatment techniques can be separated into two broad categories; those that address suspended substances, and those that address dissolved substances. Suspended substances in water form heterogeneous mixtures, with visible particles. The resulting mixture is called a suspension.

Dissolved substances in water are evenly dispersed in a given volume. They form solutions, which are homogeneous mixtures that contain particles not visible to the naked eye. Ionic substances may undergo a chemical reaction with water, resulting in a separation of these substances into their component ions. This process is known as ionization.

Suspended substances are typically treated with physical techniques such as filtration. When particles are too small to be removed by physical treatment, techniques that cause agglomeration of these particles are used.

Removal of dissolved substances requires technologies capable of chemical interaction, and some examples include lime softening, oxidation, ion exchange, adsorption, and the treatment of chlorine with activated carbon. By this definition, reverse osmosis may be considered a physical technique that can effect separation on an atomic level.

A number of water contaminants can move between the two categories of suspended and dissolved substances. For some applications, this can be beneficial as it allows the use of less expensive treatment technologies. A good example is the removal of dissolved iron by the combination of aeration and filtration. In other applications, the formation of solids from dissolved substances can be detrimental to both water-using devices and water treatment equipment. Examples include the formation of scale in a water heater or the unintended precipitation of iron compounds in an ion exchange resin tank.

At the chemical level, substances may be classified as either ionic or covalent, although some will demonstrate both types of behavior. Ionic compounds consist of positively-charged cations and negatively-charged anions. The valence electrons are localized on the ions and the electrostatic attraction of the opposite charges holds the compound together. Purely covalent substances share valence electrons over the molecule and do not separate into ions.

Solubility of any substance is dependent both on the nature of that substance, also known as the solute, and on the nature of the substance in which it is being dissolved, or the solvent. Water is considered a strongly polar solvent, meaning that the electrons in each H₂O molecule are arranged such that the overall molecule has a slightly positively-charged end, or pole, and a slightly-negatively charged end, as illustrated in Figure 1.

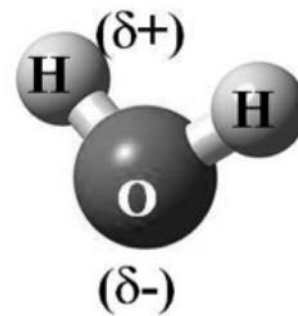


Figure 1: Polarization behavior of a water molecule

Since like dissolves like, ionic compounds are more likely to be separated into their ionic components in water than covalent substances. Figure 2 depicts the interaction between the polar molecules of water and the ions of a sodium chloride crystal that lead to the crystal dissolving into sodium cations and chloride anions.

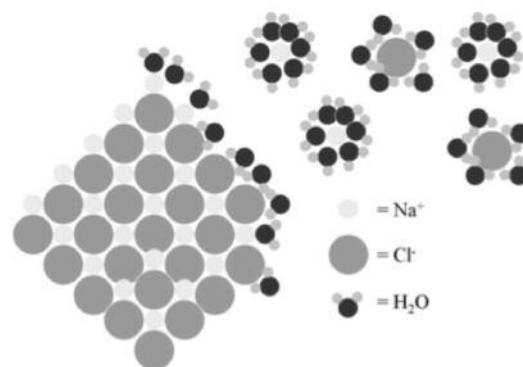


Figure 2: Sodium chloride crystal dissolving

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Most mineral salts and inorganic acids and bases are in the category of ionic compounds. Nonpolar organic molecules, made up mainly of carbon/hydrogen chains, are in the category of covalent compounds. Some organic molecules - such as acetic acid - have ionizable portions and will dissolve in water by ionizing. Polar organic molecules, short-chain alcohols like ethanol, are also very comfortable in the polar environment of water. Hydrogen bonding is another interaction by which water can stabilize the dissolution of a solute. Hydrogen bonds are attraction between atoms of hydrogen and oxygen, hydrogen and nitrogen, and hydrogen and fluorine.

Each ionic substance has a maximum solubility - a maximum amount that can be dissolved - at a specific water temperature. This amount is typically reported in grams (g) per 100 milliliters (mL) of water. Substances with solubilities greater than 1 g per 100 mL of water are considered very soluble, substances with solubilities between 1 g and 0.1 g in 100 mL of water are slightly soluble, and substances with less than 0.1 g solubility per 100 mL of water are insoluble.

Maximum solubilities for a number of ionic compounds have been measured and can be found in reference books, such as the *CRC Handbook of Chemistry and Physics*. For example, sodium chloride, which is readily recognized by anyone working with ion exchange technology to be very soluble, has a maximum solubility of 36.0 g/100 mL H₂O at 25°C. Calcium sulfate is considered as having the potential to form scale, and indeed, its maximum solubility is reported as 0.2 g/100 mL H₂O at 25°C.

Solutions that contain the maximum amount of a particular solute are said to be saturated. Solutions that contain more than the maximum amount of a particular solute are said to be supersaturated and are unstable. These are typically formed when the temperature of an already saturated solution is slowly lowered. Any slight change in condition, such as an additional decrease in temperature, the addition of a seed crystal, evaporation of solvent, or turbulence, quickly leads to the precipitation of the excess solute.

Another useful tool in determining solubility of a substance is its solubility product, K_{sp} . The smaller the number, the less likely a substance will dissolve, or, conversely, the faster it will precipitate from solution if any of its component ions happen to get added to the same solution. For example, the solubility product of calcium carbonate (CaCO₃) is 8.7×10^{-9} , while the solubility product of iron(II) hydroxide [Fe(OH)₂] is 1.6×10^{-14} , a considerably smaller number. If sodium hydroxide (NaOH, caustic) is added to water containing ions of ferrous (Fe^{II}) iron, calcium, and bicarbonate alkalinity in order to raise the pH, based on the solubility product, the first substance to precipitate will be iron(II) hydroxide followed by calcium carbonate (Figure 3).

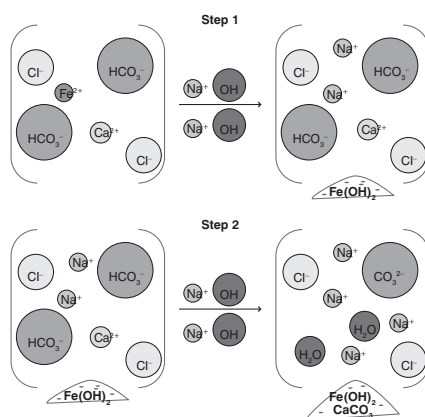


Figure 3: Solubility product and order of precipitate formation

The idea that ferrous iron could precipitate is not commonly discussed in water treatment, the focus usually being on the precipitation of ferric (Fe^{III}) iron. What the study of solubility reveals is that whether or not a substance will precipitate depends not only on the cation present, but on the anion as well.

Cations and anions do not exist separately from each other, even though they're dissociated and physically separated in water. The distance by which they're separated is relatively small, resulting in a net neutral charge on a solution. This is an important point that often gets overlooked, as in the case of iron discussed above. The balance of positive and negative charges is also illustrated in ion exchange when

removal of calcium from the raw water with the ion exchange process results in the addition of an equivalent charge of sodium ions. Likewise, on a water analysis, anytime the alkalinity concentration as calcium carbonate is greater than the hardness concentration as calcium carbonate, the difference is due to the presence of monovalent cations from the first column of the periodic table [sodium (Na⁺), potassium (K⁺), etc.].

Accounting for the monovalent cations is typically of greater importance in deionization processes. Excessive concentrations of monovalent cations can also be a problem for softening applications with resin in the sodium or potassium form. A low ratio of hardness and other polyvalent cations to total anions on a water analysis would indicate this type of situation. Because the opposite charges must be in balance, such a water analysis result could also indicate an error in the analysis itself and is worth investigating.

Common situations in water treatment explained by the solubility rules:

1. The high solubility of sodium chloride and potassium chloride in water (rules 2 and 4) precludes the possibility of these substances being removed from water with inexpensive means such as precipitation followed by filtration. Separation of water from dissolved sodium, potassium, and chloride ions requires the application of distillation, reverse osmosis, deionization, or electrodeionization technologies.
2. The addition of a base such as sodium hydroxide (NaOH) to raise the pH of slightly acidic, moderately hard water with alkalinity in proportion to or slightly higher than the concentration of hardness, causes scaling. At acidic pH the alkalinity is due to the presence of bicarbonate. The addition of a base strips a hydrogen ion off the bicarbonate, converting it to carbonate. In the presence of dissolved hardness ions, carbonate scale quickly forms.

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Keeping track of the various cations and anions in solution is also important because once dissociated, the ions from different compounds have the possibility of exchanging to form new compounds. If the new compounds are less soluble than the parent compounds, the reactions are particularly favorable, i.e. they'll happen fast, and can cause problems, as was demonstrated in the ferrous iron precipitation example in Figure 3.

Another example, illustrating the importance of considering both the cations and the anions, is a water sample that's been isolated from ambient air and contains calcium only from calcium chloride (CaCl_2). This compound will separate into its component ions, upon contact with soap anions it will form soap curd, but will not form scale if heated. Add in a little sodium carbonate (Na_2CO_3), which is also soluble, and calcium carbonate (CaCO_3) and scale will quickly form.

Forgetting to account for both the type of cation and the type of anion dissolved in a given water supply had led to the erroneous conclusion that water softening by ion exchange, with resin in the sodium form, causes a reduction in pH which then results in corrosion of metal piping. This proclamation often follows a discussion of chemical-based softening procedures, which remove both the hardness ions and the bicarbonate anions from water. As a weak base, bicarbonate can help maintain a higher pH. The removal of it from water can, indeed, result in more acidic water, which would be more corrosive to

metals. However, softening by ion exchange removes only the hardness cations, replacing them with sodium ions. The procedure does not affect the concentration of bicarbonate, carbonate, or any other anion, and, therefore, does not affect pH of the water.

Below are some rulesⁱⁱⁱ for predicting solubilities of ionic compounds in water. Temperature is assumed to be 25°C (77°F).

1. All common inorganic acids are soluble [e.g. hydrochloric (HCl), nitric (HNO_3), etc.].

Note: Only the first hydrogen of polyprotic acids will easily dissociate [e.g. carbonic (H_2CO_3), sulfuric (H_2SO_4), phosphoric (H_3PO_4)].

2. All compounds of alkali metals are soluble [sodium (Na^+), potassium (K^+), rubidium (Rb^+), cesium (Cs^+)]. Alkali metals are all located in the first column from the left on the periodic table.
3. All ammonium (NH_4^+) compounds are soluble.
4. All compounds of chloride (Cl^-) and bromide (Br^-) are soluble, except those with lead (Pb^{2+}), silver (Ag^+), and mercury (Hg^{2+}).

DEFINITIONS:

Anion = Negatively-charged ion or molecule.

Atom = The smallest part of an element that maintains the properties of an element. Atoms consist of a nucleus in the center that contains protons and neutrons and is orbited by negatively-charged electrons.

Cation = Positively-charged ion or molecule.

Compound = A substance formed from a combination of elements.

Covalent bond = A type of attraction between atoms in which valence electrons are delocalized and shared between the atoms involved in the bond.

Electron = A negatively-charged subatomic particle that orbits the nucleus in an atom.

Element = The simplest form of a substance which cannot be broken down any further by chemical means.

Ionic bond = Electrostatic attraction between ions of opposite charge in a compound.

Ionization = Separation of a compound into component ions.

Molecule = The smallest form of a compound that still maintains the properties of that compound.

Monovalent = An ion with either a negative or a positive charge of one.

Neutron = A subatomic particle without a charge that is found in the nucleus of an atom.

Nucleus = The center of an atom. The nucleus contains protons and neutrons.

Polar = A covalently-bonded compound of different elements in which the atom(s) of one element more strongly attract the delocalized valence electrons to create a slightly negative area on one end of the molecule, resulting in a slightly positive end on the opposite side of the molecule.

Polyprotic = An acid that can donate more than one positively-charged hydrogen ion (H^+). E.g. sulfuric acid, H_2SO_4 . Because a positively-charged hydrogen ion has no electrons and consists only of its single proton in the nucleus, H^+ in the terminology of acid-base reactions is often referred to as a proton. Likewise, when a base binds H^+ , it is said to be "protonated".

Polyvalent = An ion with a positive or negative charge greater than one.

Precipitate, precipitation (↓) = Precipitate is the solid formed when oppositely-charged dissolved ions combine to form an insoluble substance. Precipitation is the act of formation of the solid. In chemical reactions, the formation of a precipitate is indicated by a downward arrow, written after its molecular formula.

Proton = A positively-charged subatomic particle found in the nucleus of an atom. In acid-base terminology, a positively-charged hydrogen ion (H^+). (See Polyprotic)

Solute = The substance being dissolved to form a solution. Solutes may be gases, solids, or liquids.

Solution = Homogenous mixture of two or more substancesⁱⁱⁱ. Solutions where water is the solvent are called aqueous.

Solvent = The substance performing the dissolving of the solute to form a solution.

Valence electrons = The electrons in the outermost electron shell of an atom. These are the electrons furthest from the nucleus. When an atom becomes an ion, the number of valence electrons either increases or decreases. An increase in valence electrons results in a negatively-charged ion – anion – and a decrease in valence electrons results in a positively-charged ion – cation.

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- All compounds containing nitrate (NO_3^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), and acetate (CH_3COO^-) are soluble.
- Most sulfates (SO_4^{2-}) are soluble. Compounds with calcium (Ca^{2+}) and silver (Ag^{2+}) are slightly soluble. Compounds with barium (Ba^{2+}), mercury (Hg^{2+}), and lead (Pb^{2+}) are insoluble.
- All compounds of **carbonate** (CO_3^{2-}), phosphate (PO_4^{3-}), sulfide (S^{2-}), and sulfite (SO_3^{2-}) are insoluble, except those of ammonium (NH_4^+) and alkali metals.
- All alkali metal hydroxides (MOH , where M=metal) are soluble. Barium hydroxide [$\text{Ba}(\text{OH})_2$] is soluble. Calcium hydroxide [$\text{Ca}(\text{OH})_2$] is slightly soluble. All other hydroxide compounds are insoluble.
- All compounds of bicarbonate (HCO_3^-) are soluble.**

Solubility can be affected by both the temperature of the water and the pH. Higher temperature generally increases the solubility of ionic substances in water, however the reverse is true for the formation of calcium carbonate scale. Conversely, colder temperature will decrease solubility.

Acidic pH also, typically, enhances solubility of substances, because it reacts with the anion portion of the ionic compound and converts it to the more soluble form. An example is the reaction of acid with calcium carbonate. The carbonate binds the free hydrogen ion in the acidic water to become bicarbonate, and the resulting calcium bicarbonate compound dissolves (rule 9).

The ions already present in solution will affect the extent to which additional such ions are dissolved, especially if the second source of these ions is only slightly soluble. A solution containing sodium carbonate will severely limit how much calcium carbonate will dissolve into it. This is known as the common ion effect and is a function of equilibrium and Le Chatelier's principle, both of which are beyond the scope of this article.

A water analysis for dissolved substances is the best place to start when approaching a water treatment problem. Knowledge of the solubility rules will help in determining how to best apply and troubleshoot water treatment technologies to either take advantage of the possibility for solid formation or to avoid formation of solids.

ⁱ D. Lide, ed, *CRC Handbook of Chemistry and Physics*, 77 ed, CRC Press, Inc.: Boca Raton, 1996.

ⁱⁱ Ibid.

ⁱⁱⁱ R. Chang, *General Chemistry*, Random House: New York, 1986.

QUIZ 4: "Solubility Rules Help Avoid Water Treatment Pitfalls" (0.25 CPD)

- What type of behavior is required for a compound to be considered dissolved in water?
 - Formation of large, visible particles
 - Separation into cations and anions
 - Precipitation of a solid
 - Surface tension
- What is meant by maximum solubility?
 - The point at which a solute is fully hydrogen-bonded with water
 - The point beyond which a precipitate forms
 - The point at which a solution contains the maximum amount of solute
 - The relative solubility of all ionic compounds to that of sodium chloride
- An excess of sodium sulfate and sodium carbonate are added to water containing calcium chloride, magnesium chloride, and iron(II) chloride. Use the solubility products, K_{sp} , listed below to determine what substance will precipitate first.

$\text{CaCO}_3 K_{sp} = 3.36 \times 10^{-9}$	$\text{CaSO}_4 K_{sp} = 4.93 \times 10^{-5}$
$\text{FeCO}_3 K_{sp} = 3.13 \times 10^{-11}$	$\text{MgCO}_3 K_{sp} = 6.82 \times 10^{-6}$

 - CaCO_3
 - CaSO_4
 - FeCO_3
 - MgCO_3
- Based on the solubility rules, which of the following substances is insoluble?
 - Calcium acetate [$\text{Ca}(\text{CH}_3\text{COO})_2$]
 - Iron(III) bicarbonate [$\text{Fe}(\text{HCO}_3)_3$]
 - Copper chloride (CuCl_2)
 - Iron(II) hydroxide [$\text{Fe}(\text{OH})_2$]
- Which of the following calcium compounds is insoluble?
 - Calcium sulfite (CaSO_3)
 - Calcium chloride (CaCl_2)
 - Calcium bromide (CaBr_2)
 - Calcium perchlorate [$\text{Ca}(\text{ClO}_4)_2$]
- Which of the following does NOT/do NOT influence solubility of a substance?
 - Concentration units
 - Presence of component ions
 - Temperature changes
 - Turbulence of flow
- Which water treatment process must account for interference from potential precipitation of even the highly soluble compound of sodium chloride?
 - Oxidizing filter
 - Chemical softening
 - Reverse osmosis
 - Ozone disinfection