Physical Properties of Solutions

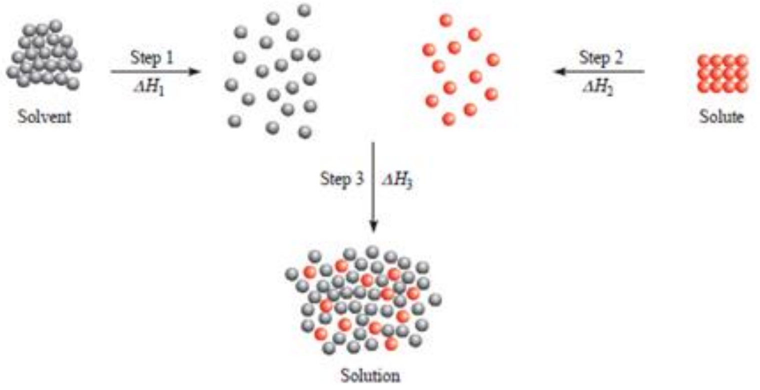
Types of Solutions

When ions and molecules dissolved in water or other solvents is formed a solution as a homogeneous or heterogeneous mixture of two or more substances.

It can be distinguished six types of solutions, depending on the solid, liquid, or gas of the solution components. In this subject, It is focued on solutions involving at least one liquid component— that is, gas-liquid, liquid-liquid, and solid-liquid solutions.

Water will investigated as the liquid solvent in most of the solutions. In addition to, solutions is characterized by their capacity to dissolve a solute. First type, a solution that contains the maximum amount of a solute in a given solvent, at a specific temperature, is called a **saturated solution. Unsaturated solution** is that contains less solute *than it has the capacity to dissolve.* A third type, a **supersaturated solution,** contains more solute than is present in a saturated solution.

Crystallization process is also formation of crystals in solution of dissolved solute.



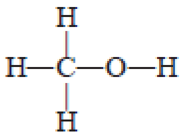
A molecular view of the solution process taken place in three steps.

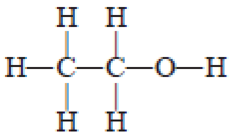
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

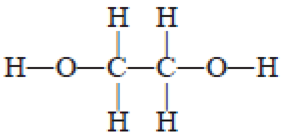
The solution process is governed by two factors. One is energy, which determines whether a solution process is exothermic or endothermic. The second factor is an inherent tendency toward disorder in all natural events.

When solute and solvent molecules mix to form a solution, there is an increase in randomness or disorder. Much of this order observed in pure state is destroyed when the solute dissolves in the solvent. Therefore, the solution process is accompanied by an increase in disorder or randomness. It is the increase in disorder of the system that favors the solubility of any substance, even if the solution process is endothermic.

When two liquids are completely soluble in each other in all proportions, as in this case, they are said to be **miscible.** Alcohols such as methanol, ethanol, and ethylene glycol are miscible with water because of their ability to form hydrogen bonds with water molecules:


methanol


ethanol


1,2-ethylene glycol

When sodium chloride dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction. In general, we predict that ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride.

Solvation is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. When the solvent is water, this process is called *hydration*.

Types of Concentration Units

Concentration is quantitative study of a solution, that is, the amount of solute present in a given amount of solution. Several different concentration units are used. the three most common units of concentration such as percent by mass, molarity, and molality will investigated here.

Percent by Mass

The ***percent by mass*** is also called the *percent by weight* or the *weight percent* and is calculated as follows

$$\text{percent by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$

Molarity (M) unit is defined as the number of moles of solute in 1 L of solution according to as follows,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

Molality (m) is the number of moles of solute dissolved in 1 kg (1000 g) of solvent, that is,

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 mL.

Comparison of Concentration Units

The choice of a concentration unit is based on the purpose of the experiment. The advantage of molarity is that it is generally easier to measure the volume of a solution. For this reason, molarity is often preferred over molality.

On the other hand, molality is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent. This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

Percent by mass is similar to molality in that it is independent of temperature. Furthermore, because it is defined in terms of ratio of mass of solute to mass of solution, we do not need to know the molar mass of the solute to calculate the percent by mass.

Sometimes it is desirable to convert one concentration unit of a solution to another; for example, the same solution may be employed for different experiments that require different concentration units for calculations.

Effect of Temperature on Solubility

The solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent at a defined temperature. For most substances of solids and gases, temperature affects solubility.

Solid Solubility and Temperature

The temperature dependence of the solubility of some ionic compounds in water is observed by increasing form. In most but certainly not all cases, sometimes the opposite situation is encountered.

However, there is no clear correlation between the sign of ΔHsoln and the variation of solubility with temperature. In general, the effect of temperature on solubility is best determined experimentally.

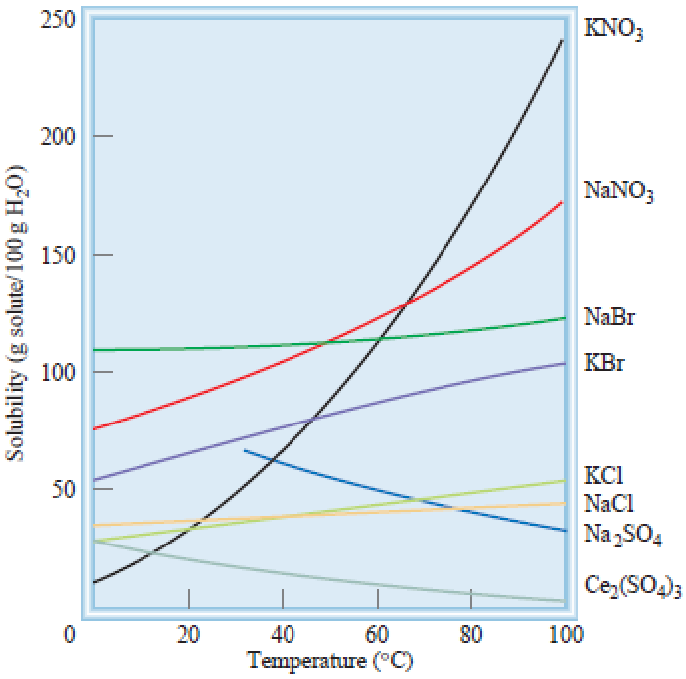


Figure Dependence on temperature of the solubility of some ionic compounds in water.

Gas Solubility and Temperature

The solubility of gases in water usually decreases with increasing temperature. When water is heated in a beaker, you can see bubbles of air forming on the side of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.

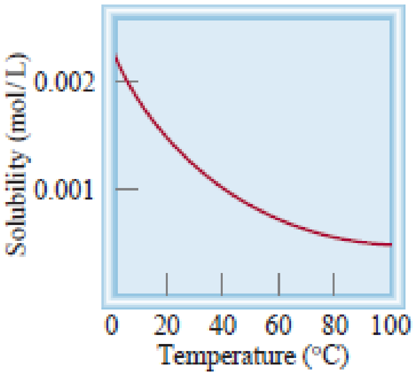


Figure Dependence on temperature of the solubility of O_2 gas in water. Note that the solubility decreases as temperature increases. The pressure of the gas over the solution is 1 atm.

Effect of Pressure on the Solubility of Gases

External pressure has no influence on the solubilities of liquids and solids, but it greatly affect the solubility of gases. The quantitative relationship between gas solubility and pressure is given by ***Henry's law,*** which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

$$c \propto P$$

$$c = kP$$

The constant *k* has the units mol/Latm. You can see that when the pressure of the gas is 1 atm, *c* is numerically equal to k.

The amount of gas that will dissolve in a solvent depends on how frequently the molecules in the gas phase collide with the liquid surface and become trapped by the condensed phase.

When the partial pressure is increased, more molecules dissolve in the liquid because more molecules are striking the surface of the liquid. This process continues until the concentration of the solution is again such that the number of molecules leaving the solution per second equals the number entering the solution.

Colligative Properties of Solutions

Some important properties of solutions depend on the number of solute particles in solution, whether these particles are atoms, ions, or molecules. However not on the nature of the solute particles. These properties are called as ***colligative properties*** or *collective properties.*

The colligative properties are vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure. We will first discuss the colligative properties of nonelectrolyte solutions.

Vapor-Pressure Lowering

If a solute is ***nonvolatile***, the vapor pressure of its solution is always less than that of the pure solvent. Thus, the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution. This relationship is given by ***Raoult's law*** which states that the partial pressure of a solvent over a solution (P_1), the mole fraction of the solvent in the solution is shown by X_1, P^o_1 also shows vapor pressure of püre solvent.

$$P_1 = X_1 P_1^\circ$$

It can be see that the *decrease* in vapor pressure, ΔP, is directly proportional to the concentration of the solute present.

$$P_1 = (1 - X_2)P_1^\circ$$

$$P_1^\circ - P_1 = \Delta P = X_2 P_1^\circ$$

in which X_2 is the mole fraction of the solute.

Vaporization increases the disorder of a system because molecules in a vapor have less order than those in a liquid. Because a solution is more disordered than a pure solvent, the difference in disorder between a solution and a vapor is less than that between a pure solvent and a vapor.

If both components of a solution are ***volatile*** the vapor pressure of the solution is the sum of the individual partial pressures. Raoult's law holds equally well in this case:

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

$$P_T = P_A + P_B$$

In which PA and PB are partial pressures over the solution for components A and B, P^o_A and P^o_B are the vapour pressures of the pure substances; and X_A and X_B are their mole fractions. The total pressure is given by Dalton's law of partial pressure.

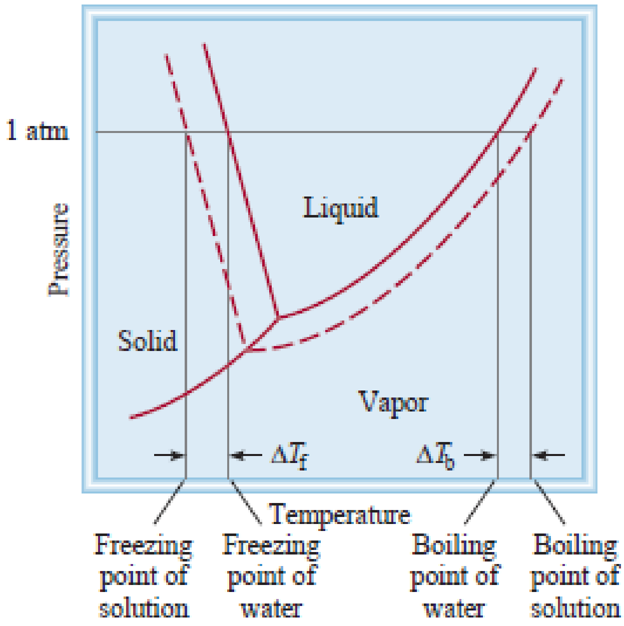


Figure Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions. The dashed curves pertain to the solution, and the solid curves to the pure solvent.

As it can be seen, the boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water.

Boiling-Point Elevation

The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure. The presence of a *nonvolatile* solute lowers the vapor pressure of a solution, it also increases the boiling point of the solution.

Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the liquid-vapor curve for the solution lies below that for the pure solvent.

The *boiling-point elevation,* ΔT_b, is defined as

$$\Delta T_b = T_b - T_b^\circ$$

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

in which *m* is the molality of the solution and *K*b is the *molal boiling-point elevation constant.*

Freezing-Point Depression

A nonscientist may remain forever unaware of the boiling-point elevation phenomenon, but a careful observer living in a cold climate is familiar with freezing-point depression. Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl2. This method of thawing succeeds because it depresses the freezing point of water.

Figure shows that lowering the vapor pressure of the solution shifts the solidliquid curve to the left. Consequently, this line intersects the horizontal line at a temperature *lower* than the freezing point of water. The *freezing-point depression,* _*T*f, is defined as

$$\Delta T_f = T_f^\circ - T_f$$

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

in which *m* is the concentration of the solute in molality units, and Kf is the molal freezing-point depression constant.