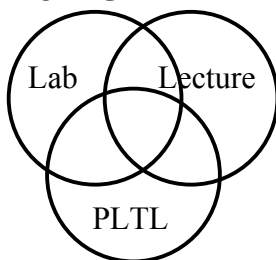


UMCHEM



"It is clear that under these circumstances the classical theory can not be retained. All experimental material indicates that its fundamental starting point should be abandoned, and that, in particular, an equilibrium calculated on the basis of the mass action law does not correspond to the actual phenomena."

P. Debye and E. Hückel

Workshop for Chapter 13: Solutions

To a chemist, a solution is nothing more than a homogeneous mixture. The defining phrase is comprised of two words, each of which has a very specific meaning in chemistry: Homogeneous, meaning that the sample has a uniform appearance and composition throughout, plus mixture, a sample that consists of two or more substances. If both of these definitions are met, a sample is a solution.

You encounter solutions frequently, both in the chemistry laboratory and in everyday life. In the laboratory, solutions are an excellent medium for promotion of chemical reactions. The particles are much closer together than in a gas, and they have more freedom of movement than in a solid. Outside of the laboratory, the process of life itself depends on solutions. The air we breathe and the oceans, lakes, and streams that cover most of our planet are examples of solutions.

Solution Terminology

A specialized vocabulary is used when discussing solutions. Let's look at some of these terms and see how they are applied.

In general, the component of the solution that is present in the greatest amount is called the *solvent*. The substance with the smaller amount in the solution is called the *solute*. These terms are not precise, however, and their usage varies among different specialties in chemistry. For example in water solutions, water is almost always referred to as the solvent no matter its relative amount. Also when a solid or a gas is dissolved in a liquid, the liquid is generally called the solvent.

It is often useful to know the maximum amount of a solute that will dissolve in a given solvent at a specified temperature. This measure is known as the *solubility* of that solute. Reference sources often report solubilities in grams of solute per 100 grams of solvent. When a solution contains a solute amount less than the solubility limit, it is said to be *unsaturated*; if it is at the solubility limit, it is *saturated*. Under certain special conditions, a solution can contain more solute than its normal solubility limit, and in this case, it is called *supersaturated*.

The terms concentrated and dilute are often used to describe solutions. It is important to keep in mind that these terms are valid only in a relative sense. A *concentrated* solution has a relatively large amount of solute per given amount of solvent when compared with a *dilute* solution. The comparison is only valid for systems of the same solute and solvent.

When discussing solutions of liquids in liquids, the term *miscible* is used to describe two liquids that will dissolve in one another in all possible combinations. When liquids will not dissolve in one another, they are said to be *immiscible*. A chemist would say that oil and water are immiscible, whereas alcohol and water are miscible.

Solution Concentration Units

A number of different units are used to express the quantity of solute dissolved in a given amount of solvent. Common units include percentage by mass, parts per million, molarity, and molality. The definition of each provides the basis for calculations with that unit.

$$\% \text{ by mass} = \frac{\text{mass solute}}{\text{mass solution}} \times 100 \quad (13.1)$$

$$\text{parts per million} = \text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \quad (13.2)$$

$$\text{molarity} = M = \frac{\text{moles solute}}{\text{liters solution}} \quad (13.3)$$

$$\text{molality} = m = \frac{\text{moles solute}}{\text{kilograms solvent}} \quad (13.4)$$

The choice of concentration unit is largely a matter of convenience. There are some technical considerations that must be made, however. Percentage by mass, parts per million, and molality are applicable at any temperature. Molarity, in contrast, is temperature dependent because the volume of the solution, measured in liters, varies with temperature.

Solution Formation

Two processes contribute to the formation of a solution—or the lack thereof. The effects of the change in the heat energy content (*enthalpy*) of the system plus the change in the *entropy* of the system must result in an overall release of *free energy* (energy available to do work) if a solution is to form [ΔG must be negative]. Let's consider each of these processes separately.

The heat energy (enthalpy) changes in the formation of a solution consist of interactions (1) among the solute particles, (2) among the solvent particles, and (3) between the solute and solvent particles. Consider the process by which table salt, sodium chloride, dissolves in water. The positively-charged sodium ions and the negatively-charged chloride ions are attracted to one another. When a solution forms, these ions must be separated from each other, and thus energy is required to separate the solute particles so $\Delta H_1 > 0$. A similar situation occurs with the solvent particles. The water molecules are clumped together in hydrogen-bonded groups. These groups

must be “pulled apart” so that solute ions can fit between them. This process also requires an input of energy or $\Delta H_2 > 0$. Energy is released when the solute and solvent particles interact, $\Delta H_3 < 0$. The negative ends of water molecules surround positively-charged sodium ions and the positive ends of water molecules surround negatively-charged chloride ions. The enthalpy change for the solution process is written as the sum of these terms:

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

(+), (+), (-) *typical sign of each contribution*

The other process to consider when analyzing solution formation is the increase in entropy ΔS of the system. In most cases, when solutions form, there is an increase in entropy that results from mixing the solute and solvent. This increase in entropy favors solution formation. As we'll see in greater detail in Chapter 18 of Burdge, enthalpy and entropy effects contribute to the overall Gibbs free energy change of a solution process as follows:

$$\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T \Delta S_{\text{soln}}$$

(J/mol) (J/mol) K x (J/mol•K) *typical units of each contribution*

If the quantity ΔG_{soln} is negative, the solution forms spontaneously. Otherwise the dissolution process does not occur. If ΔS_{soln} is positive then increasing temperature will make ΔG_{soln} more negative. Thus in some cases where you cannot dissolve a substance in cold solvent, raising the temperature allows the solution process to occur (or a more of the substance to dissolve)

Colligative Properties of Solutions

Solutions are unique in that some of their properties depend only on the concentration of solute particles without regard to their identity. These are called *colligative properties*. The colligative property concept has important limitations, however. It applies only to the *change* in the properties of *dilute* solutions.

Probably the most commonly-utilized application of colligative properties is the ethylene glycol and water solution found in automobile radiators. The ethylene glycol solute is usually labeled as “winter antifreeze and summer coolant.” Its effect is to both lower the freezing temperature and raise the boiling temperature when compared to pure water alone. Both freezing-point depression and boiling-point elevation are colligative properties.

Freezing-point depression is the change in freezing point that occurs when comparing a solution to the pure solvent. It is directly proportional to the molality of the solution:

$$\Delta T_f \propto m \quad (13.5)$$

If we introduce a proportionality constant, we have an equation:

$$\Delta T_f = K_f \times m \quad (13.6)$$

where K_f is the *molal freezing point depression constant*. This constant is valid for any solute in a dilute solution of the specified solvent.

Boiling-point elevation is the change in boiling point for a solution when compared with the pure solvent. As with freezing-point depression, boiling-point elevation is proportional to the molality of the solution. The proportionality constant is called the *molal boiling point elevation constant*.

$$\Delta T_b \propto m \quad (13.7)$$

$$\Delta T_b = K_b \times m \quad (13.8)$$

Given that water is the most common solvent, the freezing- and boiling-point constants for water are those most frequently encountered. $K_f = 1.86^\circ\text{C} \cdot \text{kg solvent/mol solute}$ and $K_b = 0.52^\circ\text{C} \cdot \text{kg solvent/mol solute}$. A bit of common sense comes in handy here when working with these cumbersome units. As long as calculations involving Equations 13.6 and 13.8 are not mixed with other calculations, we can substitute 1.86°C/m and 0.52°C/m .

Another solution colligative property is found when comparing measurements of the vapor pressure of a solution and the pure solvent. Before discussing the colligative property, however, we must introduce a new concentration unit called the *mole fraction* which is, by definition

$$\text{mole fraction} = X = \frac{\text{moles solute}}{\text{total moles of solution}} \quad (13.9)$$

The vapor pressure of a solution is directly proportional to the mole fraction of the solvent particles:

$$P_{\text{soln}} = X_{\text{solvent}} \times P_{\text{solvent}} \quad (13.10)$$

However, we will be interested in the change in vapor pressure that occurs by addition of a solute. Subtracting both sides of Equation 13.10 from the identity $P_{\text{solvent}} = P_{\text{solvent}}$, we have

$$P_{\text{solvent}} - P_{\text{soln}} = P_{\text{solvent}} - (X_{\text{solvent}} \times P_{\text{solvent}}) \quad (13.11)$$

Notice how the left side of Equation 13.11 is the difference between the vapor pressure of the pure solvent and the solution. This is the change in vapor pressure that will occur upon addition of the solute, which we can symbolize as ΔP . We can also factor out P_{solvent} from the right side of Equation 13.11 to obtain

$$\Delta P = P_{\text{solvent}} \times (1 - X_{\text{solvent}}) \quad (13.12)$$

If we add the mole fraction of the solvent plus the mole fraction of the solution, the total must be equal to one:

$$X_{\text{solvent}} + X_{\text{solute}} = 1 \quad (13.13)$$

Solving Equation 13.13 for the mole fraction of the solute,

$$X_{\text{solute}} = 1 - X_{\text{solvent}} \quad (13.14)$$

Finally, substituting Equation 13.14 into Equation 13.12,

$$\Delta P = P_{\text{solvent}} \times X_{\text{solute}} \quad (13.15)$$

Thus we see that the change in vapor pressure for a solution depends on the mole fraction of *solute* particles. The more solute particles, the greater the change in vapor pressure.

The final colligative property that we will consider in this unit is *osmotic pressure*, the pressure required to prevent the phenomenon known as osmosis, which is discussed below. Consider the illustration shown in Figure 13.1, which shows a particulate-level view of a solution on the right side of a semi-permeable membrane and pure solvent on the left side. The membrane has pores large enough to allow passage of water molecules, symbolized by the smaller light circles, but small enough to prevent the passage of solute molecules, symbolized by the larger shaded circles. The pressure required on the right side of the apparatus to balance the rate of movement of solvent particles between the two compartments is the osmotic pressure of the solution.

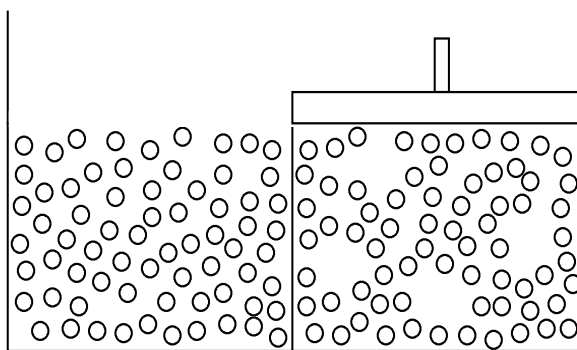


Figure 13.1. Osmotic pressure. The pressure that must be applied to the right side of the apparatus, the side that holds the solution, to prevent net movement of pure solvent from the left side is the osmotic pressure of the solution.

Osmotic pressure, symbolized by π , is directly proportional to the molarity of the solution:

$$\pi \propto M \quad (13.16)$$

The proportionality constant that changes this relationship into an equation is RT , the product of the ideal gas constant and the absolute temperature.

$$\pi = RT \times M \quad (13.17)$$

Molarity is moles per liter, which is moles, n , per volume, V , or $M = n/V$. Substituting this, we find that osmotic pressure is similar to ideal gas pressure in the ideal gas equation:

$$\pi = RT \times \frac{n}{V} \quad \text{or} \quad \pi V = nRT \quad (13.18)$$

<i>Self Test</i>

- A) Which of the following in each pair is likely to be the more soluble in water: (a) $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; (b) CCl_4 or CaCl_2 ; (c) benzene, C_6H_6 or phenol, $\text{C}_6\text{H}_5\text{OH}$? Explain your answer in each case.

B) Which of the following in each pair is likely to be the more soluble in hexane, C_6H_{14} : (a) cyclohexane C_6H_{12} , or glucose, $\text{C}_6\text{H}_{12}\text{O}_6$; (b) propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, or sodium propionate, $\text{CH}_3\text{CH}_2\text{COONa}$; (c) HCl or ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$? Explain your answer in each case.
- A solution is made by dissolving 1.00 g of sodium chloride in 1.00 L of water. Assume that the volume of the resulting solution is 1.00 L and that the density of water and the resulting solution is 1.00 g/mL. Determine the concentration of the solution in molarity, and molality.
- Determine the freezing and boiling points of a solution made by dissolving 30.0 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in 100.0 g of water.
- Ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is used as an antifreeze. Calculate the vapor pressure of water above a solution of 100.0 mL ethylene glycol and 100.0 mL water at 90 °C. Densities: ethylene glycol, 1.15 g/mL; water, 1.00 g/mL. The vapor pressure of pure water at 90 °C is 525.8 mm Hg.
- List the following aqueous solutions in the order of decreasing freezing point: 0.075M glucose; 0.075 M LiBr; 0.030 M $\text{Zn}(\text{NO}_3)_2$.

<i>Workshop: Solutions</i>

1. Use the round robin approach to complete the following table.

Compound	Mass of compound	Mass of water	Mole Fraction of Solute	Mass percent of solute	Ppm of Solute	Molality
Table salt	52 g	175 g				
glucose	15				7×10^4	
Ethylene glycol		100 g		2.5 %		

What information would be needed to calculate the molarity of these solutions?

2. Consider the formation of a solution of ammonia with water as the solvent. Divide into two sub-groups, and draw a diagram, which shows the *enthalpy changes* between the following states: (i.e. convey whether the system is at a higher or lower enthalpy state)
- The starting point - a container of liquid ammonia, NH_3 (the solute), and a container of water.
 - The solute molecules separated from each other, and the container of water.
 - The solute molecules separated from each other, and the water molecules separated from each other.
 - The solute molecules dissolved in the solvent molecules.
 - The heat of solution for the reaction:

$$\text{NH}_3(l) \rightarrow \text{NH}_3(aq)$$
 is $\Delta H_{\text{soln}} = -12.8 \text{ kJ/mole}$. Now consider the intermolecular bonds broken or formed in each step and try to give a qualitative explanation for your answer to part e. (You may consider the NH_3 to be present as a minority species and focus on the number and strength of the hydrogen bonds formed by each NH_3 molecule.)
 - Commercial concentrated aqueous ammonia is 28 percent NH_3 by mass and has a density of 0.90 g/mL. What is the molarity of the solution? What is the mole fraction of this solution? How many water molecules are there for each ammonia molecule?

Compare the diagrams and explanations of the two sub-groups.

3. How would you prepare 5.00 L of a 0.75 molal solution of table sugar, $C_{12}H_{22}O_{11}$?
4. The UMaine facilities and grounds supervisor has asked you to evaluate alternative materials for use on sidewalks on campus to melt the snow and ice this winter. Divide the compounds in the figure below amongst the group and, using information from this figure, determine:
- The molecular weight of each compound
 - The maximum molality of the compound in its fully dissociated state
 - The maximum freezing point lowering that can be achieved for each compound.

Reconvene as a group and compare your results.

- Which compound is capable of lowering the freezing point the most? Is the order the same as the solubility? Why or why not? Generalize the trends you see in the data.
- Are there any compounds that you can eliminate as suitable materials for other reasons?

