Unit 2

SOLUTIONS

2.1 Heterogeneous and Homogeneous Mixtures

Mixtures are combinations of two or more substances where each substance retains its own properties. Unlike compounds, the components of a mixture can be physically separated, and their proportions can vary. Mixtures are commonly found in everyday life, such as the air we breathe, the food we eat, and the products we use.

Mixtures can be classified into two main types: **homogeneous** and **heterogeneous**.

2.1.1 Homogeneous Mixtures

A **homogeneous mixture** is one that has a uniform composition throughout. In this type of mixture, the different components are not visibly distinguishable, and the mixture appears as a single phase. An example of a homogeneous mixture is a solution of salt in water, where the salt is evenly dissolved, making the mixture appear uniform.

Characteristics of Homogeneous Mixtures:

- Uniform appearance and composition.
- Components are not visibly distinguishable.
- The properties are consistent throughout the mixture.

Examples include:

- **Saltwater**: A solution where salt is dissolved in water.
- **Air**: A mixture of gases, such as nitrogen, oxygen, and carbon dioxide.

2.1.2 Heterogeneous Mixtures

A **heterogeneous mixture** consists of visibly different substances or phases. In these mixtures, the components are not evenly distributed, and different parts of the mixture have different properties.

Characteristics of Heterogeneous Mixtures:

- Non-uniform composition.

- Distinct phases or layers are often visible.
- The properties vary from one part of the mixture to another.

Examples include:

- **Oil and Water**: A mixture where oil and water do not mix and form separate layers.
- **Sand and Iron Filings**: A mixture where sand and iron filings are visibly distinct and can be separated by a magnet.

2.2 The Solution Process

A solution is formed when solute particles completely dissolve in a solvent. This process is more straightforward for gases, which mix freely, but in the case of liquids and solids, it requires overcoming the inter-particle forces of attraction both within the solute and the solvent.

When forming a liquid or solid solution, the solute and solvent particles are held together by intermolecular forces. To create a solution, the process involves three key steps:

1. **Breaking up the solute-solute inter-particle forces**: The forces holding the solute particles together must be overcome.
2. **Breaking up the solvent-solvent inter-particle forces**: Similarly, the forces between solvent particles must be broken.
3. **Formation of solute-solvent interactions**: New interactions form between the solute and solvent particles, allowing the solution to form.

The extent to which a solute dissolves in a solvent depends on the intermolecular forces at play. The energy change during the dissolution process, as well as the increase in entropy (disorder) when solute and solvent molecules mix, are the driving forces behind the solution process.

Important Note: The formation of a solution from a solute and a solvent is a physical process, not a chemical change.

2.2.1 Liquid Solutions and Inter-particle Forces of Attraction

When a solute dissolves in a solvent, its particles spread throughout the solvent, taking up positions that solvent molecules usually occupy. The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of the following interactions:

- **Solute-solute interaction**

- **Solvent-solvent interaction**
- **Solute-solvent interaction**

For a solution to form, the inter-particle forces between solute molecules and solvent molecules must be replaced by solute-solvent interactions. A helpful rule of thumb is "like dissolves like," meaning that substances with similar types of intermolecular forces will dissolve in each other. For example, ionic compounds like NaCl and polar compounds like ethanol dissolve in polar solvents such as water, while nonpolar compounds like oil dissolve in nonpolar solvents like hexane.

Predicting the Likeness of a Substance:

One way to predict whether a solute will dissolve in a solvent is by understanding the polarity of the substances involved. Ionic compounds, which have high polarity due to the transfer of electrons between atoms, typically dissolve in polar solvents. Covalent bonds can be polar if the atoms involved have different electronegativities, leading to an unequal sharing of electrons and a net dipole moment. However, not all molecules with polar bonds are themselves polar; molecular shape and the distribution of atoms must also be considered.

For example, carbon dioxide (CO_2) has polar bonds, but the molecule is nonpolar overall because its linear shape causes the dipole moments to cancel out. In contrast, water (H_2O) is polar because its bent shape results in a net dipole moment.

2.2.2 Inter-particle/Intermolecular Forces

Intermolecular forces, or noncovalent interactions, are the forces that occur between molecules, holding them together in liquids and solids. These forces include:

- **Dipole-dipole interaction**: Occurs between polar molecules due to electrostatic interactions among dipoles.
- **Dipole-induced dipole interaction**: Happens when a polar molecule distorts the electron cloud of a nonpolar molecule.
- **Dispersion forces (London forces)**: Arise from the constant movement of electrons, creating temporary dipoles in all molecules.
- **Ion-dipole interaction**: A key force when ionic compounds dissolve in water.
- **Ion-induced dipole interaction**: Arises when an ion's charge distorts the electron cloud of a nearby nonpolar molecule.

- **Hydrogen bonding**: A particularly strong type of dipole-dipole interaction involving hydrogen and electronegative atoms like oxygen, nitrogen, or fluorine.

The relative strengths of these forces, from weakest to strongest, are:

- Dispersion forces < dipole-induced dipole < dipole-dipole < hydrogen bonding < ion-dipole interaction

These forces are crucial in the formation of solutions.

2.2.3 Solutions of Ionic Solids in Water

Many ionic compounds are soluble in water, meaning that at least 1 gram of the compound can dissolve in 100 mL of water. However, not all ionic compounds are equally soluble. For example, potassium chloride (KCl) is highly soluble, while silver chloride (AgCl) is insoluble, and calcium hydroxide (Ca(OH)$_2$) is only slightly soluble. When ionic compounds dissolve in water, they dissociate into hydrated cations and anions.

2.2.4 Solubility Rules for Ionic Solids

Solubility is defined as the maximum amount of a substance that can dissolve in a given volume of solvent at a specific temperature. The solubility rules for common ionic compounds are:

1. **Salts of Group 1A elements** (e.g., Na^+, K^+, Li^+) and ammonium (NH_4^+) are soluble.
2. **Salts containing acetate (CH_3COO^-), nitrate (NO_3^-), and most perchlorates (ClO_4^-)** are soluble.
3. **Common chlorides (Cl^-), bromides (Br^-), and iodides (I^-)** are soluble, except for those of Ag^+, Pb^{2+}, Cu^{2+}, and Hg_2^{2+}. **Fluorides (F^-)** are soluble except for those of Pb^{2+} and Group 2A elements.
4. **Most hydroxide salts** are only slightly soluble. Hydroxides of Group 1 elements are soluble, while hydroxides of Group 2 elements (Ca, Sr, Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble.
5. **Sulfate salts (SO_4^{2-})** are soluble, except for those of barium (Ba), strontium (Sr), lead (Pb), calcium (Ca), silver (Ag), and mercury (Hg).
6. **Carbonates (CO_3^{2-}), sulfides (S^{2-}), oxides (O^{2-}), and phosphates (PO_4^{3-})** are insoluble, except for those in Rule 1.

2.2.5 Solutions of Molecular Solids

Molecular solids, which are composed of molecules held together by London forces, dipole-dipole forces, or hydrogen bonds, also dissolve according to the principle of "like dissolves like." Polar molecular solids like ice and sucrose dissolve in polar solvents such as water, while nonpolar molecular solids like sulfur and hydrocarbons dissolve in nonpolar solvents like benzene.

2.2.6 Solution of Liquids in Liquids

Solutions can also be formed by mixing two liquids. The liquid in the lower concentration is termed the solute, while the one in higher concentration is the solvent. If two similar liquids (in terms of polarity) mix, they are considered miscible. For example, alcohol (CH_3CH_2OH) is miscible with water because both are polar. On the other hand, oil and water are immiscible because oil is nonpolar, and water is polar.

2.3 Solubility as an Equilibrium Process

Solubility refers to the maximum amount of a substance that can dissolve in a given amount of solvent at a specific temperature. When a solute dissolves in a solvent, it dissociates into its constituent ions or molecules. As more solute is added, a point is reached where no more solute can dissolve, resulting in an equilibrium between the dissolved and undissolved solute. This state is known as **solution equilibrium**.

At this equilibrium, the rate of dissolution (where solute particles enter the solution) equals the rate of recrystallization (where solute particles leave the solution and return to the solid phase). Therefore, the concentration of the solute in the solution remains constant even though the dynamic processes of dissolution and recrystallization continue to occur.

Unsaturated, Saturated, and Supersaturated Solutions

1. **Unsaturated Solution**: A solution that can still dissolve more solute, meaning it has not reached its maximum solubility.
2. **Saturated Solution**: A solution that contains the maximum amount of dissolved solute at a given temperature. At this point, the solution is in equilibrium, and any additional solute will not dissolve but will remain in the solid form.
3. **Supersaturated Solution**: A solution that contains more solute than it would normally dissolve at a given temperature. This can be created by dissolving solute at an elevated temperature and then slowly cooling the

solution. A supersaturated solution is unstable and will precipitate excess solute when disturbed.

Factors Affecting Solubility

1. **Inter-particle Forces**: The interactions between particles of the solute and solvent significantly influence solubility. Stronger interactions, such as hydrogen bonds or ionic bonds, may either increase or decrease solubility depending on the nature of the substances involved.
2. **Temperature**:
   o **Solids**: Typically, the solubility of solids in liquids increases with temperature. For example, sugar dissolves more readily in hot water.
   o **Gases**: The solubility of gases in liquids usually decreases with increasing temperature because higher temperatures give gas molecules more kinetic energy to escape the solution.
3. **Pressure** (mainly for gases): According to **Henry's Law**, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. An increase in pressure will increase the gas's solubility in the liquid.

Henry's Law

Henry's Law states that the amount of dissolved gas in a liquid is proportional to the partial pressure of that gas above the liquid. The relationship can be expressed mathematically as:

$$C = kP$$

Where:

- C is the concentration of the dissolved gas.
- k is the Henry's law constant, unique for each gas-solvent combination.
- P is the partial pressure of the gas.

For instance, in carbonated beverages, carbon dioxide is dissolved under high pressure, which increases its solubility in the liquid. Upon opening the bottle, the pressure decreases, causing the gas to escape, thus reducing its solubility.

2.4 Ways of Expressing Concentration of Solutions

Concentration is a measure of how much solute is present in a given quantity of solution. It can be expressed in various ways, including percent by mass or

volume, mole fraction, molarity, molality, and normality. Understanding these methods helps in accurately describing and calculating the concentration of solutions in different contexts.

2.4.1 Percent by Mass/Volume

Percent by Mass
Percent by mass (or weight percent) is calculated using the formula:

$$\text{Percent by Mass} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100\%$$

Where the mass of the solution is the sum of the mass of solute and mass of solvent.

Example 2.5
If a rubbing alcohol solution contains 70 mL of isopropanol in 100 mL of solution, the percent by volume (% v/v) is:

$$\%(v/v) = \frac{70 \ mL}{100 \ mL} \times 100\% = 70\%$$

Percent by Volume
Volume percent is calculated as:

$$\text{Volume Percent} = \frac{\text{Volume of Solute}}{\text{Volume of Solution}} \times 100\%$$

Example 2.6
For an isotonic solution containing 0.9 g of NaCl in 100 mL of solution, the percent by weight/volume (% w/v) is:

$$\%(w/v) = \frac{0.9 \ g}{100 \ mL} \times 100\% = 0.9\%$$

Note: For dilute solutions, parts per million (ppm) and parts per billion (ppb) are used to express trace amounts.

- **ppm** $= \dfrac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^6$
- **ppb** $= \dfrac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^9$

Example Calculation
If there is lead contamination of 4 ppm in water, this means there are:

$$4 \ ppm = 4 \ mg \ lead/1 \ L \ solution$$

Thus, 1 ppm equals 1 mg/L for dilute solutions.

2.4.2 Mole Fraction

The mole fraction of a component in a solution is the ratio of the number of moles of that component to the total number of moles of all components in the solution. It is expressed as:

Mole Fraction of A$(X_A)=\dfrac{Moles\ of\ A}{Total\ Moles\ of\ Solution}$

The sum of the mole fractions of all components equals 1:

$X_A+X_B=1$

Mole Percent
To convert mole fraction to mole percent:

Mole Percent$=X_A\times100\%$

2.4.3 Molarity

Molarity (M) is the number of moles of solute per liter of solution:

Molarity$=\dfrac{Number\ of\ Moles\ of\ Solute}{Volume\ of\ Solution\ (L)}$

Example 2.9
To find the molarity of a solution with 16.0 g of CH_3OH in 200 mL (0.20 L) of solution:

1. Molar mass of CH_3OH = 32 g/mol
2. Moles of CH_3OH = $\dfrac{16\ g}{32\ g/mol}$ =0.5 moles
3. Molarity =$\dfrac{0.5\ moles}{0.20\ L}$ =2.50 M

Example Calculation
To find the moles of NaOH needed to make 2.50 L of 0.100 M NaOH:

Number of moles$=M\times V=0.1\ M\times2.50\ L=0.25$ moles

2.4.4 Molality

Molality (m) is the number of moles of solute per kilogram of solvent:

$$\text{Molality}(m)=\frac{\textit{Moles of Solute}}{\textit{Mass of Solvent (kg)}}$$

Advantages

- **Temperature Independence:** Unlike molarity, molality is not affected by temperature changes because it is based on mass, not volume.
- **Additivity of Masses:** Masses are additive, so mixing 500 g of one solution with 500 g of another results in a total of 1000 g.

2.4.5 Normality

Normality (N) is the number of gram equivalents of solute per liter of solution. It is used in acid-base and redox reactions:

$$\text{Normality}(N)=\frac{\textit{Number of Gram Equivalents of Solute}}{\textit{Volume of Solution (L)}}$$

Gram Equivalent

$$\text{Number of Gram Equivalents}=\frac{\textit{Mass of Solute}}{\textit{Equivalent Weight}}$$

Example 2.11

For HCl, NaOH, and H_2SO_4:

(a) For HCl: $z=1$, so:

$$\text{Number of Equivalents}=\frac{18.25\ g}{36.5\ g/mol}\times1=0.5\ eq$$

(b) For NaOH: $z=1$, so:

$$\text{Number of Equivalents}=\frac{20\ g}{40\ g/mol}\times1=0.5\ eq$$

(c) For H_2SO_4: $z=2$, so:

$$\text{Number of Equivalents}=\frac{98\ g}{98\ g/mol}\times2=2\ eq$$

Example 2.12

To calculate normality and equivalents for various forms of H_3PO_4 and Na_2CO_3 solutions, you need to consider the number of equivalents per reaction type and the volume of solution.

2.4.6 Conversion of Concentration Units

To convert between different concentration units, follow these steps:

- Convert percent concentration to volume or mass as needed.
- Use molarity and molality formulas to switch between concentration types.
- For unit conversions, adjust the volume or mass units according to the concentration unit being used.

Example 2.15
Convert 0.273 m KCl to molarity:

$$\text{Molarity}=\frac{0.273\ m\times mass\ of\ solute\ (74.6\ g/mol)+1000\ g}{1.011\times10^3\ g/L}\approx0.270\ M$$

Example 2.16
Convert 36.5% (w/w) HCl to molarity:

$$\text{Molarity}=\frac{36.5\ g/36.5\ g/mol}{0.0833\ L}=12.0\ M$$

2.5 Preparation of Solutions

Molarity and Dilution Formula

- **Molarity (M):** A measure of concentration, defined as the number of moles of solute per liter of solution. It is expressed as:

$$M=\frac{Moles\ of\ solute}{Volume\ of\ solution\ (L)}$$

- **Dilution Formula:** Used to prepare a dilute solution from a more concentrated one. The relationship between the concentrations and volumes before and after dilution is:

$$M_1V_1=M_2V_2$$

Where:

  - M_1 and V_1 are the molarity and volume of the concentrated solution.
  - M_2 and V_2 are the molarity and volume of the dilute solution.

Important Note: When preparing dilutions, particularly of concentrated acids like sulfuric acid, always add the acid slowly to water with frequent stirring to avoid splattering.

Example Problem

To dilute a 7.41 M sulfuric acid solution to 250 mL of a 2.25 M solution:

1. Use the dilution formula to calculate the volume of the concentrated solution needed.
2. Add this volume to a 250 mL flask half-filled with distilled water.
3. Dilute with more water to the 250 mL mark.

2.6 Stoichiometry in Solutions

Stoichiometry involves calculating the amounts of reactants and products in chemical reactions. When dealing with solutions, the relationship between molarity (M), volume (V), and moles (n) is essential.

Steps for Stoichiometric Calculations:

1. **Balance the chemical equation.**
2. **Calculate moles** from the given volume and molarity using n=MV.
3. **Use the balanced equation** to relate the moles of one substance to another.
4. **Convert moles** to the desired units (mass, volume, etc.).

Example Problems:

1. **Mole-Mole Calculation:** For the reaction $H_2SO_4+2NaOH \rightarrow Na_2SO_4+2H_2O$:
   o Calculate the number of moles of H_2SO_4 and relate it to NaOH using the balanced equation.
2. **Mole-Mass Calculation:** For the reaction $2NaOH(aq)+1Mg(NO_3)_2(aq) \rightarrow Mg(OH)_2(s)+2NaNO_3(aq)$:
   o Find the mass of $Mg(OH)_2$ precipitated from a given volume of NaOH and $Mg(NO_3)_2$.
3. **Mole-Volume Calculation:** Example: To find the volume of a 0.35 M $AgNO_3$ solution required to react with 55 mL of 0.24 M NaCl, use:

$$V_{AgNO3} = \frac{M_{NaCl} \times V_{NaCl}}{M_{AgNO3}}$$

2.7 Describing Reactions in Solution

Molecular Equation

A molecular equation represents the complete chemical reaction where all reactants and products are written as if they were molecular substances, even if they exist as ions in solution.

Example: $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Ionic Equation

An ionic equation shows the reactants and products as ions, emphasizing the actual species involved in the reaction.

For the reaction above:
$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

Spectator Ions: Ions that do not participate in the actual reaction and appear unchanged on both sides of the equation. In the example above, Na^+ and NO_3^- are spectator ions.

Net Ionic Equation

A net ionic equation removes the spectator ions, showing only the species that participate in the reaction.

For the above example: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Steps for Writing Net Ionic Equations:

1. Write the balanced molecular equation.
2. Write the complete ionic equation.
3. Cancel the spectator ions to get the net ionic equation.

Unit Summary:

- **Solutions** are homogeneous mixtures of two or more substances.
- **Colloids** and **suspensions** are types of heterogeneous mixtures with distinct properties.
- **Concentration** describes the amount of solute in a solution, with various methods to express it, including molarity.
- **Stoichiometry** in solutions involves using molarity to relate the amounts of reactants and products.
- **Molecular, ionic, and net ionic equations** help describe reactions in solution at the molecular level.