

9.1.2 AQUEOUS SOLUTIONS AND CHEMICAL REACTIONS

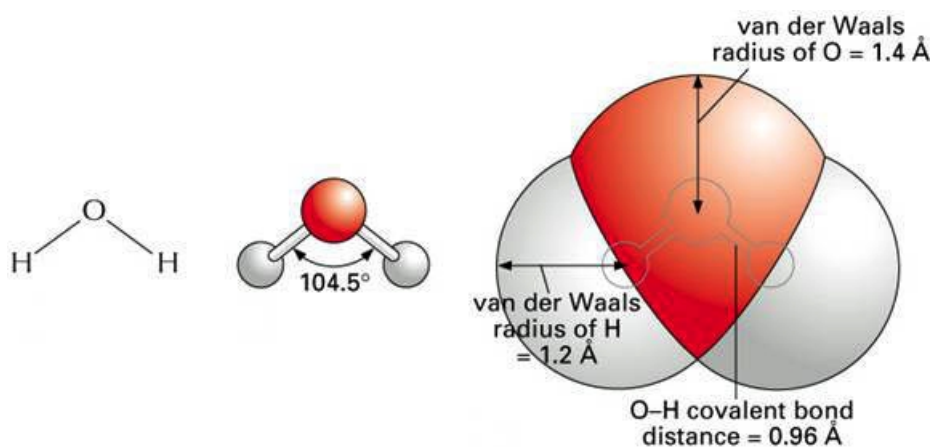
Work directly from Zumdahl (Chapter 4). Work through exercises as required, then summarise the essentials of the section when complete.

To understand the chemistry that occurs in such diverse places as the human body, the atmosphere and water bodies in general, we must understand how substances dissolved in water react with each other.

We first need to consider the nature of solutions in which water is the dissolving medium, or *solvent*. These solutions are known as **aqueous solutions**.

9.1.2.1 Water, the Common Solvent

Liquid water consists of a collection of H_2O molecules. Individual H_2O molecules are bent, or V-shaped, with an $\text{H}-\text{O}-\text{H}$ angle of 104.5° :



The $\text{O}-\text{H}$ bonds in water molecules are covalent bonds formed by electron sharing between the respective oxygen and hydrogen atoms. However, for reasons we will discover when we delve more deeply into the subject of chemical bonding, the [negatively charged] electrons of the bond are not shared equally between the two atoms. Since oxygen has a greater affinity for electrons, they tend to spend more time close to the oxygen than to the hydrogen. Further, the oxygen atom also possesses two pairs of non-bonding electrons. The result is that the oxygen 'end' of the water molecule is slightly negative, and the hydrogen 'end' is slightly positive. Because of this unequal charge distribution, water is said to be a **polar molecule**, and it is this polarity that gives water its great ability to dissolve compounds.

When an ionic solid, known generally as a **salt**, dissolves in water, the positive 'ends' of water molecules are attracted to the negatively charged anions, and the negative ends are attracted to the positively charged cations. This process is called **hydration**, and it tends to cause the salt crystal lattice to fall apart and the salt to **dissolve**. When a salt dissolves, it breaks up into individual cations and anions. When, for example, **NaCl** dissolves in water, the resulting solution contains Na^+ and Cl^- ions moving around independently, and the process is described by the equation:



The solubility of ionic substances in water varies greatly. Sodium chloride, for example, is quite soluble in water, while silver chloride is only very slightly soluble.

Many non-ionic substances, ethanol ($\text{C}_2\text{H}_5\text{OH}$) for example, are also soluble in water. Wine, beer and spirits are all aqueous solutions of ethanol and other substances. Ethanol contains a polar O—H bond, like water, making it somewhat polar, like water.

There are also many substances that do not dissolve in water. Animal fat, for example, will not dissolve in pure water. Fat molecules are non-polar and thus do not interact effectively with polar water molecules.

In general, “Like dissolves like”, so that polar and ionic substances dissolve more readily in water than do non-polar substances.

9.1.2.2 The Nature of Aqueous Solutions

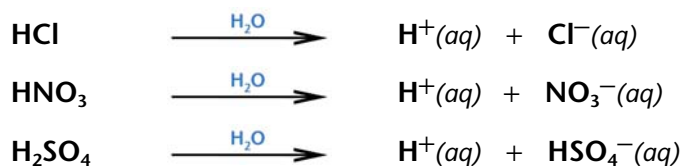
When making an aqueous solution, we dissolve a substance, the **solute**, in water, the **solvent**.

One useful property for characterising a solution is its electrical conductivity, its ability to conduct an electrical current, a property first identified by Swedish physicist Svante Arrhenius (1859–1927).

9.1.2.2.1 Strong Electrolytes

Strong electrolytes are substances that are completely ionised when they are dissolved in water. Soluble salts, strong acids and strong bases are all strong electrolytes.

Arrhenius proposed that an **acid** was *a substance that produces H^+ ions (protons) when dissolved in water*. For example, hydrochloric acid, nitric acid and sulphuric acid:



Similarly, a base is a substance that produces OH^- (hydroxide) ions when dissolved in water. For example, sodium hydroxide and potassium hydroxide:



9.1.2.2.2 Weak Electrolytes

Weak electrolytes are substances that exhibit a small degree of ionisation in water.

The main acidic component of vinegar is acetic acid (CH_3COOH). The dissociation reaction for acetic acid in water can be written as follows:



Because acetic acid is a weak electrolyte, it is called a **weak acid**.

The most common weak base is ammonia (NH_3). When ammonia is dissolved in water, it reacts as follows:



The solution is basic because OH^- ions are produced, and ammonia is called a **weak base** because *the resulting solution is a weak electrolyte*.

9.1.2.2.3 Nonelectrolytes

Nonelectrolytes are substances that dissolve in water but do not produce any ions. For example, when ethanol is dissolved in water, entire $\text{C}_2\text{H}_5\text{OH}$ molecules are dispersed in the water—they do not break up into ions, and the resulting solution does not conduct electricity.

9.1.2.3 The Composition of Solutions

The concentration of solutions is defined in terms of **molarity** (M), the number of *moles of solute per volume (in litres) of solution*:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{litres of solution}}$$

A solution that is 1.0 molar (written as 1.0M) contains 1.0 mole of solute per litre of solution.

Complete sample exercises 4.1 – 4.6 to develop an understanding of this concept and the underlying mathematics.

9.1.2.3.1 Dilution

When more water is added to an aqueous solution, it is said to have been diluted—there will then be more solvent, and less solute, per litre of solution. Nonetheless, the following equality applies in any dilution process:

$$M_1V_1 = \text{moles of solute before dilution} = \text{moles of solute after dilution} = M_2V_2$$

Complete sample exercise 4.7 on concentration and volume.

9.1.2.4 Types of Chemical Reactions

Virtually all reactions that occur in solution can be classed as one of the following three types.

9.1.2.4.1 Precipitation Reactions

This is the name given to reactions that yield an insoluble substance, or **precipitate**, when two solutions are mixed.

Most ionic substances (also known as salts) dissolve in water, although there are some notable exceptions.

Simple Rules for the Solubility of Salts in Water

- 1 Most nitrate (NO_3^-) salts are soluble
- 2 Most salts containing the alkali metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Rb^+) and the ammonium ion are soluble
- 3 Most chloride, bromide and iodide salts are soluble. Notable exceptions are salts containing the ions Ag^+ , Pb^{2+} and Hg_2^{2+}
- 4 Most sulphate salts are soluble. Notable exceptions are BaSO_4 , PbSO_4 , Hg_2SO_4 and CaSO_4
- 5 Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH . The compounds $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ are marginally soluble
- 6 Most sulphide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}) and phosphate (PO_4^{3-}) are only slightly soluble

When two solutions, each containing one of the ions of an insoluble salt, are mixed together, the insoluble salt precipitates out. For example, when solutions of the salts potassium chromate and barium nitrate are mixed together, the insoluble salt barium chromate precipitates out of solution:

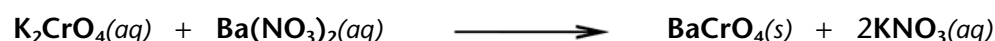


Sample exercise 4.8

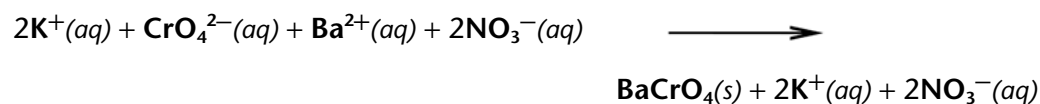
Describing Reactions—Chemical Equations

Three types of equations are used to describe reactions in solution:

- 1 The **formula equation**, which we have already encountered above, gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants:



- 2 The **complete ionic equation** represents as ions all reactants and products that are strong electrolytes:



- 3 The **net ionic equation** includes only those solution components undergoing change (spectator ions are not included):



Sample exercise 4.9

Solving Stoichiometry Problems for Reactions in Solution

- 1 Identify the species present in the combined solution, and determine what reaction occurs;
- 2 Write the balanced net ionic equation for the reaction;
- 3 Calculate the moles of reactants;
- 4 Determine which reactant is limiting;
- 5 Calculate the moles of product or products, as required;
- 6 Convert to grams or other units, as required.

Sample exercises 4.10 & 4.11

9.1.2.4.2 Acid-Base Reactions

There are a number of different ways to view acids and bases. In the present context, the two most relevant models are:

Arrhenius Model

An acid is a substance that produces H^+ ions when dissolved in water, and a base is a substance that produces OH^- ions.

Brønsted-Lowry¹ Model

An acid is a *proton donor*, and a base is a *proton acceptor*. This model of a base is broader than the Arrhenius

¹ After Johannes N. Brønsted (1879 – 1947) and Thomas M. Lowry (1874 – 1936), Danish and English chemists respectively, who independently formulated this theory in 1923.

model because it includes substances that do not contain OH^- ions.

An acid-base reaction is often called a **neutralisation reaction**. When just enough base is added to react exactly with the acid in a solution, we say the acid has been *neutralised*.

Performing Calculations for Acid-Base Reactions

- 1 List the species present in the combined solution *before any reaction occurs*, and decide what reaction will occur;
- 2 Write the balanced net ionic equation for this reaction;
- 3 Calculate the moles of reactants. For reactions in solution, use the volumes of original solutions and their molarities;
- 4 Determine the limiting reactant where appropriate;
- 5 Calculate the moles of the required reactant or product;
- 6 Convert to grams or volume (of solution), as required.

Sample exercises 4.12 & 4.13

Acid-Base Titrations

Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration. A **titration** involves delivery (from a burette) of a measured volume of a solution of known concentration (the **titrant**) into a solution containing the substance being analysed (the **analyte**). The titrant contains a substance that reacts in a known manner with the analyte. The point in the titration where enough titrant has been added to react exactly with the analyte is called the **equivalence point** or the **stoichiometric point**. This point is often marked by an indicator, a substance added at the beginning of the titration that changes colour at (or very near) the equivalence point. The point where the indicator *actually* changes is called the **endpoint** of the titration. Ideally, the endpoint of the chosen indicator will be at exactly the equivalence point of the reaction.

Sample exercises 4.14 & 4.15

9.1.2.4.3 Oxidation-Reduction Reactions

The term oxidation is often used to describe the specific class of reactions that involve the reaction of an element or compound with oxygen. These reactions are, however, just one type of oxidation reaction in the present context.

Oxidation, or more generally Oxidation-Reduction reactions, also known as **redox reactions**, are those that involve a change in **oxidation state** of, or the transfer of electrons between, the reacting species. For example, when sodium metal, containing neutral **Na** atoms, reacts with chlorine gas, containing diatomic **Cl₂** molecules, electrons are transferred from the sodium atoms to the chlorine atoms to form **Na⁺** and **Cl⁻** ions, which then combine to form an ionic crystal lattice of **NaCl**:



Most reactions used to produce energy in living organisms—photosynthesis in plants, for example—are redox reactions. Combustion reactions, used extensively in power generation, also involve oxidation and reduction. The combustion of methane, for example, even though it does not involve any ionic species, does involve the transfer of electrons from carbon to oxygen:



The most common redox reactions, however, involve the transition metals, most of which have several stable oxidation states.

To better understand all these reactions, we need to look more closely at the concept of oxidation states.

Oxidation States

The oxidation state is an indication of the degree of oxidation of an atom in a chemical element or compound. It is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic.

Rules for Assigning Oxidation States

The Oxidation State of ...	Summary	Examples
An atom in an element is zero	Element: 0	Na(s), O₂(g), O₃(g), Hg(l)
A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na⁺, Cl⁻
Fluorine is -1 in its compounds	Fluorine: -1	HF, PF₃
Oxygen is usually -2 in its compounds. Exception: peroxides (containing O₂²⁻) in which oxygen is -1	Oxygen: -2	H₂O, CO₂
Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H₂O, HCl, NH₃

Note that *the sum of the oxidation states in an electronically neutral compound must be zero*. For an ion, the sum of the oxidation states must equal the charge on the ion.

Sample exercise 4.16

Characteristics of Oxidation-Reduction Reactions

Oxidation-reduction reactions are characterised by a transfer of electrons. In some cases the transfer is more obvious, such as in the reaction between metallic sodium and gaseous chlorine. In other cases it is less obvious, as in the combustion of methane:



In any case, an **increase in oxidation state** of an atom (**net gain of electrons**) during a reaction is known as **oxidation**, a **decrease in oxidation state (net loss of electrons)** is known as **reduction**. The species that accepts electrons, the **electron acceptor**, is called the **oxidising agent**, and the species that donates electrons, the **electron donor**, is called the **reducing agent**.

Sample exercises 4.17 & 4.18

Balancing Oxidation-Reduction Equations

For oxidation-reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions**: one involving oxidation and the other involving

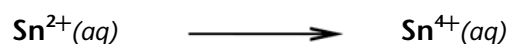
reduction. For example, consider the *unbalanced* equation for the oxidation-reduction reaction between cerium(IV) and tin(II) ions:



This reaction can be separated into a half-reaction involving the substance being reduced:



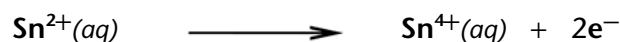
and one involving the substance being oxidised:



The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation. To balance the above half-reactions, we need to add electrons to balance the charges on each side of each equation. For the reduction half-reaction:

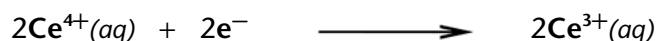


Note that the net charge on each side of the half-reaction is now 3^{+} . For the oxidation half-reaction:

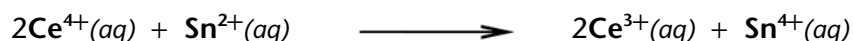


In this case, the net charge on each side is now 2^{+} .

The next step is to multiply one, or both if necessary, of these equations by an integer so that the number of electrons in each is the same. In the present case, we simply need to multiply the reduction half-reaction by 2, so that in each case we are transferring 2 electrons:



Finally, we add the two half-reactions together, cancelling the species (in this case, the 2e^{-} components) common to both sides, to yield the balanced oxidation-reduction reaction equation:



The half-reaction method for balancing more complex oxidation-reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution. The respective procedures are summarised below, but we will defer a more detailed discussion of the process until later in our studies.

*The Half-Reaction Method for Reactions Occurring in **Acidic Solution***

- 1 Write separate equations for the oxidation and reduction half-reactions;
- 2 For each half-reaction,
 - a. Balance all the elements except hydrogen and oxygen;
 - b. Balance oxygen using H_2O ;
 - c. Balance hydrogen using H^+ ;
 - d. Balance the charge using electrons;
- 3 If necessary, multiply one or both balanced half-reactions by an integer to equalise the number of electrons transferred in the two half-reactions;
- 4 Add the half-reactions and cancel identical species;
- 5 Check that the elements and charges are balanced.

*The Half-Reaction Method for Reactions Occurring in **Basic Solution***

- 1 Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present*;
- 2 To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions (we want to eliminate H^+ by forming H_2O);
- 3 Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation;
- 4 Check that elements and charges are balanced.

Exercises

Zumdahl Ch. 4 Exercises

References

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