

Solution: Homogeneous Mixture

Solute: That which dissolves

Solvent: Dissolving medium (usually water)

The solute can be solid, liquid, or gas. The solvent can also be solid, liquid, or gas. However, solvent is usually a liquid.

Solute/solvent	Examples
gas/gas	Air, natural gas
gas/liquid	CO <sub>2</sub> /water (soda) HCl/water (hydrochloric acid) NH <sub>3</sub> /water (aqueous ammonia)
liquid/liquid	Ethanol/water (alcoholic beverages)
solid/liquid	NaCl/water (salt water) naphthalene/benzene
solid/solid	Ag/Au (14 karat gold) Zn/Cu Brass Pb/Sn Solder

Air is not usually described as a solution, but it does fit the definition of a homogeneous mixture (assuming the air is in a reasonably small space, since the air spread over a large distance is not homogeneous).

In a liquid/liquid solution, it is unclear as to what dissolves in what (which is the solute, which is the solvent). The two liquids are said to be mutually soluble, or miscible.

An ethanol-water mixture is miscible in all proportions. Any amount of ethanol can mix with any amount of water to form a homogeneous mixture.

On the other hand, when a solid dissolves in a liquid, there is a limit to its solubility. When maximum solubility has been reached, the solution is said to be saturated.

### Solution Concentration

Solutions are mixtures with variable composition. We describe the composition of the solution in terms of concentration. In general:

$$\text{Concentration} = \frac{\text{quantity of solute}}{\text{quantity of solvent or solution}}$$

where "solution" = solute + solvent

Some common units of concentration are:

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

This is equivalent to “parts per hundred.” where “parts” refer to mass. For really small concentrations (trace amounts), we sometimes use ppm (parts per million) or even ppb (parts per billion).

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

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

Other units used by chemists are molarity, molality and mole fraction.

$$\text{Molarity} = \frac{\text{moles solute}}{\text{Liter of solution}}$$

$$\text{Molality} = \frac{\text{moles solute}}{\text{kg solvent}}$$

$$\text{Mole fraction} = \frac{\text{moles solute}}{\text{moles solute} + \text{moles solvent}}$$

Add 5.00 g NaCl to 100 g of water. Calculate the percent by mass, molality and mole fraction.

$$\text{Percent by mass} = \frac{5.00 \text{ g NaCl}}{105 \text{ g solution}} \times 100 = 4.76\%$$

$$\text{Molality} = \frac{5.00 \text{ g} \times \frac{1 \text{ mol}}{58.5 \text{ g}}}{0.100 \text{ kg water}} = 0.855 \text{ m}$$

$$\text{Mole fraction} = \frac{5.00}{\frac{5.00}{58.5} + \frac{100}{18.0}} = 0.0152$$

In the above expression  $\frac{5.00}{58.5}$  represents mol NaCl and  $\frac{100}{18.0}$  represents mol water.

What additional information must be given in order to calculate the molarity of this solution?

We would need to know the solution's density. Since molarity is  $\frac{\text{moles}}{\text{liter}}$ , we require information relating volume to amount. The density relates volume to mass, and molar mass can then be used to relate mass to moles. This is illustrated in the next example.

Concentrated hydrochloric acid is 37.0% HCl by mass. Its density is  $1.19 \frac{\text{g}}{\text{mL}}$ . Calculate the molarity, molality, and mole fraction of HCl.

The density of  $1.19 \frac{\text{g}}{\text{mL}}$  is equivalent to  $1190 \frac{\text{g}}{\text{L}}$ . Each liter has a mass of 1190 g, and 37.0% of that mass is HCl. Thus:

$$\text{Molarity} = 0.37 (1190 \frac{\text{g}}{\text{L}}) \times \frac{1 \text{ mol}}{36.5 \text{ g}} = 12.1 \text{ M}$$

An alternate, equivalent way of solving is to start with thinking of 37% as

$$\frac{37 \text{ g HCl}}{100 \text{ g solution}}$$

$$\frac{37.0 \text{ g HCl}}{100 \text{ g solution}} \times \frac{1190 \text{ g solution}}{\text{L}} \times \frac{1 \text{ mol}}{36.5 \text{ g}} = 12.1 \text{ M}$$

To calculate molality, we again remember that 37.0% HCl means 37.0 g HCl per 100 g solution. That 100 g solution will contain 37.0 g HCl and (100-37) or 63 g of water. Molality is the only common concentration unit in which the denominator is solvent alone.

$$\text{Molality} = \frac{\frac{37.0 \text{ g} \times 1 \text{ mol HCl}}{36.5 \text{ g}}}{0.063 \text{ kg water}} = 16.1 \text{ m}$$

$$\text{Mole fraction HCl} = \frac{\frac{37.0}{36.5}}{\frac{37.0}{36.5} + \frac{63.0}{18.0}} = 0.225$$

In the above expression,  $\frac{37.0}{36.5}$  represents mol HCl, and  $\frac{63.0}{18.0}$  represents mol H<sub>2</sub>O.

Book example:

Battery acid is 3.75 M  $\text{H}_2\text{SO}_4$  and has a density of  $1.230 \frac{\text{g}}{\text{mL}}$ . Calculate the percent by mass and molality of  $\text{H}_2\text{SO}_4$  in the solution.

Each L contains 3.75 mol  $\text{H}_2\text{SO}_4$  and has a mass of 1230 g.

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

$$\frac{3.75 \text{ mol } \text{H}_2\text{SO}_4 \times 98.1 \frac{\text{g}}{\text{mol}}}{1230 \text{ g solution}} \times 100 = 29.9\%$$

$$\text{Molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

Each 3.75 mol  $\text{H}_2\text{SO}_4$  is in 1230 g of solution. The mass of 3.75 mol  $\text{H}_2\text{SO}_4$  is  $3.75 \times 98.1 = 368 \text{ g}$   
Of the 1230 g solution, the mass of solvent alone is  $1230 - 368 = 862 \text{ g}$  or 0.862 kg

$$\text{Molality} = \frac{3.75 \text{ mol } \text{H}_2\text{SO}_4}{0.862 \text{ kg water}} = 4.35 \text{ m}$$

Energetics of Solution Formation

When solute and solvent mix to form a homogeneous mixture, we can imagine this process taking place in three steps:

(1) Solute molecules must separate from each other. Intermolecular attractions break. Identify the  $\Delta H$  for this process as  $\Delta H_1$ , which must be positive (energy required to break intermolecular attractions between solute molecules).

(2) Solvent molecules must separate from each other. Intermolecular attractions break. Identify the  $\Delta H$  for this process as  $\Delta H_2$ , which must be positive (energy required to break intermolecular attractions between solvent molecules).

(3) Solute molecules and solvent molecules interact and join together. Intermolecular attractions form.

Identify the  $\Delta H$  for this process as  $\Delta H_3$ , which must be negative (energy is released in forming intermolecular attractions between solute and solvent molecules).

This process is illustrated in figure 11.1 of your textbook.

In this description, solvent molecules get in-between solute molecules (solute-solute bonds break and solvent-solute bonds form), and similarly, solute molecules get in-between solvent molecules (solvent-solvent bonds break and solvent-solute bonds form).

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

An **ideal solution** is one where the solute-solute, solvent-solvent, and solute-solvent interactions are all equal. The intermolecular forces between solute-solute, solvent-solvent, and solute-solvent are equal. In such a case, the energy required to break solute-solute and solvent-solvent bonds ( $\Delta H_1 + \Delta H_2$ ) will be equal to the energy released in forming solute-solvent bonds ( $-\Delta H_3$ ). Then the overall heat of solution will be 0.

The solution process will be most successful when the solution is ideal or close to ideal. This gives rise to the general rule: **Like dissolves like**. Here “like” refers to polar or non-polar. A polar solute will be more soluble in a polar solvent than a non-polar solvent. A non-polar solute will be more soluble in a non-polar solvent than a polar solvent.

Oil and water are immiscible. Why?

Oil is a mixture of non-polar hydrocarbons. The oil-oil intermolecular attractions are dispersion forces. Representing oil as component 1,  $\Delta H_1$  represents the energy to separate the oil molecules (break the dispersion force bond)

Water is a polar molecule with hydrogen-bonds as the main intermolecular force. Representing water as component 2,  $\Delta H_2$  represents the energy to separate the water molecules (break the hydrogen bond).

The oil-water attractions are represented by  $\Delta H_3$ .

In this case,  $\Delta H_2$  would be much higher than  $\Delta H_1$  or  $\Delta H_3$ . The water-water attractions are much stronger than the oil-oil attractions, or the oil-water attractions.

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

In this case,  $\Delta H_2$  (breaking hydrogen bonds between water molecules) is much higher than  $\Delta H_1$  and much more positive than  $\Delta H_3$  is negative. That is, the water-water bonds are much stronger than oil-oil or oil-water bonds.  $\Delta H_{\text{soln}}$  would be a high positive number (highly endothermic), and the dissolving process would be energetically unfavorable. The polar water and the non-polar oil are immiscible.

Ethanol and water are miscible. Why?

Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is a polar molecule with hydrogen bonds between the molecules. Water,  $\text{H}_2\text{O}$  is a polar molecule with hydrogen bonds between the molecules.

$\Delta H_1$ : ethanol molecules separate

$\Delta H_2$ : water molecules separate

$\Delta H_3$ : ethanol-water solution forms.

$\Delta H_1$ ,  $\Delta H_2$ , will be positive (break hydrogen bonds between ethanol-ethanol and water-water).

$\Delta H_3$  will be negative (form hydrogen bonds between ethanol-water).

The similar bonds broken and formed leads to close to an ideal solution.  $\Delta H_{\text{soln}}$  will be close to zero. Both liquids are polar, with similar intermolecular forces. Like dissolves like; the liquids are miscible.

Benzene,  $\text{C}_6\text{H}_6$  and carbon tetrachloride,  $\text{CCl}_4$ , are miscible. Why?

Benzene,  $\text{C}_6\text{H}_6$ , is a non-polar molecule with dispersion forces between the molecules.

Carbon tetrachloride,  $\text{CCl}_4$ , is a non-polar molecule with dispersion forces between the molecules.

$\Delta H_1$ :  $\text{C}_6\text{H}_6$  molecules separate.

$\Delta H_2$ :  $\text{CCl}_4$  molecules separate.

$\Delta H_3$ :  $\text{C}_6\text{H}_6$ - $\text{CCl}_4$  solution forms.

$\Delta H_1$ ,  $\Delta H_2$ , will be positive (break dispersion forces between  $\text{C}_6\text{H}_6$ - $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$ - $\text{CCl}_4$ )

$\Delta H_3$  will be negative (form dispersion forces between  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$ ).

The similar bonds broken and formed leads to close to an ideal solution.  $\Delta H_{\text{soln}}$  will be close to zero. Both liquids are non-polar with similar intermolecular forces. Like dissolves like; the liquids are miscible.

Compare the structures of vitamin A and vitamin C. Why is vitamin A fat-soluble and vitamin C water-soluble?

Refer to Figure 11.4 of your textbook, which shows the structures of vitamin A and vitamin C.

Vitamin A, except for a single O-H group, is a hydrocarbon. It is virtually non-polar, since the polar O-H group is only a small part of the overall large molecule.

Vitamin C, ascorbic acid, contains six O-H groups which occupy a large part of the overall smaller molecule. It is a polar molecule which can hydrogen-bond with water.

The ascorbic acid-water hydrogen bonds which form in dissolving ascorbic acid are strong enough to compete with the water-water hydrogen bonds which must break when the solution forms. Like dissolves like. Polar ascorbic acid is soluble in water.

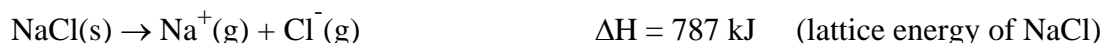
Non-polar vitamin A would have only weak dispersion forces with water, much weaker than the hydrogen bonds between water molecules. It has very little solubility in water, but is soluble in the non-polar fat molecules, where the dispersion forces between fat and vitamin A (solute-solvent interactions) are approximately equal in strength to the dispersion forces between vitamin A/vitamin A and fat/fat (solute/solute and solvent/solvent interactions). Like dissolves like. Non-polar vitamin A is soluble in the non-polar fat.

Being fat soluble, vitamin A can be stored in the fatty tissues of the body. Being water soluble, vitamin C (ascorbic acid) is excreted by the body and must be consumed regularly. Scurvy, the disease caused by vitamin C deficiency, was once suffered by sailors, whose salt-pork diet had an absence of vitamin C. Fresh fruit eaten regularly prevents scurvy.

Sodium chloride is soluble in water. Why?

Sodium chloride is an ionic lattice. We can analyze the energetics of dissolving an ionic solid by thinking of it as the sum of a two-step process:

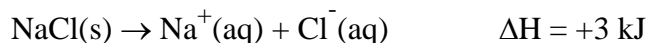
1. Break the ionic solid into its individual gaseous ions (lattice energy required).



2. Join the gaseous ions to water (ion-dipole attractions). The  $\Delta\text{H}$  for this process is negative (bonds form) and is known as the hydration energy of the ions.



3. Add steps 1 and 2 to get the overall process:



The dissolving process for NaCl is slightly endothermic. The energy released by the hydration energy bonds (between the ions and water) is close to the lattice energy (energy to separate the lattice into gaseous ions). Even though the lattice is strong, the relatively strong hydration energy between the ions and water make the process energetically feasible.

Note that the overall  $\Delta\text{H}$  is close to zero, and is the difference between two large numbers ( $787-784 = +3$ ). The ability of ionic solids to dissolve in water depends on the lattice energy (strength of the lattice) compared to the hydration energy (strength of the ion-water bonds). Some ionic solids are not too soluble due to either too large a lattice energy or too weak a hydration bond.

Sodium chloride is highly insoluble in benzene. Why?

Since benzene is a non-polar solvent, there would be no ion-dipole bonds between the ions and benzene. The NaCl ionic lattice is too strong, and the dissolving process is energetically unfavorable.

When  $\Delta\text{H}_{\text{soln}} = 0$  (ideal solution), or even when  $\Delta\text{H}_{\text{soln}}$  is slightly endothermic (NaCl dissolving in water), the dissolving process does occur. Since there is no energy effect ( $\Delta\text{H}_{\text{soln}} = 0$ ) or even an unfavorable energy effect requiring adding of energy ( $\Delta\text{H}_{\text{soln}} > 0$ ), why does the solution process occur?

The extent of a reaction depends on two thermodynamic quantities:

$\Delta\text{H}$  enthalpy change for reaction

$\Delta\text{S}$  entropy change of reaction

S, entropy, refers to randomness or disorder. A more random system is more probable. A positive  $\Delta S$  (go to a more random, more disordered state) is favorable for a spontaneous reaction. A negative  $\Delta H$  (go to a state of lower enthalpy) is also favorable.

A reaction with large positive  $\Delta H$  is likely to be energetically unfavorable. But a small  $\Delta H$ , or  $\Delta H = 0$  can still be spontaneous, if the entropy change is favorable and the system becomes more disordered.

Solution processes are primarily driven by the entropy effect, since mixing solute and solvent creates a more disordered, more random condition. Even if  $\Delta H = 0$  or slightly positive, the process may still be spontaneous.

This concept of spontaneity as affected by changes in enthalpy and entropy ( $\Delta H$ ,  $\Delta S$ ), will be studied in more detail later in the semester, in chapter 16 (“Spontaneity, Entropy, and Free Energy”). This is the study of thermodynamics, which is very important in determining whether a reaction is possible, and the extent of such reactions.