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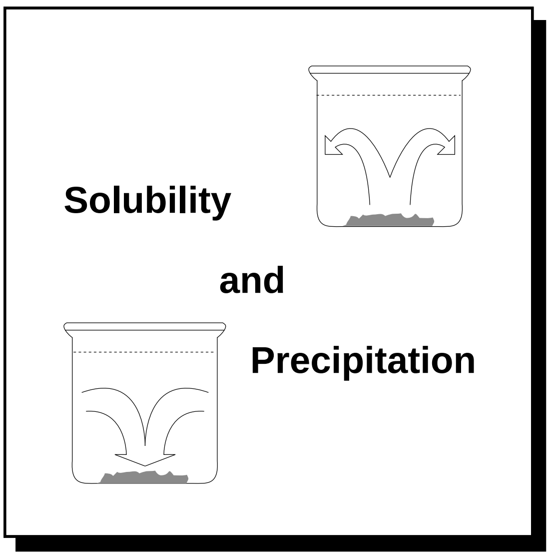


ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

SOLUBILITY AND PRECIPITATION

Topic Overview

Content in a Nutshell

Life on earth depends upon the fact that certain substances dissolve in other substances. We constantly deal with solutions. We enjoy cola drinks because dissolved carbon dioxide gives them an effervescence. Fish can live because oxygen gas is dissolved in lakes and oceans. We grow and develop because nutrients dissolved in our blood can reach cells and tissues.

The process of dissolving has always been fascinating. Early alchemists searched for the "universal solvent"—that mythical liquid that would dissolve everything. Perhaps it never occurred to them that, if they found it, it would be difficult to contain! Of course, there is no universal solvent. Water is perhaps the closest thing we have to a universal solvent; its truly unique properties make it one of our most important chemical substances.

We now know much more about the process of dissolving than did early chemists. We now understand that particles (ions and molecules) are held together within solids and liquids by certain attractive forces. Some of these are weak and some are relatively strong. For a solution to form, bonds must be broken and reformed, involving changes in energy. Solution formation is most likely to happen when the solute and solvent have certain similar chemical properties. We often generalize this fact by saying that "like dissolves like."

When a solute dissolves in a solvent in a closed system, the process continues until a certain amount of solute enters solution. After that point, particles return to the solute at the same rate they leave the solute and dissolve. Thus, dissolving is a dynamic equilibrium process. It has often been stated that "everything is somewhat soluble in everything else," and every substance has a characteristic solubility. When the solubility of a solid is exceeded, the substance comes out of solution in the form of a precipitate. The word *precipitate* comes from the Latin and means "cast down." Interestingly enough, chemists a hundred years ago knew little about ions and atoms and how they recombine in solution. When a precipitate formed in solution, they would say that a substance was "thrown down."

Some substances show very limited solubility in solvents like water. We can express this small solubility quantitatively as the "solubility product constant" (K_{sp}). This is a useful expression since it allows a chemist to predict if and when a precipitate may occur when solutions are mixed.

The solubility of a substance can be changed by altering the conditions that affect equilibrium. Temperature and pressure affect the solubility of gases in liquids. The solubility of solids in liquids is affected by temperature.

If we collect enough data regarding the solubility of certain substances, especially ionic compounds, we can formulate a set of rules or generalizations that help us predict whether or not certain compounds will form solutions.

Place in the Curriculum

Students can understand and appreciate the ideas of solubility and precipitation with even greater comprehension after they have studied the concepts of bonding and equilibrium as part of class discussion on the solution process. There are many important and practical applications of these concepts.

Central Concepts

1. Certain substances have the ability to dissolve other substances.
2. The extent of solubility depends upon interparticle solute-solute, solvent-solvent, and solute-solvent attractions.
3. When the solute is only slightly soluble, the extent of solubility can be quantitatively expressed as the solubility product constant.
4. The solubility of a substance can be altered by the common ion effect, pH change, temperature change, *etc*.
5. Accumulated data allow one to predict the degree of solubility of many substances (solubility rules).

Related Concepts

1. Bonding
2. Energy
3. Entropy
4. Polar and nonpolar molecules
5. Ionization/dissociation
6. Equilibrium
7. Kinetic molecular theory

Related Skills

1. Exponents
2. Constants
3. Logarithms
4. Working with small-scale volumes
5. Measuring volumes using a graduated cylinder or other volumetric apparatus.

Performance Objectives

After completing their study of solubility and precipitation, students should be able to:

1. explain phrase "like dissolves like" as it relates to polar and nonpolar materials.
2. discuss the effect that entropy and enthalpy have on the dissolving process.
3. explain why a precipitate forms when solutions of two ionic compounds are mixed.
4. explain why gases become less soluble at higher temperatures, whereas most solids become more soluble.
5. predict the solubility of an ionic compound by applying generalizations (rules) determined by laboratory experiments.
6. give practical, personal, and everyday examples of situations that involve solubility and precipitation.
7. explain the relationship between equilibrium and solubility.
8. explain how solubilities of solids and gases are changed by changing temperature and pressure.
9. discuss effect of temperature on endothermic and exothermic solution processes.
10. describe how increase in disorder favors the solution process.
11. discuss energy required for bond breaking *vs*. energy released when new bonds are formed.
12. calculate the K_{sp} for an ionic compound if they are given the solubility of the compound.
13. calculate solubility of an ionic compound if they are given K_{sp} for that compound.

Concept/Skills Development

Laboratory Activity: Student Version

Activity 1: What Dissolves and What Does Not: Establishing Some "Rules"

Introduction

In this laboratory activity you will work with an assortment of solutions of ionic substances, divided into five sets. Your teacher will assign specific sets of solutions for your work. You will compile your data with that of classmates to generate some 'rules' regarding solubilities of certain ionic compounds. Using very small quantities, you will mix all possible combinations of solutions in each set and observe any reactions that occur.

Purpose

When you mix certain solutions, you will find that some combinations produce precipitates. By comparing data with other students, you should find distinctive patterns developing as certain ions react with each other. From such class data, some generalizations regarding the solubilities of ionic compounds can be drawn. This activity will give you experience in (a) developing laboratory skills, (b) making and recording observations, (c) drawing conclusions and making generalizations from data, and (d) working as part of a team.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Although none of the solutions are toxic, place all waste solutions in a properly labeled container. Do not discard the waste in the sink.

Procedure

1. Prepare five grid sheets like the following one. (The numbers refer to numbered solutions in each set.)

Set No. _____	6	5	4	3	2
1					
2					
3					
4					
5					

2. Select a set of solutions for the laboratory activity. (Your teacher may select one for you.) Indicate the number of the solution set on the sheet. For each solution in the set, identify the ions present in the solution and record them on the sheet. For example, the sheet for Solution Set No. 1 would look like the one shown. Prepare two sheets for each set of solutions.

Set No. 1	K^+/Cl^- 6	Na^+/NO_3^- 5	Ag^+/NO_3^- 4	Na^+/I^- 3	Ba^{2+}/Cl^- 2
Ba^{2+}/NO_3^- 1					
Ba^{2+}/Cl^- 2					
Na^+/I^- 3					
Ag^+/NO_3^- 4					
Na^+/NO_3^- 5					

3. Place an acetate sheet, or a small glass plate, over one of the sheets. (Your teacher may prefer that you use cell well plates.)
4. Carefully add one drop of each solution, where it is indicated on the grid. When you have finished, you will have two drops of solution in each square, and you will have mixed all possible combinations of solutions in the set.
5. Note any precipitates that form, and record their colors on the second grid sheet that you prepared. Write a net ionic equation for each reaction that produced a precipitate.
6. Carefully rinse the acetate sheet, or glass plate, with a small amount of water into the waste container provided by your teacher. Wash your hands.
7. Repeat the procedure for the other solution sets assigned to you.
8. Thoroughly wash your hands before leaving the laboratory.
9. Compile your data with that of your classmates on the large data table on the chalkboard.

Data Analysis and Concept Development

1. Observe the patterns in precipitation. What conclusions can you draw regarding the solubility of various combinations of ions in solution?
2. Which of the following pairs of ions should produce a precipitate in water solution?

    a. $Ag^+ + NO_3^-$

    b. $Mg^{2+} + OH^-$

    c. $K^+ + SO_4^{2-}$

    d. $Al^{3+} + Na^+$

    e. $Ag^+ + CO_3^{2-}$

    f. $NH_4^+ + Cl^-$

Laboratory Activity: Teacher Notes

Activity 1: What Dissolves and What Does Not: Establishing Some "Rules"

Level

This activity may used with basic, general, and honors students.

Safety

These solutions include some heavy metal ions that are toxic in the environment. Although they are safe to use when handled properly, you must dispose of these ions carefully. A small-scale approach is suggested to reduce the volume of solutions required.

Materials

	Set I	Set II	Set III	Set IV	Set V
Solution 1:	$Ba(NO_3)_2$	Na_2SO_4	$FeCl_3$	$CoCl_2$	$BaCl_2$
Solution 2:	$BaCl_2$	$Al_2(SO_4)_3$	$Co(NO_3)_2$	$MgCl_2$	$Sr(NO_3)_2$
Solution 3:	NaI	$Sr(NO_3)_2$	$CoCl_2$	K_2SO_4	Na_2CO_3
Solution 4:	$AgNO_3$	$BaCl_2$	NaOH	NaOH	$Al_2(SO_4)_3$
Solution 5:	$NaNO_3$	$Ba(NO_3)_2$	KOH	$Ba(OH)_2$	$K(CH_3COO)$
Solution 6:	KCl	$AlCl_3$	$NaNO_3$	$MgSO_4$	$AgNO_3$

Advance Preparation

1. Prepare 10% solutions of the reagents by dissolving 10 g of each in 90 mL water. If all of the sample does not dissolve let it settle and use the clear solution.
2. Place the solutions in dropper bottles and arrange in sets. Prepare at least five complete set-ups. These solutions are stable and can be used many times. **Assign only one set to each student pair.** (Beral™ pipets in an audio cassette case are also a convenient arrangement.)
3. Acetate sheets, or small glass plates work well. Acetate sheets are inexpensive and eliminate the risk of glass cuts. You may wish to photocopy copies of the grid and give several to each student, or make transparencies of the grid. Small-scale cell well plates work nicely. Students can rinse them and dry with Q-tips. Grid sheets on colored paper enhance visibility of white precipitates.
4. You might find it convenient to provide a large chart on the chalkboard and have students record their data as they complete each part of the laboratory activity. The following chart is suggested as a possible format.

	Cl^-	CH_3COO^-	CO_3^{2-}	OH^-	NO_3^-	I^-	SO_4^{2-}
Ag^+							
Al^{3+}							
Ba^{2+}							
Co^{2+}							
Fe^{3+}							
K^+							
Mg^{2+}							
Na^+							
Sr^{2+}							

Place an (I) for Insoluble in the space where a precipitate was formed. Place an (S) in spaces where there was no precipitate.

Generally, we consider anything insoluble if it has a solubility of less than 0.1 g per 100 mL. You may find it necessary to declare some compounds as “slightly soluble” (ss). Silver sulfate fits this category.

Pre-Laboratory Discussion

1. When students compile their data and compare their observations, it will become apparent that certain combinations of solutions produce precipitates. Further, it can be determined that only certain pairs of ions react to produce precipitates. When class data are gathered, some generalizations regarding the solubility of ionic compounds can be drawn. It is important that the general rules for solubility be developed as a result of student observations, and not presented as something to be “memorized”.
2. This activity gives students experience in (1) developing laboratory skills, (2) making and recording observations, (3) drawing conclusions and making generalizations from data, and (4) working as part of a team.
3. Students should be introduced to dissociation, the separation of ions in aqueous solution. They should identify all ions present in a solution and write correct ionic symbols. They must understand that precipitates form only when an insoluble product results from the recombination of ions in solution. They should also be able to write net ionic equations for precipitation reactions, eliminating “spectator” ions.
4. You might select, as an example, the combination of silver nitrate and sodium chloride solutions. Do this as a demonstration—simply add one to the other; a dense white precipitate of silver chloride will form. Ask students to list all ions present in the combined solutions and eliminate those that would not precipitate. Show students that the precipitate could not be sodium nitrate by dissolving a small amount of this compound in water to show that it is very soluble. Stress that the “process of elimination” to determine that the precipitate must be silver chloride is based on all four potential salts in each reaction plus recording all six solution salts as soluble in the beginning of the activity.

Teacher-Student Interaction

Having students pool and compare their data provides an opportunity to discuss experimental error and the need to collect a large quantity of data before establishing conclusions. Students should be prepared to support their conclusions with careful observations and data collection. They should also realize that the rules, theories, and hypotheses that chemists use are the direct or indirect result of laboratory experimentation. This laboratory activity allows every student to contribute to forming the “rules” by which chemists try to describe and understand their surroundings.

Anticipated Student Results

Student results will be encouragingly consistent. If some question arises as to whether or not a precipitate formed, you can mix several milliliters of the solutions in question in front of the class and ask for their observations.

Answers to Data Analysis and Concept Development

1. The patterns match those found in general rules for water solubilities of ionic substances.
2. a. No precipitate
   b. Precipitate
   c. No precipitate
   d. No precipitate
   e. Precipitate
   f. No precipitate

Post-Laboratory Activities

1. After discussing student data and creating a set of generalizations regarding solubilities of certain compounds, call attention to the "solubility rules" in the textbook, or distribute a copy. Compare these two sets of "rules." Spot check student understanding by posing possible combinations of solutions. (What would happen if solutions of lead nitrate and potassium carbonate were mixed? What would the precipitate be?)
2. You may find that barium hydroxide and sodium hydroxide (Set 4) produce a precipitate due to dissolved carbon dioxide in the sodium hydroxide, forming barium carbonate. If this happens, explain to students that it is not due to the combination of ions from the original compounds.

Assessing Laboratory Learning

1. It is important that students understand what their laboratory activity has produced regarding knowledge of solubility rather than having students simply memorize solubility rules. Allow students to refer to the class-generated solubility chart and predict the solubility of various ionic compounds, or the precipitate formed when various ionic solutions are mixed.
2. Ask students to design sets of solutions to check the solubility of compounds not included on their charts.
3. Have students write net ionic equations, eliminating all spectator ions.

DEMONSTRATIONS

Demonstration 1: Solubility and Immiscibility

Description

Polar solvents dissolve polar and ionic solids, and nonpolar solvents generally dissolve nonpolar solids. This can be easily demonstrated and projected on an overhead projector.

Materials

Trichlorotrifluoroethane (TTE), 5 mL
Solid iodine, $I_2(s)$, several crystals
Solid copper(II) sulfate, $CuSO_4 \cdot 5\ H_2O(s)$, several crystals
Petri dishes
Overhead projector

Procedure

Place two Petri dishes on the stage of an overhead projector. Add enough water to each dish to cover the bottom. In each dish, carefully add about 2 mL TTE. (Notice that it forms a "pool".) Carefully drop a few crystals of iodine in the TTE pool of one Petri dish, and the same number in the water near the pool. What do you observe? Now, in the second dish add a few crystals of copper(II) sulfate in the TTE pool, and the same amount in the water near the pool. Stir each gently with a toothpick. What do you observe?

Reactions

TTE is a nonpolar solvent; it does not dissolve in polar water. Iodine is a nonpolar solid; it does not dissolve in polar water, but does dissolve in nonpolar TTE. Copper(II) sulfate is an ionic solid that dissolves in polar water, but not in nonpolar TTE.

Disposal

TTE is an acceptable and safe organic solvent. All of these materials can be disposed of according to directions given in the *SourceBook Safety* section.

Demonstration 2: Negative Coefficient of Solubility

Description

The solubility of most solids increases with an increase in temperature. Some compounds, however, show a decrease in solubility with increased temperature. Calcium acetate, $Ca(CH_3COO)_2$, is such a compound—it has a negative coefficient of solubility.

Materials

Calcium acetate solution, saturated (about 60 g/150 mL water)
Thermometer
Erlenmeyer flask, 250-mL
Hot plate or burner

Procedure

Place about 150 mL calcium acetate solution in a 250-mL flask and cool it overnight. Heat the flask gently and note that a precipitate begins to form as it is heated (at about 80 °C). Remove the flask from the heat and cool it by placing it in a stream of tap water. Notice that the precipitate goes back into solution as the temperature decreases.

Disposal

Collect waste chemicals in a special container and dispose of them according to the acceptable procedure for your school. (This solution can be stoppered and saved from year to year. You may need to readjust the amount of water as needed after long periods of standing.)

Demonstration 3: Producing a Blue Precipitate

Description

Students often get the impression that all precipitates are white, since this is what they usually see. This demonstration produces a nice blue precipitate.

Materials

Limewater (saturated calcium hydroxide solution), ~0.5 g in 200 mL H_2O
0.1 M Cobalt(II) nitrate solution [2.9 g Cobalt(II) nitrate hexahydrate, $Co(NO_3)_2 \cdot 6\ H_2O$, per 100 mL solution] in dropping bottle

Procedure

Place the limewater in a large beaker. Add a few drops of cobalt nitrate solution. Note the immediate formation of a blue precipitate.

Precautions

Cobalt nitrate should be handled with care. Wear gloves and dispose of the precipitate by drying and following directions in the *SourceBook Safety* section.

Reactions

Cobalt ion reacts with the basic limewater solution to produce cobalt hydroxide, a blue precipitate.

$$Co^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons Co(OH)_2(s)$$

Demonstration 4: Precipitation and Purification of Water

Description

Water that we use in our homes often comes from rivers, lakes, or ground deposits, and contains impurities such as bacteria, soil, and toxic substances that must be removed before we can use it. After water is allowed to stand in large tanks to allow large particles to fall to the bottom, it is treated to remove smaller suspended particles. This demonstration duplicates that treatment.

Materials

Lime solution (calcium hydroxide; about 3 tsp per liter water)
Alum solution (potassium aluminum sulfate, or aluminum sulfate, or ammonium aluminum sulfate; about 3 tsp per liter water)
Red litmus paper
Soil
Containers

Procedure

Add enough soil to a container of water to make a muddy solution. Divide this in half—one will be treated and one will serve as a control. Place a piece of red litmus paper in one container. Add lime solution, a dropperful at a time, stirring after each addition until the paper turns blue. Add a dropperful of alum solution to the container. What do you observe? Continue adding alum solution until a thick, white gelatinous precipitate forms. Stir the solution thoroughly and observe the two containers side-by-side for several minutes.

Reactions

The addition of lime solution, $Ca(OH)_2$, produced a basic solution. Aluminum ions reacted with this solution to produce aluminum hydroxide. This compound has a low solubility, so it forms a gelatinous precipitate that settles to the bottom, taking with it much of the suspended matter, leaving clear water.

$$Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_3(s)$$

Disposal

This material can be flushed down the sink.

Counterintuitive Examples and Discrepant Events

1. Can you prepare a saturated solution of bromine in carbon tetrachloride? Ethyl alcohol in water? *[No, bromine, which is ordinarily a liquid, is infinitely soluble in carbon tetrachloride; thus it is impossible to form a saturated solution of these two liquids. Ethyl alcohol is also infinitely soluble in water.]*
2. When sugar dissolves in water, why is the resulting solution clear? Why has the sugar become "invisible?" *[You cannot see anything that is smaller than the wavelength of visible light (about 10^{-5} cm). When solid, visible sugar dissolves, it releases individual sugar molecules. These have a diameter of about 10^{-7} cm. Even when surrounded by water molecules, their size is less than the wavelength of visible light. Since lightwaves pass through them, they are, indeed, "invisible."]*
3. Why do the particles in a true solution never settle? *[Particles in solution have extremely low mass. A sugar molecule, for example, has a mass of about 5×10^{-22} g. Although even a particle this small is affected by gravity, it is constantly bombarded by water molecules. As it begins to fall, water molecules below hit it and tend to drive it upward, keeping it in solution. Particles large enough to overcome this bombardment will settle, and will not form a true solution.]*
4. Do all solids that lose their physical state in aqueous solution dissolve in water? *[No. Salts dissolve, but metals react with acids and then dissolve because salts are formed.]*

Analogies

1. Ions separating from compounds and recombining to form precipitates may be compared to couples (cations + anions) going to a "dance." During the dance, couples exchange partners to form "new combinations."
2. Increase in entropy during the dissolving process is somewhat like a small group of students going into a large auditorium, where they have a tendency to spread out, rather than bunch together.

Pictures in the Mind

The Dissolving Process

1. Draw a picture of the water molecule, showing its positive and negative "ends."
2. Draw a picture of a sodium chloride crystal, showing its positive and negative ions.
3. Draw a picture of several water molecules attracted to a negative chloride ion.
4. Draw a picture of several water molecules attracted to a positive sodium ion.

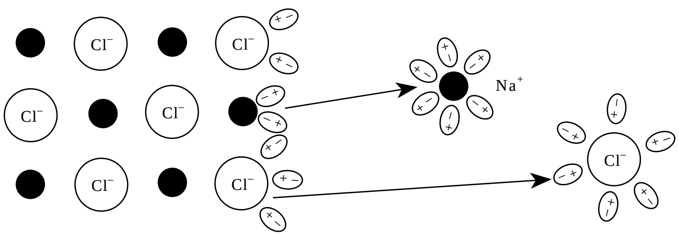


Figure 1. The dissolving process.

The Precipitation Process

1. Draw a picture of two different ions in a solution.
2. Draw a picture of a different solution with two different ions.
3. Draw a picture of all these ions in the two solutions mixed together.
4. Draw a picture to show how a precipitate might form from a new combination of these ions.

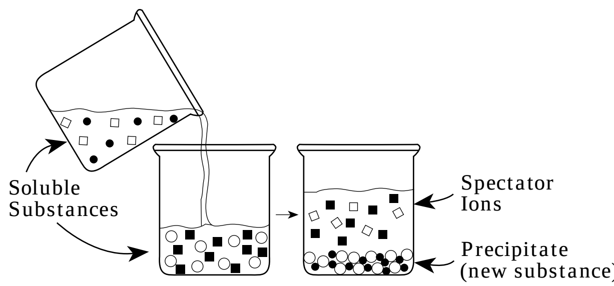


Figure 2. The precipitation process.

Language of Chemistry

Vocabulary

precipitate solid formed in solution by a reaction.

solubility amount of a substance that dissolves in a given quantity of solvent (for example water) at a given temperature.

solubility-product constant (K_{sp}) equilibrium constant for the dissolving of a slightly soluble (or nearly insoluble) ionic compound.

tincture an alcohol solution, as in "tincture of iodine."

TIPS FOR THE TEACHER

Major Factors in the Dissolving Process

$$\Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mixing} = \Delta H_{solution}$$

If ΔH in "A" is GREATER than ΔH in "B," then

- $\Delta H_{solution}$ is Endothermic
- Solution gets colder as it forms
- Heating will cause more solid to dissolve
- Energy needed to break old attractive forces > Energy released by formation of new forces

If ΔH in "A" is LESS than ΔH in "B," then

- $\Delta H_{solution}$ is Exothermic
- Solution gets warmer as it forms
- Heating will decrease the amount of solid dissolved
- Energy needed to break old attractive forces < Energy released by formation of new forces

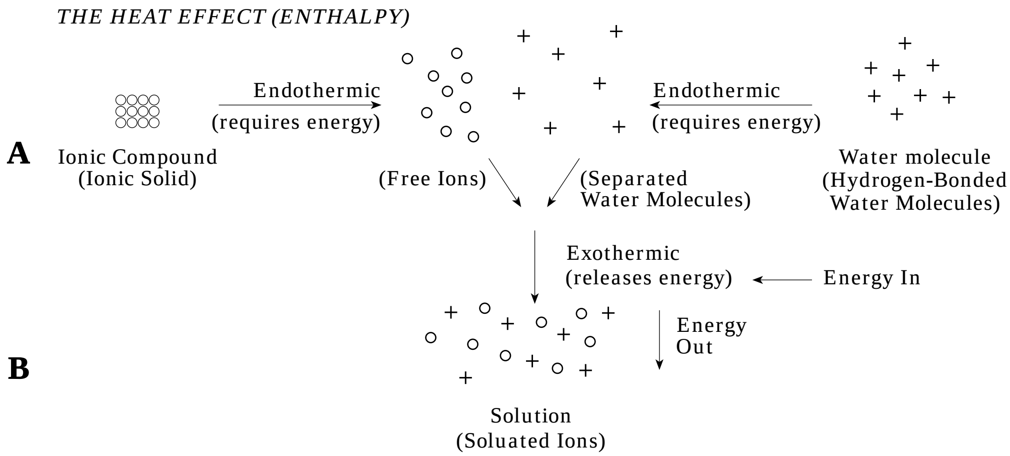


Figure 3. The effect of heat (enthalpy).

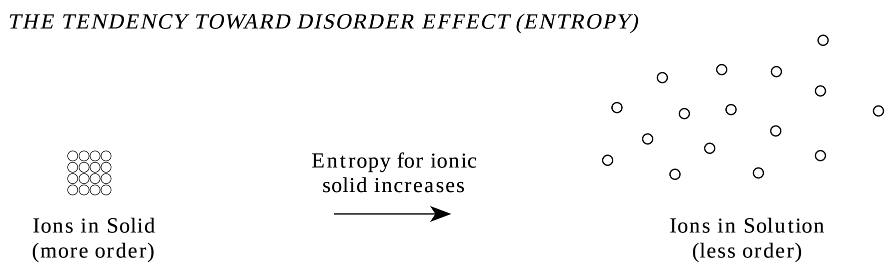


Figure 4. The effect of entropy.

There is a tendency for entropy to increase when solutions form.

If ΔS is positive, solution is favored.
ΔS is large enough, it can overcome ΔH effects and substance will go into solution.

These conditions for dissolving can also be represented by the following charts.

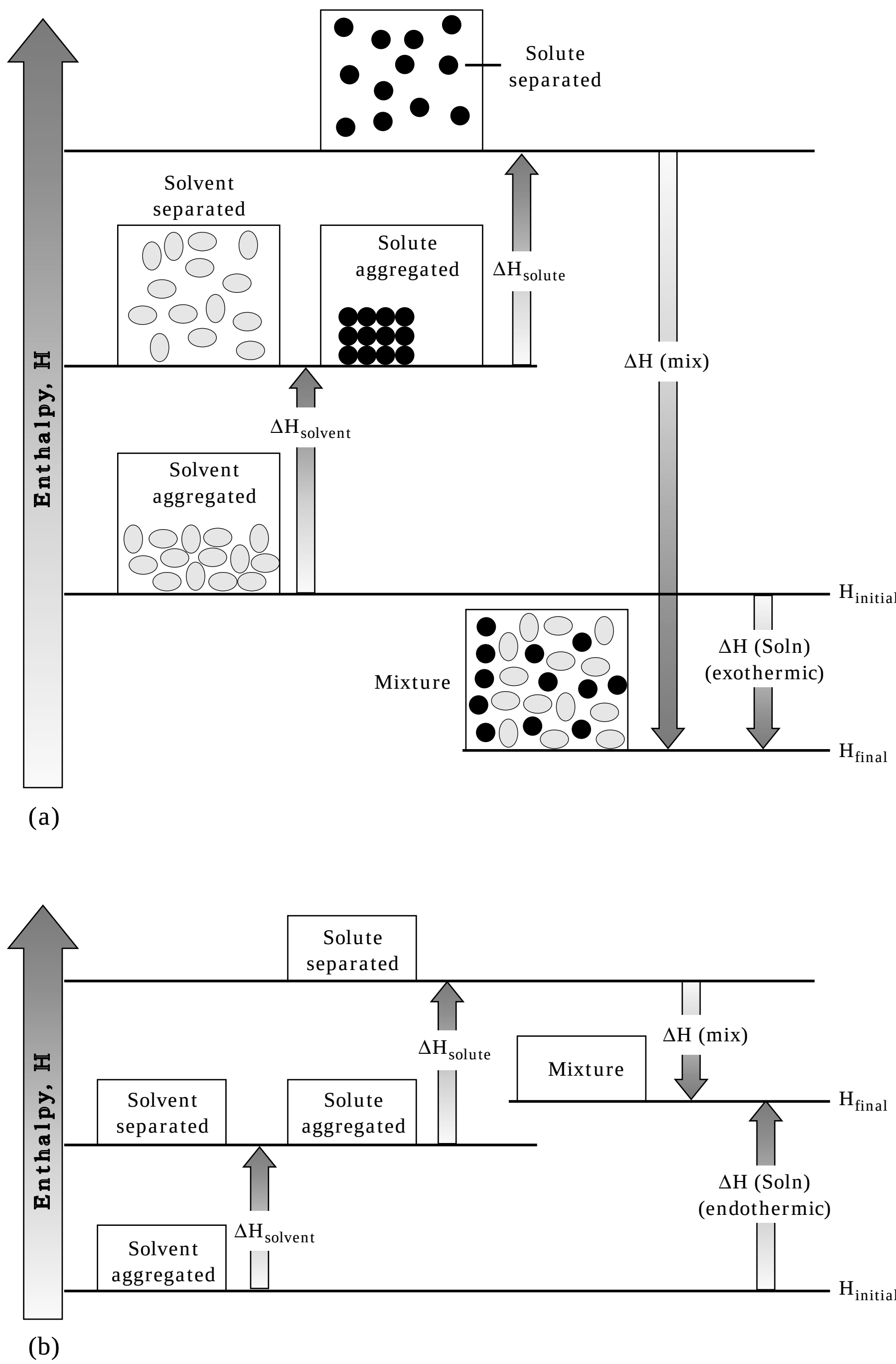


Figure 5. The conditions for dissolving.

Pattern Recognition

What Dissolves and What Does Not: Some General Rules. Charts similar to this appear in most chemistry texts.

What Dissolves and What Does Not: Some General Rules

After making a large number of observations on the solubility of compounds, chemists have devised some helpful "rules" to determine whether an ionic compound is soluble or insoluble in water. These generalizations are listed in the following chart.

The chart is easy to read. For example, it tells us that compounds containing ammonium ion (NH_4^+) are soluble (no exceptions). This means that NH_4Cl, $(NH_4)_2S$, $(NH_4)_3PO_4$, and so on are all soluble. It also tells us that compounds containing hydroxide (OH^-) are insoluble, except the alkali metals, calcium, barium, and strontium. For example, magnesium hydroxide, $Mg(OH)_2$, is insoluble, but calcium hydroxide, $Ca(OH)_2$, is soluble. With a little practice, students can make predictions about solubility of ionic compounds.

Compounds containing	Are	Except
Alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+)	Soluble	
Ammonium (NH_4^+)	Soluble	
Nitrate (NO_3^-)	Soluble	
Chlorate (ClO_3^-)	Soluble	
Perchlorate (ClO_4^-)	Soluble	
Acetate ($C_2H_3O_2^-$)	Soluble	
Chloride (Cl^-), Bromide (Br^-), Iodide (I^-)	Soluble	Lead (Pb^{2+}), Silver (Ag^+), and Mercury(I) (Hg_2^{2+}), NH_4^+
Sulfate (SO_4^{2-})	Soluble	Strontium (Sr^{2+}), Barium (Ba^{2+}), Mercury(I) (Hg_2^{2+}), Mercury(II) (Hg^{2+}), Lead (Pb^{2+}), NH_4^+
Hydroxide (OH^-)	Insoluble	Alkali metals, Ca^{2+}, Ba^{2+}, and Sr^{2+}
Sulfite (SO_3^{2-}), Chromate (CrO_4^{2-})	Insoluble	Alkali metals and NH_4^+
Carbonate (CO_3^{2-}), and Phosphate (PO_4^{3-})	Insoluble	Alkali metals and NH_4^+
Sulfide (S^{2-})	Insoluble	Alkali metals, Beryllium (Be^{2+}), Magnesium (Mg^{2+}), Calcium (Ca^{2+}), Strontium (Sr^{2+}), Barium (Ba^{2+}), and NH_4^+

Common Student Misconceptions

1. **"Like always dissolves like."**

   This is only a generalization and there are exceptions. For example, acetic acid is totally miscible in water due to the formation of hydrogen bonds, but it is also soluble in nonpolar solvents such as benzene and carbon tetrachloride.

2. **"The solubility of a solid in a liquid increases with an increase in temperature."**

   This is not always true. For example, sodium sulfite, calcium acetate, and lithium sulfate have solubilities that decrease with an increase in temperature.

3. **"Insoluble compounds do not dissolve."**

   This is not really true. All ionic compounds, even those that we classify as "insoluble" dissolve to some slight extent in water.

4. **"Hydration means the attachment of any solvent molecules to solute molecules."**

   Hydration is used only when the solvent is water. Solvation is the term used to describe any solvent molecule that surrounds and becomes attracted to solute molecules.

Problem Solving

Calculations

1. The solubility of $PbCrO_4$ is 1.34 x 10^{-7} mol/L at 25°C. Calculate the value of K_{sp}.

   Solution: $PbCrO_4(s) \rightleftarrows Pb^{2+}(aq) + CrO_4^{2-}(aq)$

   $K_{sp} = [Pb^{2+}][CrO_4^{2-}]$

   $K_{sp} = (1.34 \times 10^{-7})(1.34 \times 10^{-7})$

   $K_{sp} = 1.80 \times 10^{-14}$

2. The K_{sp} for AgCl is 1.7 x 10^{-10} at 25 °C. What is the solubility of AgCl?

   Solution: Let's represent the concentration of Ag^+ as "x". Since there will be an equal concentration of Cl^-, this can be represented as "x" also. Then,

   $AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$

   $K_{sp} = [Ag^+][Cl^-]$

   $K_{sp} = [x][x]$

   $K_{sp} = x^2$

   $1.7 \times 10^{-10} = x^2$

   $x = \sqrt{1.7 \times 10^{-10}}$

   $x = 1.3 \times 10^{-5}$ mol/L

Decision Making

1. Taking both entropy and enthalpy into consideration, explain why a gas is less soluble in water, whereas certain solids are more soluble in warm water. *[When a gas dissolves in water it forms weak bonds to the water and occupies less space. It also has slightly more order than it would as a free gas. Thus dissolving of a gas is exothermic (bond forming) and decreases entropy. Solids also generally dissolve exothermically but become considerably disordered as they move freely in the water. Since processes are favored by increased entropy and lower energy, solids tend to dissolve in water. Gases dissolving are favored by energy but not by entropy, so lower solubility is expected.]*

   $$\Delta G = \Delta H - T\Delta S$$

   $$\Delta G < 0 \text{ if } \Delta H < 0 \text{ and } \Delta S < 0$$

   (Note that increasing T makes ΔG smaller)

2. Refer to the accompanying table of solubility product constants to answer these questions:

   a. Although the ionic solids listed in the table are considered insoluble, which compound is the least soluble? *[CdS has the smallest Ksp and is therefore least soluble.]* Which is the most soluble? *[$CaSO_4$ is largest, thus most soluble.]*

   b. Which three compounds are the most insoluble? *[PbS, CdS, ZnS have the lowest K_{sp}'s.]* Does this suggest a generalization? *[Sulfides in general have low solubility.]*

NOTE: When a different number of ions per mole of slightly soluble salt form, the magnitude of the solubility product constant is not an immediately comparable value to determine relative solubility. For example, the K_{sp}'s of $CaCO_3$ and CaF_2 are 4.95 x 10^{-9} and 1.61 x 10^{-10}, respectively, but their molar solubilities are 7.04 x 10^{-5} and 3.43 x 10^{-4}, respectively.

Formula	K_{sp}	Formula	K_{sp}
AgBr	7.7 x 10^{-13}	$CaSO_4$	6.1 x 10^{-5}
AgCl	1.7 x 10^{-10}	$MgCO_3$	1 x 10^{-5}
AgCN	2 x 10^{-12}	MnS	1.4 x 10^{-15}
AgI	8.3 x 10^{-17}	$PbCO_3$	1.6 x 10^{-13}
$BaCO_3$	4.9 x 10^{-9}	$PbCrO_4$	1.8 x 10^{-14}
$BaSO_4$	1.5 x 10^{-9}	$PbSO_4$	1.9 x 10^{-6}
$CdCO_3$	2.5 x 10^{-14}	PbS	7 x 10^{-28}
CdS	1 x 10^{-28}	$SrSO_4$	2.8 x 10^{-7}
$CaCO_3$	4.8 x 10^{-9}	ZnS	4.5 x 10^{-24}

c. Certain toxic metal ions, including lead and mercury, are precipitated as a sulfide and then buried in an EPA approved landfill. Why is this an acceptable way to treat these toxic substances? *[Because these sulfides have such low solubility it is unlikely that they would dissolve and leach into the environment.]*

Graph Interpretation

Refer to Figure 6 to answer the following questions:

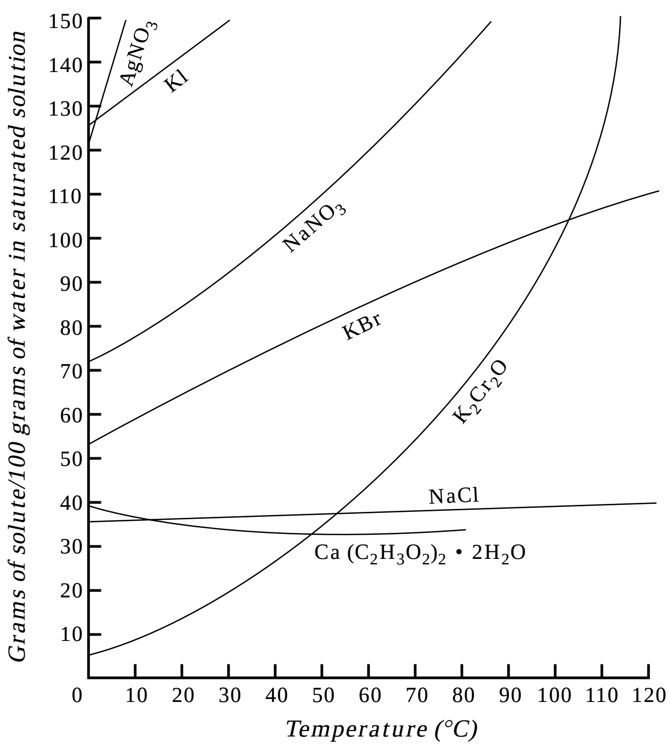


Figure 6. Solubilities of ionic compounds in water with respect to temperature.

1. Which substance decreases in solubility with increasing temperature? [$Ca(C_2H_3O_2)\cdot 2\ H_2O$]
2. Which substance has a solubility that is least affected by a change in temperature? [NaCl]

Additional Problem Solving

1. Suppose you were given a bottle of a solution that contained either magnesium, mercury(II), or barium ions. If you only had solutions of sodium hydroxide, sodium sulfate, and sodium chromate in your laboratory, devise a scheme to determine which ion is present in the mystery solution. You may find the chart "What Dissolves and What Does Not" (see Pattern Recognition) useful. *[Magnesium sulfate is soluble; barium hydroxide is soluble.]*
2. If you had a solution that contained a mixture of silver ions and strontium ions, devise four reactions that would allow you to precipitate one ion but leave the other in solution. *[Combine with hydroxide, sulfate, sulfide, halide ions.]*

History: On the Human Side

Drinking Water

When considering the topic of solubility and solutions, one inevitably must discuss the role of water as the 'universal' solvent. While this property is necessary to sustain life, impurities can be dissolved or suspended in water and are often dangerous or even fatal to humans. The earliest records of water treatment and purification have been traced to approximately 2000 B.C. in the Sus'ruta Samhita, a body of Indian Sanskrit medical knowledge. Although not written down until 400 A.D., this oral tradition described a process to purify water by boiling over a fire, or being heated in the sun, or by dipping a heated iron into it; another way was to purify by filtration through sand and coarse gravel. During the period from the 15th to 13th centuries B.C. the Egyptians developed an apparatus for filtering and siphoning fluids and recorded images of them on the walls of the tombs of Amenophis II and Ramses II. By the eighth century A.D., Arabian alchemists had developed methods of distillation that provided a safer product than that of filtration.

Most of Europe did not begin to recognize the need for water purification until the end of the Middle Ages. Sir Francis Bacon conducted numerous experiments on filtration, boiling, distillation, and clarification by coagulation. In 1685 an illustrated description of sand filters was published by Lucas Antonius Portius, an Italian physician. Portius had participated in efforts at mass sanitation for soldiers fighting the Austro-Turkish War of 1685. He proposed straining and sedimentation followed by multiple filtration through sand. Nevertheless, most Europeans continued to get their drinking water from streams, rivers, and rainwater collecting bins. They then brought these simple methods to the new world with them.

Until the end of the 19th century, Americans obtained drinking water from local ponds, wells, and rainwater holding tanks. Waste water was discarded in dry wells, leaching cesspools (pits lined with broken stones), or was simply dumped on the ground. Human defecation was usually collected in receptacles lined with brick or stone that were periodically emptied. However by the mid 1880s, flush toilets were beginning to find common use in urban settings. As a result, municipal sewer systems were constructed to carry the sewage. Until 1909 these sewer wastes were released without treatment into streams and lakes from which either the same urban center or others drew their drinking water. It was believed that rivers and large bodies of water would purify themselves.

As a result of disease epidemics that were striking urban centers at the turn of the century through the 1920s, urban centers began treating both the raw sewage from household wastes as well as chlorinating drinking water. Thus water is cleaned twice, once before being used, and again after use. The before-use cleaning, known as water treatment, takes place at municipal treatment plants. After its use, municipal water must again be treated, this time at a sewage treatment plant.

Humor: On the Fun Side

1. Message on a T-shirt: ***Front***: If you're not part of the solution...
   Back: You're part of the precipitate.
2. When students are deficient in note taking, ask them to precipitate some graphite.
   CHEM 13 NEWS, December 1976, p. 11.23
3. *CHEM 13 NEWS, January 1983, p. 11*

4. **THE GREEN LITTLE CHEMIST**

A green little chemist
On a green little day,
Mixed some green little chemicals
In a green little way.
The green little grasses
Now tenderly wave,
O'er the green little chemist's
Green little grave.

CHEM 13 NEWS, February 1981, p. 10

5. Word Search (see *Appendix* for master copy)

```
N N K N U F W J D Y I W J Q L V H
W P Z D C O T W O L L E Y G M A T
L Q W H I T E H K C R N R A D C E
P S O C X B K M S U W V E C S V T
K S P V V E Y T T N U U D R C C A
M R T C L X X A R O A S E Z S X T
Y X V V F E R C I M L G E R I R I
X B S X O E O G Q M C Q R A L O P
H K N G P B X B P O Z M H A V Y I
C U A M M O N I U M X T T M E J C
D J E L P J B Y Q P D Y W I R B E
Y T I L I B U L O S X C L B L F R
X A S A C A O W O E S N G F E U P
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Ability of a substance to dissolve in a given quantity of solvent.
2. Solid formed by reaction in aqueous solution.
3. Color of solid formed when solutions of silver nitrate and sodium chloride are mixed.
4. Color of solid formed when solutions of lead nitrate and potassium iodide are mixed.
5. Ionic solids dissolve in this kind of solvent.
6. Solubility of most solids increases as this factor is increased.
7. Symbol for solubility product constant.
8. For PbI_2, Ksp = $[Pb^{2+}]^x [I^-]^y$. The sum of x + y is this number.
9. Compounds containing this polyatomic cation are soluble.
10. Halides of this metal are used in photography.

Answers: 1. SOLUBILITY 2. PRECIPITATE 3. WHITE 4. YELLOW 5. POLAR 6. TEMPERATURE 7. KSP 8. THREE 9. AMMONIUM 10. SILVER

6. See cartoons at end of module.

Links/Connections

Within Chemistry

1. Equilibrium
2. Analytical chemistry
3. Organic chemistry (especially organic solvents)
4. Chemical bonding

Between Chemistry and Other Disciplines

1. **Environmental Sciences**
   Air pollution
   Water pollution
   Acid rain
   Eutrophication in lakes and rivers (from dissolved nitrates and phosphates)
2. **Geochemistry**
   Formation of sink holes by solution of underground limestone
   Crystal formation
3. **Biochemistry**
   Biochemical reactions
   Fat-solubility of DDT, other pesticides
4. **Medicine**
   Artificial kidneys for hemodialysis
   Kidney and gallstone formation
   Preparation of intravenous fluids
5. **Meteorology**
   Rain, snow formation

To the Contemporary World

1. **The Process of Life Depends upon Solutions**
   a. Oxygen and carbon dioxide are carried in solution in blood.
   b. Nutrients from foods we eat (simple sugars, amino acids, water soluble vitamins, *etc.*) are absorbed as particles dissolved in water.
   c. Fat-soluble vitamins are ingested as part of fatty substances and are stored in fat in the body.
   d. Urea and other excretory products are water soluble.
   e. Bones and teeth are composed primarily of insoluble phosphates, which contribute to their strength and durability.
2. **Altering Solubilities Often Results in Health Problems**
   a. Bacteria in the urinary tract can hydrolyze urea, producing ammonia and changing urine's pH. This lowers the solubility of magnesium ammonium phosphate ($MgNH_4PO_4$). This mineral (called struvite) precipitates as one type of kidney stone and must be removed surgically or broken up by ultrasound.

b. High-protein intake increases the production of uric acid and urates. When their concentration exceeds their solubility, they often precipitate in various joints of the body. This condition is known as gout.

c. Water-soluble vitamins are excreted in urine and must be replenished daily, or deficiency symptoms may result. Fat-soluble vitamins (A, D, E) are stored in body fat. One generally has enough of these vitamins stored to last several years.

3. **Formation of Caves**. Caves are formed because most rocks (especially limestone, gypsum, and dolomite) are soluble in water. Calcium carbonate, the primary component of limestone, dissolves in water rich in carbon dioxide to form calcium hydrogen carbonate. When the concentration of carbon dioxide decreases due to temperature change, pressure change, *etc.* as found in caves, solid calcium carbonate precipitates to form stalactites and stalagmites.

4. **Boiler Scale**. The same process described in (3) produces a deposit of calcium carbonate in water pipes and in boilers. When water saturated with carbon dioxide seeps through the ground it reacts with limestone to form soluble calcium hydrogen carbonate. When it is heated, carbon dioxide is driven off and insoluble calcium carbonate forms.

5. **Acid Rain**. Acid rain reacts with monuments, statues, buildings, *etc.* composed primarily of calcium carbonate to form the more soluble calcium sulfate.

6. **Photography**. Insoluble silver halides (AgI, AgBr, AgCl) are used to manufacture photographic film and paper.

7. **Extraction of Magnesium from Sea Water**. Hydroxide ion is added to sea-water to precipitate magnesium hydroxide, thus separating it from the more abundant sodium ions. The magnesium hydroxide is neutralized with hydrochloric acid. The resulting solid magnesium chloride is melted; electrolysis of the molten salt gives magnesium metal.

Media

1. "Solutions: Ionic and Molecular," Coronet laser videodisc (also on videocassette). Includes discussion questions.

2. "Doing Chemistry," laser videodisc set.

   Side C. DMEX C21 "Equilibrium Crystallization"
   DMEX C22 "Supersaturation"
   DEMO C25 "Aqueous and Nonaqueous Solvents"
   EXPT C28 "Solution Formation"
   EXPT C20 "Effect of Temperature on Solubility"

   Extensive hard copy descriptions and worked out experiments are provided with the disk. From American Chemical Society, 1155-16th St., N.W., Washington, D.C. 20036.

3. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

   a. For the Apple II computer running on ProDOS: AR 303

   b. For the Apple II computer: AP 310, AP 502

   c. For IBM PCs and PC-compatibles: PC 2501

References

Module developed by Robert Davis, Pat Owens, and Lee Summerlin, the Alabama team.

Laboratory activities, demonstrations, and charts in this module were adapted from the following sources:

Borgford, C., and Summerlin, L. (1988). *Chemical activities*. Washington, DC: American Chemical Society.

A variety of activities, with teaching tips and safety discussions, useful demonstrations or laboratory experiments for grades 7-12.

Schaff, J., Niedfeldt, K., and Brawders, J. (1966). *Semi-micro experiments for the chemstudy program*. Boston, MA: D.C. Heath.

Summerlin, L. (1981). *Chemistry for the life sciences*. New York, NY: Random House.

A text for the beginning college student planning a career in any health-related field, especially nursing and medical technology.

Summerlin, L., Borgford, C., and Ealy, J. (1988). *Chemical demonstrations, Volume II, Second Edition*. Washington, DC: American Chemical Society.

Summerlin, L., and Ealy, J. (1988). *Chemical demonstrations, Volume I, Second Edition*. Washington, DC: American Chemical Society.

Two good resources of demonstrations for teachers of chemistry and physics.

Appendix

- **Transparency Masters**
  1. Solution Set #1
  2. Suggested Chart for Reordering Solubility Observations
  3. Conditions for the Dissolving Process
  4. Word Search
- **Humor**

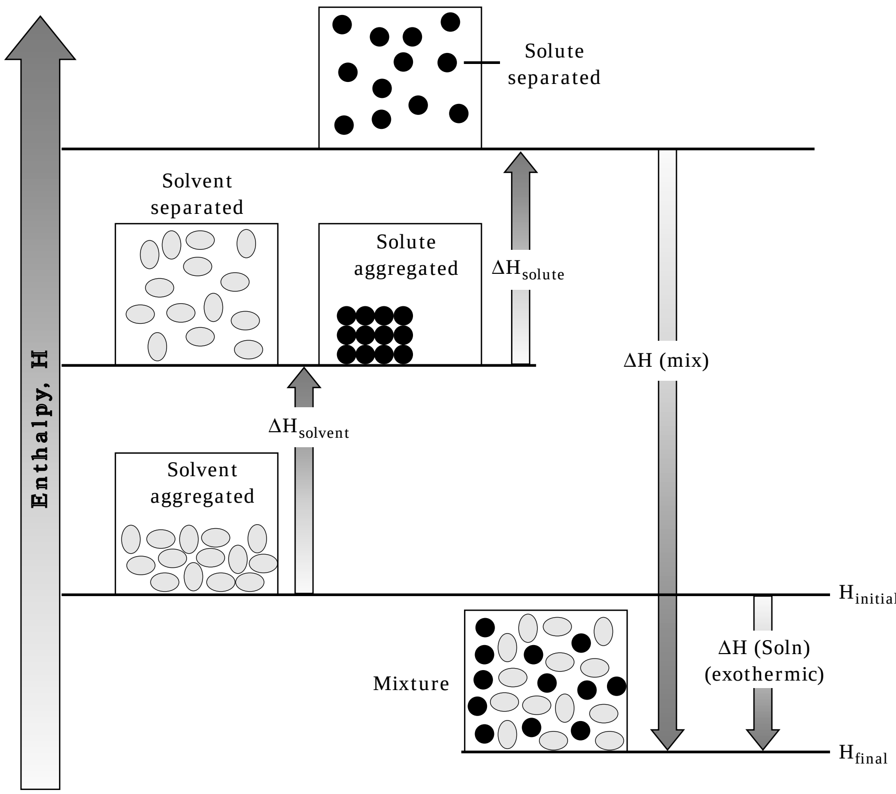
Solution Set #1

Set No. 1	K^+/Cl^- 6	Na^+/NO_3^- 5	Ag^+/NO_3^- 4	Na^+/I^- 3	Ba^{2+}/Cl^- 2
Ba^{2+}/NO_3^- 1					
Ba^{2+}/Cl^- 2					
Na^+/I^- 3					
Ag^+/NO_3^- 4					
Na^+/NO_3^- 5					

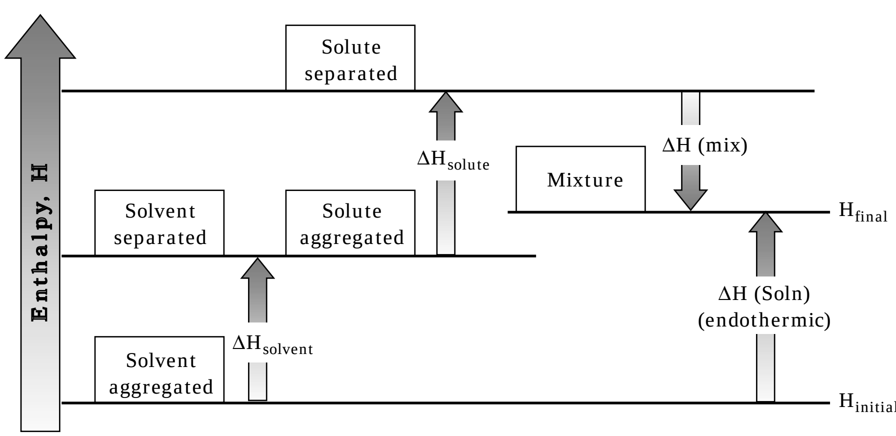
Suggested Chart for Reordering Solubility Observations

	Cl^-	CH_3COO^-	CO_3^{2-}	OH^-	NO_3^-	I^-	SO_4^{2-}
Ag^+							
Al^{3+}							
Ba^{2+}							
Co^{2+}							
Fe^{3+}							
K^+							
Mg^{2+}							
Na^+							
Sr^{2+}							

Conditions for the Dissolving Process



(a)



(b)

Word Search

N	N	K	N	U	F	W	J	D	Y	I	W	J	Q	L	V	H
W	P	Z	D	C	O	T	W	O	L	L	E	Y	G	M	A	T
L	Q	W	H	I	T	E	H	K	C	R	N	R	A	D	C	E
P	S	O	C	X	B	K	M	S	U	W	V	E	C	S	V	T
K	S	P	V	V	E	Y	T	T	N	U	U	D	R	C	C	A
M	R	T	C	L	X	X	A	R	O	A	S	E	Z	S	X	T
Y	X	V	V	F	E	R	C	I	M	L	G	E	R	I	R	I
X	B	S	X	O	E	O	G	Q	M	C	Q	R	A	L	O	P
H	K	N	G	P	B	X	B	P	O	Z	M	H	A	V	Y	I
C	U	A	M	M	O	N	I	U	M	X	T	T	M	E	J	C
D	J	E	L	P	J	B	Y	Q	P	D	Y	W	I	R	B	E
Y	T	I	L	I	B	U	L	O	S	X	C	L	B	L	F	R
X	A	S	A	C	A	O	W	O	E	S	N	G	F	E	U	P

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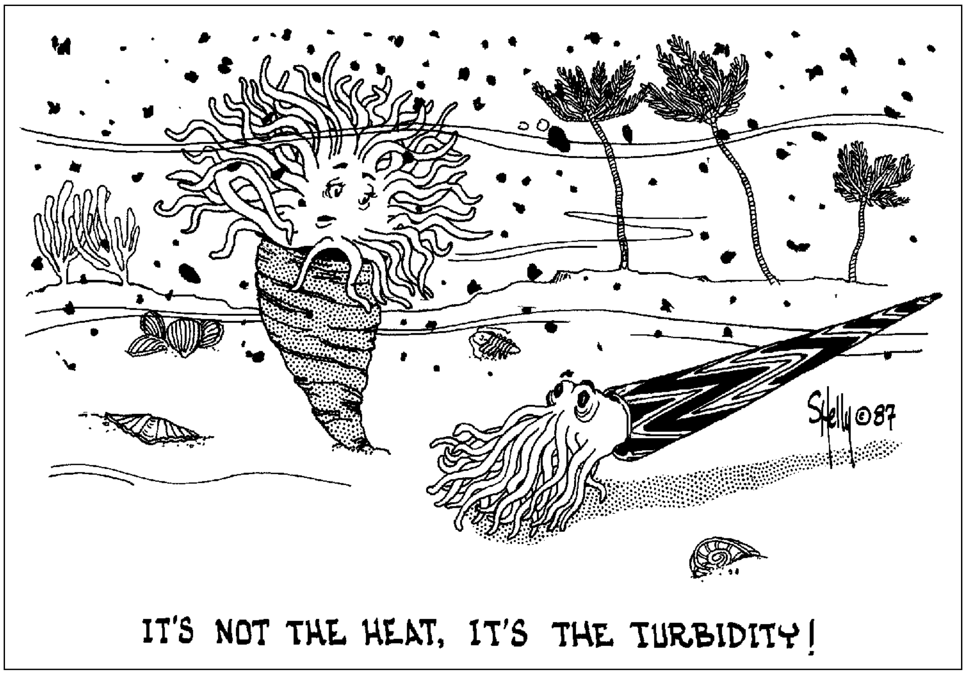

Cartoon by Shelly Fischman. Reprinted with permission.

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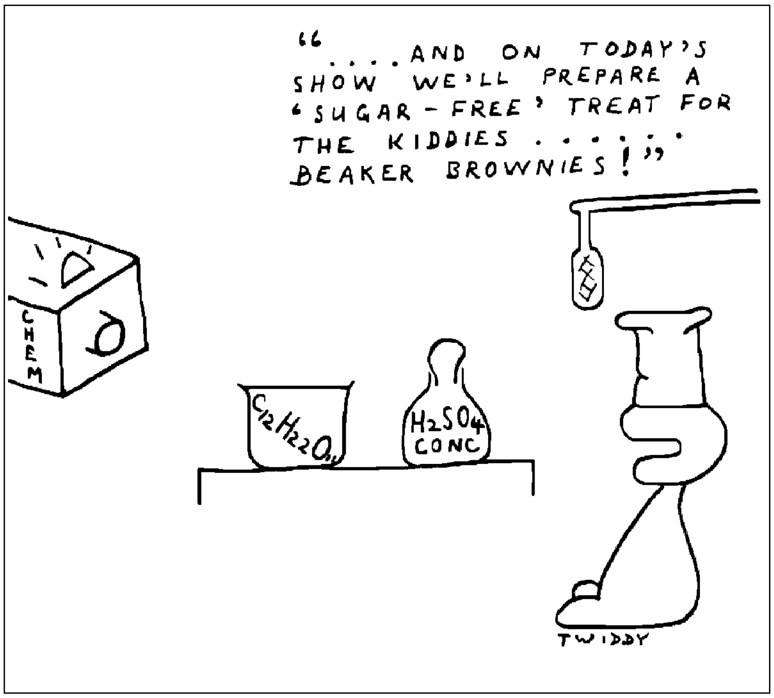

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