MISCIBILITY OF LIQUIDS:

As the saying goes, "oil and water don't mix." This is fortunate for the makers of salad dressing! The makers of alcoholic beverages, on the other hand, take advantage of the fact that ethyl alcohol and water do mix together. The tendency of some liquids to "mix" -- that is, to form homogeneous mixtures -- is referred to as their miscibility. Two liquids are miscible if they are each soluble in the other, regardless of the relative proportions used.

Why are some liquids miscible and other liquids are not miscible? The answer has to do with the intermolecular forces of attraction between molecules of the liquids in question. For two liquids to be miscible, their intermolecular attractive forces must be of approximately equal strength. Any attempt to mix two liquids whose intermolecular attractive forces are of unequal strengths will result in the molecules of the liquid with the stronger intermolecular attractive forces tending to form relatively strong bonds to each other, leaving the molecules of the liquid with the weaker intermolecular attractive forces to form a separate layer. In short, no mixing takes place.

A simple rule which summarizes all of this is the "like dissolves like" rule, which says that liquids of similar polarity are miscible with each other, while liquids with different polarities are not miscible. For example, water (H₂O) is a polar molecule -- water molecules tend to connect to each other by forming hydrogen bonds. Liquids such as ethyl alcohol (CH₃CH₂-O-H), which also tend to form hydrogen bonds, are generally miscible with water. However, liquids which do not tend to form hydrogen bonds (such as the "oil" in salad dressing) are usually immiscible with water. (The "oil" in salad dressing is composed largely of carbon and hydrogen, which are similar in electronegativity. Thus, "oil" is nonpolar, and its molecules are attracted to each other by relatively weak London forces.)
SOLUBILITY OF GASES IN LIQUIDS:

Gases are soluble in liquids to some extent, as a moment's thought will make obvious. For example, oxygen \((\text{O}_2, \text{a gas})\) is transported to the brain by the blood (a liquid). The solubility of a gas in a liquid depends mostly on two properties of the gas in question -- its pressure and its temperature.

Not surprisingly, the solubility of a gas in a liquid increases as the pressure of the gas increases. Again, this should be obvious from everyday experience. For example, when you open a can of a "carbonated" beverage, you see bubbles come to the surface of the liquid. The bubbles are made of carbon dioxide \((\text{CO}_2, \text{a gas})\) which was dissolved in the liquid until you opened the can. Cans of carbonated beverages are sealed so as to contain a slightly higher pressure of gas than atmospheric pressure. Exposing the carbonated beverage to a lower pressure (atmospheric pressure) causes the dissolved gas \((\text{CO}_2)\) to be less soluble in the liquid than it was, with the result that bubbles form.

Somewhat surprisingly, the solubility of a gas in a liquid decreases as the temperature of the liquid increases. (For solids, the opposite is true -- for example, sugar (a solid) is more soluble in hot water than in cold water.) Once again, you've probably seen this phenomenon before. For example, if you heat a pan of water on a stove, you will notice that just before the water boils, some relatively small bubbles will form along the insides of the walls of the pan. These bubbles are not made of water vapor (like the "boiling bubbles" are), but are actually made of oxygen gas which had been dissolved in the water before you heated it. This phenomenon is the basis for the environmental problem known as thermal pollution -- if the temperatures of the lakes and ponds where fish live rise above certain levels, the amount of oxygen dissolved in the water will be reduced below the point at which the water can support fish and other marine life.
SOLUBILITY OF SOLIDS IN WATER:

When a crystalline solid dissolves in water, it does so because water molecules strike the crystal lattice with enough force to dislodge particles of the solid, whether these particles are molecules (such as the \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) molecules of which sugar is made) or ions (such as the \( \text{Na}^+ \) and \( \text{Cl}^- \) ions of which table salt -- sodium chloride -- is made). The water molecules then surround the particles of the solute, forming a "solvent cage" around them which is held in place by ion-dipole or dipole-dipole attractive forces. These "solvent cages" keep the solute particles separated from each other, preventing recrystallization of the solid.

Not all ionic compounds are soluble in water. The reasons for this are not well understood, but a series of empirical rules for predicting whether an ionic compound is soluble in water has been developed. The solubility rules given below are numbered 1 through 6 for future reference.

The following ionic compounds are soluble in water:

1. All salts containing \( \text{Na}^+ \), \( \text{K}^+ \), or \( \text{NH}_4^+ \) ions.
2. All salts containing \( \text{NO}_3^- \), \( \text{ClO}_4^- \), \( \text{ClO}_3^- \), or \( \text{C}_2\text{H}_3\text{O}_2^- \) ions.
3. All salts containing halide ions (\( \text{Cl}^- \), \( \text{Br}^- \), \( \text{I}^- \)) except:
   - \( \text{Ag}^+ \), \( \text{Hg}_2^{2+} \), and \( \text{Pb}^{2+} \) halides.
4. All salts containing sulfate (\( \text{SO}_4^{2-} \)) ions, except:
   - \( \text{CaSO}_4 \), \( \text{BaSO}_4 \), \( \text{RaSO}_4 \), \( \text{SrSO}_4 \), \( \text{PbSO}_4 \), and \( \text{Hg}_2\text{SO}_4 \).

The following ionic compounds are insoluble in water, but are salts of weak acids and are therefore soluble in acid:

5. All salts containing oxide (\( \text{O}^{2-} \)) and hydroxide (\( \text{OH}^- \)) ions, except:
   - \( \text{Ca}^{2+} \), \( \text{Ba}^{2+} \), \( \text{Na}^+ \), \( \text{K}^+ \), and \( \text{NH}_4^+ \) oxides and hydroxides.
6. All salts containing \( \text{CO}_3^{2-} \), \( \text{PO}_4^{3-} \), \( \text{S}^{2-} \), or \( \text{SO}_3^{2-} \) ions, except those which are soluble according to Rule # 1 above.
USING THE SOLUBILITY RULES:

**Problem:** Convert pure, crystalline CaCO₃ into pure, crystalline CaCl₂.

**Solution:** CaCO₃ is insoluble in water, but soluble in acid (Rule # 6). Therefore, dissolve the CaCO₃ in acid to get Ca²⁺ ions into solution. A good acid to choose would be HCl, since this will also get Cl⁻ ions into solution. CaCl₂ is soluble in water (Rule # 3), so simply heating this solution until all of the water has boiled away will leave a residue of pure, crystalline CaCl₂. The equation of the reaction which occurs is: CaCO₃ + 2 HCl → CaCl₂ + H₂O + CO₂.

(Carbonates (CO₃²⁻) give off bubbles of CO₂ gas whenever they react with acids.)

**Problem:** Separate a mixture of MgCl₂ and BaCl₂, obtaining pure MgCl₂ and pure BaCl₂ at the end of the separation process.

**Solution:** Both MgCl₂ and BaCl₂ are soluble in water (Rule # 3). Thus, dissolving them in water produces a solution which contains Mg²⁺ ions and Ba²⁺ ions. These ions can be separated by adding NaOH to the solution. Mg(OH)₂ is insoluble in water (Rule # 5), so it emerges from the solution as a solid. The Ba²⁺ ions remain in solution, since Ba(OH)₂ is soluble in water (Rule # 5). The Mg(OH)₂ can be isolated, acidified with HCl, and heated to dryness to give pure MgCl₂. The remaining solution can be acidified with HCl and boiled to give pure BaCl₂.

**Problem:** An unknown crystalline solid may contain any or all of the following: Ca(NO₃)₂, CuCl₂, K₂CO₃, SrI₂. Adding water to the unknown solid gave a solid residue. Treating this residue with H₂SO₄ caused the residue to dissolve completely and produced bubbles of a gas. Identify the unknown solid.

**Solution:** The bubbles suggest that the residue is a water-insoluble carbonate salt, but it can't be CaCO₃ or SrCO₃, since either of these would react with H₂SO₄ to produce water-insoluble sulfate salts (Rule # 4). Therefore, it must be CuCO₃, and the unknown solid was a mixture of CuCl₂ and K₂CO₃.
ELECTROLYTES:

As you probably already know, it's not a good idea to go swimming in the ocean during a thunderstorm! Neither is it a good idea to drop an electrical appliance into your bathtub while you're bathing! This is because both the ocean and your bath water conduct electricity, which could harm you if you're careless.

Pure water does not conduct electricity, but water which contains ions does conduct electricity. Any substance which produces ions when dissolved in water, thereby creating a solution which conducts electricity, is called an electrolyte. All water-soluble ionic compounds (such as NaCl in salty ocean water) are electrolytes, but some water-soluble covalent compounds are also electrolytes. An example is HCl, which is normally a gas, but reacts with water to form ions:

$$\text{HCl (g)} + \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{Cl}^- (\text{aq})$$

Some covalent compounds are nonelectrolytes -- their aqueous solutions do not conduct electricity. A common example of a nonelectrolyte is table sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$), whose aqueous solutions contain sucrose molecules, but not many ions.

Compounds such as NaCl and HCl are examples of strong electrolytes -- their aqueous solutions are good conductors of electricity. Some covalent compounds which are electrolytes produce aqueous solutions which are relatively poor conductors of electricity. These compounds are called weak electrolytes. Examples include ammonia (NH$_3$) and acetic acid (HC$_2$H$_3$O$_2$, found in vinegar). The reactions these compounds undergo when dissolved in water are shown below.

$$\text{NH}_3 (\text{g}) + \text{H}_2\text{O (l)} \rightarrow \text{NH}_4^+ (\text{aq}) + \text{OH}^- (\text{aq})$$
$$\text{HC}_2\text{H}_3\text{O}_2 (\text{aq}) + \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^- (\text{aq})$$

Compounds such as ammonia and acetic acid are weak electrolytes because the reactions shown above do not go to completion -- a relatively small number of ions is formed, resulting in a solution which is a relatively poor conductor.
COLLIGATIVE PROPERTIES:

In the winter, when snow and ice make the highways slippery and thus dangerous for travel purposes, rock salt is spread out over the roads in order to "melt" the ice. Actually, the salt doesn't "melt" the ice -- that is, it doesn't supply any additional heat. What happens is that the rock salt dissolves in the ice, forming a solution whose freezing point (or melting point, if you like) is lower than the freezing point of pure water. Since colder temperatures are needed for freezing to occur, the ice-salt mixture melts more readily than pure ice does.

The lowering of the freezing point of an aqueous solution of a salt is one example of several properties of solutions referred to collectively as colligative properties. What distinguishes a colligative property from any of the other properties of solutions is that colligative properties depend only on the numbers of particles of solute and solvent present in the solution, and not on the identities of the solute and the solvent. For example, the freezing point of any aqueous solution will be lower than the freezing point of pure water -- it doesn't matter whether the solute is NaCl, CaCl₂, C₁₂H₂₂O₁₁, or any other solid. However, the identity of the solute does help determine the extent to which the freezing point of the solution is lowered.

The reason for the lowering of the freezing point of a solution is that the presence of the solute particles makes it more difficult for the particles of the solvent to arrange themselves into the crystalline lattice formation needed for freezing to occur. More energy must be removed from these solvent particles -- that is, lower temperatures must be achieved -- before crystallization (freezing) can take place. Similarly, the boiling point of a solution is higher than the boiling point of the pure solvent, since the solute particles occupy some of the surface area of the solution, making vaporization of solvent less likely to occur.
MOLALITY AND FREEZING POINT DEPRESSION:

The extent to which a solute which is a non-electrolyte lowers the freezing point of a solution is given by the equation: \( \Delta T = k_f m \), where \( \Delta T \) is the freezing point depression, \( k_f \) is the freezing point depression constant, and \( m \) is the concentration of the solution, expressed as its molality. The molality of a solution is defined as the amount of solute (in moles) per kilogram of solvent present in the solution. (Spelling is very important here -- do not confuse molarity (moles/liter, symbol = M) with molality (moles/kilogram, symbol = m).)

**Problem:** What is the molality of a solution prepared by dissolving 34.23 grams of sucrose (table sugar, \( C_{12}H_{22}O_{11} \)) in 50.00 mL of water?

**Solution:** First, find the molecular weight of sucrose:

M.W. sucrose = \((12 \times 12.011) + (22 \times 1.0079) + (11 \times 15.9994) = 342.30 \) grams/mole.

Next, find the amount of sucrose which dissolved (in moles):

\[
\text{Amount of sucrose} = \frac{34.23 \text{ grams sucrose}}{342.30 \text{ grams/mole}} = 0.1000 \text{ moles sucrose}. \quad (4 \text{ sig. figs.})
\]

Next, find the mass of water used, in kilograms: (density = 1.00 g/mL)

\[
\text{Mass of water} = 50.00 \text{ mL} \times (1.00 \text{ gram/mL}) \times (0.001000 \text{ kg/gram}) = 0.05000 \text{ kg water}.
\]

Finally, compute the molality by dividing the amount of the solute used (in moles) by the mass of the solvent used (in kilograms):

\[
\text{Molality of Solution} = \frac{0.1000 \text{ moles sucrose}}{0.05000 \text{ kg water}} = 2.000 \text{ molal} = 2.000 \text{ m}.
\]

**Problem:** What would be the freezing point of the above solution? The value of \( k_f \) for water is 1.86 \(^\circ\)C/molal.

**Solution:** Use the above equation to find the freezing point depression:

\[
\text{Freezing Point Depression} = \Delta T = k_f m = (1.86 \text{ } ^\circ\text{C/molal}) \times (2.000 \text{ molal}) = 3.72 \text{ } ^\circ\text{C}.
\]

Now, since this represents a freezing point depression, subtract this number from the freezing point of pure water to get the solution's freezing point:

\[
\text{Freezing Point of Solution} = 0.00 \text{ } ^\circ\text{C} - 3.72 \text{ } ^\circ\text{C} = -3.72 \text{ } ^\circ\text{C}.
\]
BOILING POINT ELEVATION:

The extent to which a solute which is a non-electrolyte raises the boiling point of a solution is given by an equation which is very similar to the equation for determining the freezing point depression of a solution. The equation is: \( \Delta T = k_b m \), where \( \Delta T \) is the boiling point elevation, \( k_b \) is the boiling point elevation constant, and \( m \) is the molality of the solution.

Problem: Maple syrup has a boiling point of 104.6 °C. Assuming that maple syrup is essentially a solution of sucrose (\( \text{C}_{12}\text{H}_{22}\text{O}_{11} \), M.W. = 342.30 g/mole) in water, calculate the molality of maple syrup. \( k_f \) for water = 0.51 °C/molal.\(^1\)

Solution: Pure water has a boiling point of 100.0 °C, so the boiling point elevation can be found by subtracting this from maple syrup's boiling point:

\[
\text{Boiling Point Elevation} = \Delta T = 104.6 \text{ °C} - 100.0 \text{ °C} = 4.6 \text{ °C}.
\]

Now, rewriting the above equation as: \( m = \Delta T / k_b \), we can easily find the molality:

\[
\text{Molality} = \Delta T / k_b = (4.6 \text{ °C}) / (0.51 \text{ °C/molal}) = 9.0 \text{ molal}.
\]

Problem: What is the percentage by mass of sucrose in maple syrup?\(^1\)

Solution: From the above problem, maple syrup is 9.0 molal sugar in water -- that is, 9.0 moles of sugar are present for every kilogram of water that is present. Converting 9.0 moles of sugar (sucrose) into kilograms, we get:

\[
9.0 \text{ moles sucrose} \times \frac{342.30 \text{ grams}}{1 \text{ mole}} \times \frac{1 \text{ kilogram}}{1000 \text{ grams}} = 3.1 \text{ kg sucrose}
\]

The percentage by mass is simply the mass of sucrose divided by the total mass of the solution, expressed as a percentage:

\[
\text{Total Mass} = 3.1 \text{ kg sucrose} + 1.0 \text{ kg water} = 4.1 \text{ kg solution}.
\]

\[
\text{Percentage by Mass} = \frac{3.1 \text{ kg sucrose}}{4.1 \text{ kg solution}} \times 100\% = 76\% \text{ sucrose by mass}.
\]

(The next time you eat pancakes and pour a lot of maple syrup on them, you might stop to consider the fact that maple syrup is about three-fourths pure sugar!)