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 <u>do</u> mix together. The tendency of some liquids to "mix" -- that is, to form homogeneous mixtures -- is referred to as their <u>miscibility</u>. Two liquids are <u>miscible</u> 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 <u>intermolecular forces of attraction</u> between molecules of the liquids in question. For two liquids to be miscible, their intermolecular attractive forces must be of approximately <u>equal</u> strength. Any attempt to mix two liquids whose intermolecular attractive forces are of <u>unequal</u> strengths will result in the molecules of the liquid with the <u>stronger</u> intermolecular attractive forces tending to form relatively strong bonds to each other, leaving the molecules of the liquid with the <u>weaker</u> 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 <u>polarity</u> are miscible with each other, while liquids with <u>different</u> polarities are not miscible. For example, water (H_2O) is a <u>polar</u> molecule -- water molecules tend to connect to each other by forming <u>hydrogen bonds</u>. Liquids such as ethyl alcohol (CH_3CH_2-O-H), which also tend to form hydrogen bonds, are generally miscible with water. However, liquids which do <u>not</u> tend to form hydrogen bonds (such as the "oil" in salad dressing) are usually <u>immiscible</u> with water. (The "oil" in salad dressing is composed largely of carbon and hydrogen, which are similar in electronegativity. Thus, "oil" is <u>nonpolar</u>, and its molecules are attracted to each other by relatively weak <u>London forces</u>.)

1

SOLUBILITY OF GASES IN LIQUIDS:

Gases are soluble in liquids to some extent, as a moment's thought will make obvious. For example, oxygen (O_2, 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 <u>pressure</u> and its <u>temperature</u>.

Not surprisingly, the solubility of a gas in a liquid <u>increases</u> as the <u>pressure</u> of the gas <u>increases</u>. 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 (CO_2, 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 (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 <u>decreases</u> as the <u>temperature</u> of the liquid <u>increases</u>. (For <u>solids</u>, 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 <u>thermal pollution</u> -- 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 <u>molecules</u> (such as the $C_{12}H_{22}O_{11}$ molecules of which sugar is made) or <u>ions</u> (such as the Na^+ and 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 <u>solubility rules</u> given below are numbered 1 through 6 for future reference.

The following ionic compounds are <u>soluble in water</u>:

1. All salts containing Na^+, K^+, or NH_4^+ ions.

2. All salts containing NO_3^-, ClO_4^-, ClO_3^-, or $C_2H_3O_2^-$ ions.

3. All salts containing halide ions (Cl^-, Br^-, I^-) <u>except</u>:
   Ag^+, Hg_2^{2+}, and Pb^{2+} halides.

4. All salts containing sulfate (SO_4^{2-}) ions, <u>except</u>:
   $CaSO_4$, $BaSO_4$, $RaSO_4$, $SrSO_4$, $PbSO_4$, and Hg_2SO_4.

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

5. All salts containing oxide (O^{2-}) and hydroxide (OH^-) ions, <u>except</u>:
   Ca^{2+}, Ba^{2+}, Na^+, K^+, and NH_4^+ oxides and hydroxides.

6. All salts containing CO_3^{2-}, PO_4^{3-}, S^{2-}, or SO_3^{2-} ions, <u>except</u>
   those which are soluble according to Rule # 1 above.

USING THE SOLUBILITY RULES:

Problem: Convert pure, crystalline $CaCO_3$ into pure, crystalline $CaCl_2$.

Solution: $CaCO_3$ is insoluble in water, but soluble in acid (Rule # 6). Therefore, dissolve the $CaCO_3$ in acid to get Ca^{2+} ions into solution. A good acid to choose would be HCl, since this will also get Cl^- ions into solution. $CaCl_2$ 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 $CaCl_2$. The equation of the reaction which occurs is: $CaCO_3$ + 2 HCl $\longrightarrow$ $CaCl_2$ + H_2O + CO_2. (Carbonates (CO_3^{2-}) give off bubbles of CO_2 gas whenever they react with acids.)

Problem: Separate a mixture of $MgCl_2$ and $BaCl_2$, obtaining pure $MgCl_2$ and pure $BaCl_2$ at the end of the separation process.

Solution: Both $MgCl_2$ and $BaCl_2$ are soluble in water (Rule # 3). Thus, dissolving them in water produces a solution which contains Mg^{2+} ions and Ba^{2+} 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 Ba^{2+} 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 $MgCl_2$. The remaining solution can be acidified with HCl and boiled to give pure $BaCl_2$.

Problem: An unknown crystalline solid may contain any or all of the following: $Ca(NO_3)_2$, $CuCl_2$, K_2CO_3, SrI_2. Adding water to the unknown solid gave a solid residue. Treating this residue with H_2SO_4 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 $CaCO_3$ or $SrCO_3$, since either of these would react with H_2SO_4 to produce water-insoluble sulfate salts (Rule # 4). Therefore, it must be $CuCO_3$, and the unknown solid was a mixture of $CuCl_2$ and K_2CO_3.
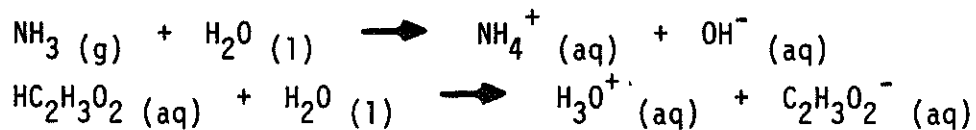
ELECTROLYTES:

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

$$HCl_{(g)} + H_2O_{(1)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Some covalent compounds are <u>nonelectrolytes</u> -- their aqueous solutions do not conduct electricity. A common example of a nonelectrolyte is table sugar (sucrose, $C_{12}H_{22}O_{11}$), whose aqueous solutions contain sucrose <u>molecules</u>, but not many ions.

Compounds such as NaCl and HCl are examples of <u>strong</u> electrolytes -- their aqueous solutions are good conductors of electricity. Some covalent compounds which are electrolytes produce aqueous solutions which are relatively <u>poor</u> conductors of electricity. These compounds are called <u>weak</u> electrolytes. Examples include ammonia (NH_3) and acetic acid ($HC_2H_3O_2$, found in vinegar). The reactions these compounds undergo when dissolved in water are shown below.

$$NH_3{}_{(g)} + H_2O_{(1)} \longrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$
$$HC_2H_3O_2{}_{(aq)} + H_2O_{(1)} \longrightarrow H_3O^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

Compounds such as ammonia and acetic acid are <u>weak</u> electrolytes because the reactions shown above do <u>not</u> go to completion -- a relatively <u>small</u> number of ions is formed, resulting in a solution which is a relatively <u>poor</u> 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, $CaCl_2$, $C_{12}H_{22}O_{11}$, 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.

6

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 ΔT 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 x 12.011) + (22 x 1.0079) + (11 x 15.9994) = 342.30 grams/mole.

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

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

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

Mass of water = 50.00 mL x (1.000 gram/mL) x (0.001000 kg/gram) = 0.05000 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):

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

Problem: What would be the freezing point of the above solution? The value of k_f for water is 1.86 ^{O}C/molal.

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

Freezing Point Depression = $\Delta T = k_f m$ = (1.86 ^{O}C/molal) x (2.000 molal) = 3.72 ^{O}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:

Freezing Point of Solution = 0.00 ^{O}C - 3.72 ^{O}C = -3.72 ^{O}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 ΔT 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 ^{o}C. Assuming that maple syrup is essentially a solution of sucrose ($C_{12}H_{22}O_{11}$, M.W. = 342.30 g/mole) in water, calculate the molality of maple syrup. k_f for water = 0.51 ^{o}C/molal.[1]

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

Boiling Point Elevation = ΔT = 104.6 ^{o}C - 100.0 ^{o}C = 4.6 ^{o}C.

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

Molality = $\Delta T/k_b$ = (4.6 ^{o}C) ÷ (0.51 ^{o}C/molal) = 9.0 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 moles sucrose x $\frac{342.30 \text{ grams}}{1 \text{ mole}}$ x $\frac{1 \text{ kilogram}}{1000 \text{ grams}}$ = 3.1 kg sucrose.

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

Total Mass = 3.1 kg sucrose + 1.0 kg water = 4.1 kg solution.

Percentage by Mass = $\frac{3.1 \text{ kg sucrose}}{4.1 \text{ kg solution}}$ x 100% = 76% 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!)

---

1) From a similar problem on page 255 in "Chemical Principles and Properties" by M. J. Sienko and R. A. Plane. 1974 by McGraw-Hill, Inc.