

Solutions:

Explain how the relative forces between molecules predict whether an ideal solution, a non ideal solution, or a heterogeneous mixture will form.

In an ideal solution the two components act as if each were pure. An ideal solution always obeys Raoult's law: The volume of the solution is the sum of the volumes of the two components. No heat is absorbed or given off when the solution forms. (The heat of solution is zero, $\Delta H_{\text{soln}} = 0$). When the forces between like molecules (A-A and B-B) are about the same as the forces between unlike molecules (A-B) the solution formed is ideal.

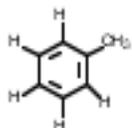
BUT the like forces (A-A) and B-B may not be the same as the un-like forces (A-B).

When the unlike forces are stronger, molecules (or ions) in solution are more strongly attracted to each other than when they are pure. The two components will mix to form a solution and the extra energy is given off as heat: $\Delta H < 0$. Likewise, the volume of the solution is expected to be less than the sum of the components volumes, since the strong forces in the solution is expected to draw the molecules and/or ions closer together.

When the unlike forces are weaker than the like ones, the molecules in solution are less strongly attracted to each other than when pure. Energy must be added during the solution process $\Delta H > 0$. The solution's volume is larger than the sum of the components volumes.

When the like forces are a great deal larger than the unlike forces, a solution does not form. A heterogeneous mixture is produced.

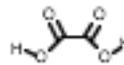
EXAMPLE: Water is a polar, hydrogen bonding mixture. It should mix well with other polar compounds. Toluene is non polar and should not be soluble in water. It forms a heterogeneous mixture. Benzaldehyde is polar, but it does not form hydrogen bonds because none of its hydrogen atoms are attached to the O, N, or F. Benzaldehyde should not be very soluble in water. Oxalic acid is polar and can form hydrogen bonds. Oxalic acid should be the most polar of these three compounds in water. Actual solubilities (%m/m) = toluene 0.67% < benzaldehyde = 0.28% < oxalic acid 14%.



toluene



benzaldehyde



oxalic acid

Be able to use percent concentration units: volume %, mass %, and mass/vol. %.

Many different concentration units exist because of the many different ways in which solutions are used. Although chemists usually are concerned with amounts (moles) of substances, others often are interested in masses or volumes. Most concentration units express the quantity of solute in a certain quantity of solution. Then we can measure out solution and know how much solute we have. All types of concentration calculations will be much easier if you use the following technique.

- Write the definition of the concentration you are using. For example, the definition of mass % is
- $$\text{mass \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$
- Determine the quantity of solute given in the statement of the problem and use this as the numerator.
- Determine the quantity of either solution or solvent (as required by definition) and use this as the denominator.
- Use the conversion factor method to separately change the units of numerator and denominator to agree with those given in the definition

Know and be able to use the definitions of molarity and molality.

Two concentration units frequently used by chemists are molarity and molality. Molality is convenient for freezing-point depression and boiling point elevation measurements as it doesn't change with temperature and is dependent on the number of particles in the solvent. Molarity does so change, since the solution volume generally expands as temperature increases. Molarity is valuable when one wishes to react two solutes. To obtain a certain amount of solute in moles, one merely measures out a definite volume of solution. Take care not to confuse concentration units with amounts of material (moles). Thinking of moles per liter as being the same as moles is similar to thinking (wrongly) that the population of a country is 5 persons per square mile is the same as 5 persons living in the country, when actually there are 16 million people living in the country 3.2 square miles large.

$$\text{molality } (m) = \frac{\text{moles solute}}{\text{kilograms of solvent}}$$

$$\text{molarity } (M) = \frac{\text{moles of solute}}{\text{liter of solution}}$$

Know and be able to use the definitions of mole fraction and mole percent.

Mole fraction is defined as the amount in moles of solute divided by the total amount of moles in the solution.

If n_A is the symbol for the amount of substance A, then
$$x_A = \frac{n_A}{n_B + n_A + \dots}$$

The mole fraction should look familiar, especially when you look at Raoult's law. Raoult's law is an expression of the relationship between the vapor pressure of a solution to the mole fraction of the solvent present. The

mathematical equation is $P_A = c_A P_A^\circ$ where P_A is the partial vapor pressure of A, c_A is the mole fraction of A in the solution, and P_A° is the vapor pressure of pure A (A not behaving as a solute or as a solvent).

(We saw an equation similar to this in gas laws, Dalton's laws of partial pressure of gases. In this case the gases were also ideal)

- The presence of a nonvolatile solute reduces the tendency of solvent molecules to escape the liquid state into the vapor state.
- Less vapor molecules means a lower vapor pressure compared to the pure solvent.
- As the mole fraction of solvent increase, the vapor pressure increases.

Apply Raoult's law. Describe the applications and the limitations of the law.

Raoult's law is true only for ideal solutions. The two components of an ideal solution often are similar in chemical nature. For dilute real solutions Raoult's law is valid for the solvent but not the solute.

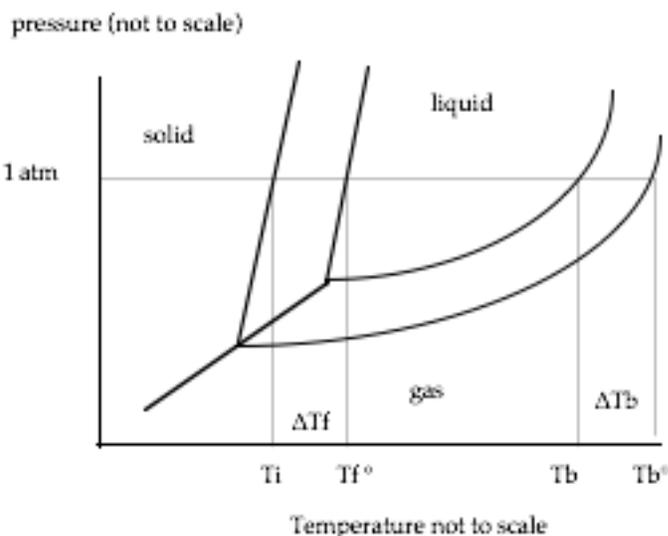
Explain how liquid-vapor equilibrium differs in non-ideal and in ideal solutions.

A solution that is not ideal does not obey Raoult's law. This can occur in two ways. If the vapor pressure of the solution is less than that predicted by Raoult's law, the solution is said to show a negative deviation from Raoult's law. This is due to the unlike forces being stronger than the like forces and the molecules being more strongly held in the solution than they were in the pure components.

If a solution's vapor pressure is greater than that predicted by Raoult's law, the solution is said to show a positive deviation from Raoult's law. In this case, the unlike forces are weaker than the like forces and the molecules are not held in solution as strongly as they were in the pure components.

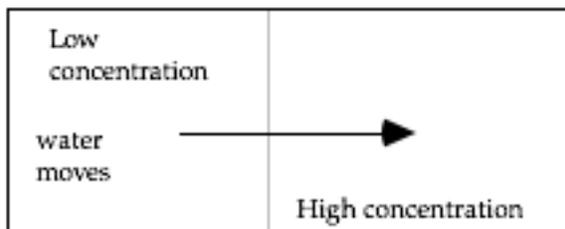
Explain how vapor pressure lowering leads to boiling point elevation and also to freezing point depression. Compute ΔT_f and ΔT_b .

According to Raoult's law, the vapor pressure of a component depends on its concentration. If the other component is nonvolatile, the vapor pressure of the solution will decrease as the concentration of the nonvolatile substance increases. Since the vapor pressure of the solution is lower at all temperatures, the liquid vapor curve on a phase diagram is lowered by the addition of a non-volatile solute. In a similar fashion, if the solute does not freeze out with the solvent (and it seldom does), the temperature at which the solution begins to freeze is lower than the freezing point of pure solvent. The constants K_b and K_f in $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$ depend only on the solvent.



Describe the process of osmosis

Osmosis occurs when two solutions of different concentrations are separated by a semi-permeable membrane. If the membrane were not present, the solutions would mix, resulting in a solution of intermediate concentration. But, only the solvent can flow through the membrane. The direction of flow is from the dilute to the concentrated solution, making it less concentrated, in the process. The pressure that must be exerted on the concentrated solution to halt the flow of solvent is the osmotic pressure.



Describe how the theory of electrolytic dissociation explains the behavior of aqueous solutions of strong, weak, and non-electrolytes, including ionic concentrations and differences in the values of colligative properties from the value computed from equations i-iv.

Colligative property data indicate that equations i-iv should be modified as follows

$$\text{boiling point elevation} \quad \Delta T_b = i K_b m$$

$$\text{freezing point depression} \quad \Delta T_f = i K_f m$$

The value of i , the van't Hoff factor, depends on the type of solute and somewhat on its concentration but not on which colligative property is measured.

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

The expected value for i can be calculated for a solute by noting the number ions per formula unit. For example, NaCl, $i = 2$; for MgCl_2 $i = 3$. These calculated values assume that when a salt dissolves, it completely dissociates into component ions, which then move around independently. This is not always true. In a concentrated solution the van't Hoff factor is lower than in a dilute solution. One explanation is **ion-pairing**. At a given instant a small percentage of cations and anions are paired and thus count as a single particle. As the solution becomes more dilute, the ions are farther apart and ion pairing occurs less.

When the electrical conductance of aqueous solutions is measured, the solutes can be grouped into three types.

I Non electrolytes

- II Weak electrolytes
- III Strong electrolytes

Non electrolytes produce aqueous solutions with a conductance equal to that of water. Non electrolytes do not form ions in solution. They are molecules. The van't Hoff factor equals 1.

Weak electrolytes produce aqueous solutions with a slightly greater conductance than that of pure water. They ionize slightly in water. The van't Hoff factor is slightly larger than 1. Both the molar conductance and the van't Hoff factor increase as the solution becomes more dilute.

Strong electrolytes produce aqueous solutions with a conductance much greater than that of pure water. The molar conductance of a strong electrolyte increase only very slightly as its solution becomes more dilute. The van't Hoff factor of its aqueous solution is a bit less than 2, 3, 4, or some whole number larger than 1, and increases slightly as the solution becomes more dilute. Most of the time one can assume that the van't Hoff