Interactions of Water with Molecules; Electrolytes and Nonelectrolytes

Interaction between Polar Molecules

Polar molecules interact with one another. This interaction is governed by the fact that like charges repel and opposite charges attract.

Polar molecules aligned by charge need not all be of the same compound. When another polar molecule such as ammonia is added to water, it dissolves because of the interaction between the two types of molecules.

Water Solutions of Ionic Compounds

When an ionic compound dissolves in water, the solution contains ions rather than neutral particles. For example, when sodium chloride, NaCl, dissolves in water, the solution contains sodium ions (Na+) and chloride ions (Cl-), rather than neutral units of NaCl. A polyatomic ion does not break up into separate atoms in solution. Thus, a solution of sodium nitrate, NaNO3, contains sodium ions and nitrate ions; no nitrogen ions or oxygen ions are present. A solution of ammonium sulfate, (NH4)2SO4, contains ammonium ions and sulfate ions.

This dissolution of ionic compounds takes place because of interactions like that between ammonia and water. Figure 7.17 shows at the molecular level what happens when sodium chloride, an ionic compound, dissolves in water. Each ion of the solid crystal becomes surrounded by water molecules, with the negative end of the water molecules approaching closest to the positive sodium ions, and the positive end of the water molecules surrounding the negative chloride ions. The water molecules pull these ions, one by one, away from the rest of the crystal. Other ionic compounds that are virtually insoluble in water have such strong interactions between their ions that the pull of the polar water molecules is not strong enough to break the ions apart.

Frequently, when a very polar molecule such as hydrogen chloride dissolves in water, there is sufficient interaction between the two molecules to cause one of them to break up into ions. With hydrogen chloride, the equation for this reaction is

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

To some extent the same process occurs when ammonia is dissolved in water. The equation for that reaction is

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Electrolytes, Non electrolytes, and Weak Electrolytes

The presence of ions in a solution of an ionic compound can be demonstrated with an apparatus consists of two electrodes--one connected to one pole of a power source and the other connected to a light bulb that is, in turn, connected to the other pole of the power source. If the two electrodes touch, an electric current flows through the completed circuit and the bulb lights. If the two electrodes are separated and then immersed in water, no current flows. Pure water cannot carry an electric current. However, if the pure water is replaced by an aqueous (water) solution of an ionic compound, the bulb lights, indicating a flow of electricity through the solution. The electric current is carried through the solution by the dissolved ions.

Compounds whose aqueous solutions conduct electricity are called electrolytes. This group of compounds includes hydroxides, salts (metal-nonmetal and metal-polyatomic ion compounds), and some acids (nitric, sulfuric, hydrochloric). Compounds that dissolve in water without forming a solution that carries an electric current are called nonelectrolytes. These compounds dissolve as molecules. Many compounds containing only nonmetals are nonelectrolytes. If a compound containing only nonmetals ionizes, its molecule will usually contain hydrogen bonded to a very electronegative atom like oxygen (as in acetic acid) or chlorine (as in hydrochloric acid).

Compounds that react somewhat but not completely with water to form ions are said to be partially ionized; their solutions are poor conductors of electricity. They are called weak electrolytes. Acetic acid is a weak electrolyte. A solution of acetic acid causes the bulb to glow only faintly, showing that not many ions are present in solution.

Other Differences between Ionic and Covalent Compounds

Ionic compounds are usually solids at room temperature. They have high melting points. They dissolve only in very polar liquids like water. Some are only sparingly soluble in water.

Covalent compounds are found in all three states - solids, liquids, and gases - at room temperature. Those of low molecular weight and those that are polar may dissolve in water, but a covalent solid is much more apt to be soluble in a non polar (carbon tetrachloride) or slightly polar (ethyl alcohol) liquid.

Chemical Reactions and Stoichiometry

Physical versus Chemical Changes

Physical properties are those properties whose observation does not involve a change in the composition of the sample. A sample of water does not change its composition if we pour it from a tall pitcher into a flat bowl. It can be frozen to a solid or vaporized to steam. Yet it remains water, with the formula H_2O. Through all these physical changes, the composition of water in unchanged. Another physical change, the crushing of limestone, is illustrated in Figure 8.1. Even though the limestone is crushed to smaller particles, the composition of the limestone does not change.

The observation of a chemical property involves a change in the composition of the sample - that is, a chemical change. When an electric current is passed through water that contains a few drops of sulfuric acid, the water decomposes to hydrogen and oxygen. Water molecules are no longer present; instead, we have two new substances, hydrogen and oxygen. When heated, limestone (known chemically as calcium carbonate) is converted into two new substances, lime (calcium oxide) and carbon dioxide, that have very different properties from those of limestone.

An equation must be balanced to show that no mass is lost or gained during the reaction. An equation may also show the physical state of each component and the energy change associated with the reaction.

Kinds of Chemical Changes

One common way of classifying chemical reactions is to separate them into four categories: combination, decomposition, displacement, and double displacement. We give several examples of each type for two reasons: (1) to ensure that you understand the scope of each category and (2) to help you gain experience in interpreting and balancing equations.

Reactants	The substances that combine in the reaction. Formulas must be correct.
Products **ΔH**	The substances that are formed by the reaction. Formulas must be correct. The enthalpy (heat energy) change accompanying the reaction. Energy is released if $\Delta H < 0$; energy is absorbed if $\Delta H > 0$
Arrows	
$\rightarrow$ $\not\rightarrow$	Found between reactants and products, means "reacts to form." Means the equation is not balanced.
$\uparrow$ $\downarrow$	Placed after the formula of a product that is a gas Placed after the formula of a product that is an insoluble solid - that is, a precipate.
Physical State	Indicates the physical state of the substance whose formula it follows. (*g*) Indicates that the substance is a gas
	(*l*) Indicates that the substance is a liquid
   Coefficients	(*s*) Indicates that the substance is a solid (*aq*) Means that the substance is in aqueous (water) solution The numbers placed in front of the formulas to balance the equation.
Conditions	Words or symbols placed over the arrow ($\longrightarrow$) to indicate conditions used to make the reaction occur. Δ Heat is added $h\nu$ Light is added elec Electrical energy is added

Combination Reactions

In a two substances combine to form a single compound. Two examples are the reaction of solid magnesium with gaseous oxygen to form magnesium oxide, a solid:

$$2\ Mg(s) + O_2(g) \longrightarrow 2\ MgO(s)$$

and the reaction of a hydrogen gas with chlorine gas to form gaseous hydrogen chloride:

$$H_2(g) + Cl_2(g) \longrightarrow 2\ HCl(g)$$

Other combination reactions have compounds as reactants. The reaction of gaseous carbon dioxide with solid calcium oxide to form solid calcium carbonate is an example of such a reaction.

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$

Example

Write balanced equations for the following combination reactions:

a. When solid phosphorus, P4, is burned in chlorine gas, solid phosphorus trichloride is formed.

b. When gaseous dinitrogen pentoxide is bubbled through a solution of water, nitric acid is formed.

Solution

a. Write the reactants, an arrow, and then the products, with the physical state of each reactant or product shown after its formula. Write conditions for the reaction over the arrow.

$$P_4(s) + Cl_2(g) \longrightarrow PCl_3(s)$$

Four atoms of phosphorus will yield four molecules of phosphorus trichloride, which will require 12 atoms (six molecules) of chlorine. Putting in thesecoefficients gives the balanced equation

$$P_4(s) + 6\ Cl_2(g) \longrightarrow 4\ PCl_3(s)$$

b. Write the reactants, an arrow, and the products.

$N_2O_5(g) + H_2O(l) \not\longrightarrow HNO_3(aq)$

Include the physical states and conditions of the reaction as given in its statement. Starting with nitrogen (it is always wise to leave hydrogen and oxygen to the last), two atoms of nitrogen in one molecule of N2O5 will form two molecules of nitric acid. Each molecule of nitric acid contains one hydrogen atom, thus two molecules will require two hydrogen atoms or one molecule of water. We then have six atoms of oxygen in the reactants - the same number of oxygen atoms required by two molecules of nitric acid. The equation is now balanced:

$N_2O_5(g) + H_2(l) \longrightarrow 2\ HNO_3(aq)$

Decomposition Reactions

In a decomposition reaction, a compound is decomposed to its component elements or to other compounds. Although some compounds decompose spontaneously, usually light or heat is needed to initiate the decomposition. Following are three examples of decomposition - one induced by light, one induced chemically by a catalyst, and the third caused by heat. The antiseptic hydrogen peroxide is sold in opaque brown bottles because hydrogen peroxide decomposes in light . The equation for this decomposition is:

$$2\ H_2O_2(aq) \xrightarrow{hv} 2\ H_2O(l) + O_2(g)$$

Oxygen can be prepared by heating solid potassium chlorate in the presence of manganese dioxide, a catalyst. A catalyst is a chemical that, when added to a reaction mixture, hastens the reaction but can be recovered unchanged after the reaction is complete.

$$2\ KClO_3(s) \xrightarrow{MnO} 2\ KCl(s) + 3\ O_2(g)$$

When slaked lime, Ca(OH)2(s), is heated, lime (CaO) and water vapor are produced:

$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(g)$

Example

Write balanced equations for the following decomposition reactions:

a. Solid amonium carbonate decomposes at room temperature to ammonia, carbon dioxide, and water. (Because of the ease of decomposition and the penetrating odor of ammonia, ammonium carbonate can be used as smelling salts.) b. On heating, lead(II) nitrate crystals decompose to yield a solid lead(II) oxide and the gases oxygen and nitrogen dioxide.

Solution

a. The unbalanced equation for the decomposition of ammonium carbonate is:

$(NH_4)_2CO_3(s) \longrightarrow NH_3(g) + CO_2(g) + H_2O(l)$

Inspection of this equation indicates that two nitrogen atoms, therefore two ammonia molecules, are needed on the right. With this change, all other atoms are balanced:

$(NH_4)_2CO_3(s)) \longrightarrow 2\ NH_3(g) + CO_2(g) + H_2O(l)$

b. Writing the formulas for the reactant and the products in the form of an equation gives:.

$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

Balance the elements in the order Pb, N, O, to leave oxygen for the last, which is in general a good practice. The lead is balanced as it stands, one atom on each side. There are two nitrogen atoms on the left, therefore we need 2 NO2 as a product. The oxygen is unbalanced, with six atoms in the reactants and five in the products. Try 2 Pb(NO3)2, which will give 2 PbO, 4 NO2, and two atoms of oxygen, making one molecule of O2. Now the equation is balanced.

$2\ Pb(NO_3)_2(s) \longrightarrow 2\ PbO(s) + 4\ NO_2(g) + O_2(g)$

Displacement Reactions

In displacement reactions, an uncombined element reacts with a compound and displaces an element from that compound. For example, bromine is found in seawater as sodium bromide. When chlorine is bubbled through seawater, bromine gas is released and a solution of sodium chloride is formed:

$2\ NaBr(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + Br_2(g)$

As another example, when an iron nail is dropped into a solution of copper(II) sulfate, iron(II) sulfate is formed in solution and metallic copper is deposited:

$CuSO_4(aq) + Fe(s) \longrightarrow FeSO_4(aq) + Cu(s)$

Example

Write balanced equations for the following displacement reactions:

a. When a piece of aluminum is dropped into hydrochloric acid hydrogen is released as a gas and a solution of aluminum chloride is formed.

b. When chlorine is bubbled through a solution of sodium iodide crystals of iodine appear in a solution of sodium chloride.

Solution

a. The unbalanced equation is:

$Al(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2(g)$

Aluminum is balanced. To balance the chlorine, we need 3 HCl on the reactant side, which will give 1 1/2 molecules of hydrogen.

$Al(s) + 3\ HCl(aq) \longrightarrow AlCl_3(aq) + 1\ 1/2\ H_2(g)$

We need whole molecules of hydrogen. To get a whole number coefficient without unbalancing the other elements, we can multiply the whole equation by 2 to get:

$2\ Al(s) + 6\ HCl(aq) \longrightarrow 2\ AlCl_3(aq) + 3\ H_2(g)$

b. The unbalanced equation is:

$Cl_2(g) + NaI(aq) \longrightarrow NaCl(aq) + I_2(s)$

to balance the chlorine, we must form 2 NaCl. Two NaCl require two sodium atoms, or 2 NaI, which gives two iodine atoms, as needed. The balanced equation then is:

$Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(s)$

Much more information is needed before you can predict whether or not a proposed displacement will take place. That information is given in Chapter 14 (Oxidation-Reduction). However, the displacement reactions we have discussed here will occur.

Double-Displacement Reactions

In double displacement, sometimes called metathesis or ion exchange, two ionic compounds react to form two different compounds. These reactions fall into a pattern that can be expressed as:

$$AB + CD \longrightarrow CB + AD$$

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in which A and C are cations, B and D are anions. These reactions are often called "exchanging-partner" reactions because the cations A and C exchange the anions with which they are associated.

Double-displacement reactions fall into two categories: (1) those in which an acid reacts with a base to form a salt and water, which are known as neutralization reactions, and (2) those in which one of the products is insoluble, which are usually precipitation reactions, although occasionally the insoluble product is a gas.

Reaction of an acid with a base: Neutralization reactions

In neutralization reactions, an acid reacts with a base to form a salt and wateran acid is a compound that liberates hydrogen ions in solution and a base (we will center here on hydroxides, a subgroup of bases) is a compound that liberates hydroxide ions in solution. A salt is defined as an ionic compound in which the cation is not hydrogen and the anion is not hydroxide. These reactions are called neutralization reactions because the base neutralizes the acid. Some examples are:

a. The reaction of sodium hydroxide with hydrochloric acid to form sodium chloride and water:

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Note that the salt formed, sodium chloride, combines the cation of the base, Na+, with the anion of the acid, Cl-. The formula of the salt is the neutral combination of these ions, here a 1:1 combination in sodium chloride, NaCl. b. The reaction of magnesium hydroxide with phosphoric acid to form magnesium phosphate and water:

$$3\ Mg(OH)_2(aq) + 2\ H_3PO_4(aq) \longrightarrow Mg_3(PO_4)_2(aq) + 6\ H_2O(l)$$

Here again the salt formed, magnesium phosphate, Mg3(PO4)2, is a neutral combination of the cation of the base, Mg2+, with the anion of the acid, PO43- .

A polyprotic acid is one whose molecules ionize to yield more than one hydrogen ion. Sulfuric acid, H2SO4, phosphoric acid, H3PO4, and carbonic acid, H2CO3, are examples of polyprotic acids. When a polyprotic acid is one of the reactants, neutralization may be incomplete and an acid salt may form. An example of this reaction is:

$$NaOH(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + H_2O(l)$$

In this reaction, only one of the hydrogens of the diprotic acid reacted; the product is an acid salt, sodium hydrogen sulfate. The addition of more sodium hydroxide neutralizes the second hydrogen of this diprotic acid:

$$NaHSO_4(aq) + NaOH(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$$

Example

Write balanced equations for the following neutralization reactions.

a. the complete reaction of sulfuric acid with calcium hydroxide

b. the complete reaction of magnesium hydroxide with hydrochloric acid

c. the reaction of sodium hydroxide with carbonic acid to form an acid salt.

Solutions

a. The reactants are H2SO4 and Ca(OH)2. The products will show Ca2+ with SO42- instead of with OH- and H+ with OH- (HOH is the same as H2O). Write these facts in the form of an equation:

$$Ca(OH)_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + H_2O(l)$$

To balance the equation, note that there are two H+ and two OH-. They will combine to give 2 H2O and the balanced equation:

$$Ca(OH)_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + 2\ H_2O(l)$$

b. The formulas of the reactants are Mg(OH)2 and HCl. The products will show Mg2+ and Cl- instead of OH- and H+ with OH- instead of Cl-. We write the equation as:

$$Mg(OH)_2(aq) + HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(s)$$

We need two chloride ions to combine with the Mg2+, so we write 2 HCl. We now have 2 H+ and 2 OH- to combine with them to form 2 H2O:

$Mg(OH)_2(aq) + 2\ HCl(aq) \longrightarrow MgCl_2(aq) + 2\ H_2O(l)$

c. The reactants are NaOH and H2CO3. If an acid salt is to be formed, only one of the H+ in carbonic acid will be replaced. The cations changing partners are Na+ and H+. The anions are HCO3- and OH-. Writing the equation we get

$NaOH(aq) + H_2CO_3(aq) \longrightarrow NaHCO_3(aq) + H_2O(l)$

Double-displacement reactions that form insoluble ionic products

Precipitation reactions, the second group of double-displacement reactions, result in the formation of insoluble ionic compounds. Ionic compounds differ enormously in the extent to which they dissolve in water, or their solubility. Table given below illustrates this point by listing the solubilities of several ionic compounds in cold water. Notice that several, such as barium iodide and silver(I) nitrate, are very soluble in water, whereas others, such as lead(II) chloride, are only slightly soluble. Others, such as silver(I) chloride, are virtually insoluble. Generally, if more than 0.1 g of an ionic solid dissolves in 100 mL (0.1 L) of water, the compound is said to be soluble. Less than 0.1 g calcium carbonate, barium sulfate, and silver(I) chloride dissolve in 100 mL water. Therefore, they are classified as insoluble compounds.

Example

Write the formulas of the following salts and predict whether each is soluble in water. a. lead(II) nitrate b. iron(II) chloride c. ammonium sulfide d. barium sulfate **Solutions**

	Formula	**Solubility**	**Reason**
lead(II) nitrate	$Pb(NO_3)_2$	soluble	It is a nitrate
iron(II) chloride	$FeCl_2$	soluble	it is a chloride, but not one of the listed exceptions.
ammonium sulfide	$(NH_4)_2S$	soluble	It is an ammonium salt.
barium sulfate	$BaSO_4$	insoluble	It is listed as an insoluble sulfate.

In precipitation reactions, solutions of two ionic compounds are combined. If two of the ions in the resulting mixture combine to form an insoluble compound or precipitate, a reaction occurs.

For example, if a solution of barium iodide is added to a solution of ammonium nitrate, no reaction takes place because the predicted products barium nitrate and ammonium iodide are both soluble.

$BaI_2(aq) + 2\ NH_4NO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + NH_4I(aq)$

A reaction would occur if a solution of barium iodide were added to a solution of silver nitrate, because one of the products, silver iodide, is insoluble.

$$BaI_2(aq) + 2\,AgNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2\,AgI(\downarrow)$$

In the equations for these reactions, the physical state of the insoluble product, the precipitate, is indicated either by (s) or by a downward-pointing arrow after its formula; the soluble components of the reaction are shown as (aq).

Example

Write the balanced equatio for the following reactions. Indicate with a downward-pointing arrow any precipitate formed; name the precipitate.

a. Solutios of lead(II) nitrate and sodium iodide react to form a yellow precipitate.

b. the reaction between a solution of copper(II) nitrate and a solution of potassium sulfide yields a heay black precipitate.

Solutions

a. The formulas for the reactants are Pb(NO3)2 and NaI. The formulas of the products of a reaction between these two compounds would have an interchange of anions, yielding PbI2 and NaNO3. Arranging these formlas in an unbalanced equation, we get:

$$Pb(NO_3)_2(aq) + NaI(aq) \not\longrightarrow PbI_2 + NaNO_3$$

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Balancing this equation requires two iodide ios and therefore 2 NaI. Two sodium nitrate are formed:

$$Pb(NO_3)_2(aq) + 2\ NaI(aq) \longrightarrow PbI2(\downarrow) + 2\ NaNO3(aq)$$

Because all sodium salts are soluble, the precipitate must be lead(II) iodide; we place an arrow after that formula.

b. The formulas of the reactants are Cu(NO3)2 and K2S. The formulas of the products are CuS and KNO3. From Table 8.3 we know that potassium nitrate is soluble, so the precipitate must be CuS, copper(II) sulfide. The unbalanced equation is:

$$Cu(NO_3)_2(aq) + K_2S(aq) \not\longrightarrow CuS(\downarrow) + KNO_3(aq)$$

Balancing this equation requires two potassium nitrate. The balanced equation is:

$Cu(NO_3)_2(aq) + K_2S(aq) \longrightarrow CuS(\downarrow) + 2\ KNO_3(aq)$

All nitrates are soluble, so the precipitate is copper(II) sulfide. A downward-pointing arrow is put after its formula.

As mentioned earlier, occasionally the insoluble product is a gas, as in the following examples:

Hydrogen chloride is released as a gas when concentrated sulfuric acid is added to solid sodium chloride. Although hydrogen chloride is very soluble in water, it is quite insoluble in concentrated sulfuric acid. The acid salt sodium hydrogen sulfate is the second product.

$NaCl(s) + H_2SO_4(l) \longrightarrow HCl(g) + NaHSO_4(s)$

1. Acetic acid may be released as a gas in a reaction similar to that in the first example. The equation for the reaction of concentrated hydrochloric acid with sodium acetate is:

$NaC_2H_3O_2(s) + HCl(aq) \longrightarrow HC_2H_3O_2(g) + NaCl(s)$

2. A carbonate reacts with an acid to form carbonic acid, which immediately decomposes to gaseous carbon dioxide and water.

$Na_2CO_3(s) + 2\ HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

Oxidation-Reduction

Another way of classifying reactions separates them into only two groups: (1) those that do not involve a change in oxidation number but do result in a decrease in the number of ions in solution and (2) those that involve a transfer of electrons and changes in oxidation number.

Those that result in a decrease in the number of ions in solution are usually double-displacement reactions In a neutralization reaction, hydrogen ion combines with hydroxide ion to form the covalent, un-ionized compound water, thus decreasing the number of ions in solution. In a precipitation reaction, the insoluble product removes ions from the solution. Other reactions in this category are those that form weak electrolytessuch as acetic acid or aqueous ammonia (ammonium hydroxide). Examples are the reaction between sodium acetate and hydrochloric acid

$NaC_2H_3O_2(aq) + HCl(aq) \longrightarrow NaCl(aq) + HC_2H_3O_2(aq)$

and the reaction between sodium hydroxide and ammonium chloride

$NaOH(aq) + NH_4Cl(aq) \longrightarrow NaCl(aq) + NH_3(aq) + H_2O(l)$

Those reactions that involve a transfer of electrons include combination, displacement, and decomposition reactions. Reactions that involve a transfer of electrons are known as oxidation-reduction or redox reactions. The reaction of sodium with chlorine is a redox reaction:

$$2\ \mathrm{Na} + \mathrm{Cl_2} \longrightarrow 2\ \mathrm{NaCl}$$

Each chlorine atom gains an electron to form a chloride ion:

$$2\,e^- + :\!\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!-\!\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!: \longrightarrow 2\ :\!\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!:^-$$

Each sodium atom loses an electron to form a sodium ion:

$$\dot{\mathrm{Na}} + \dot{\mathrm{Na}} \longrightarrow 2\ \mathrm{Na}^+ + 2\ e^-$$

The element that loses electrons is oxidized. In the reaction of sodium with chlorine, sodium is oxidized. The element that gains electrons is reduced. In this reaction, chlorine is reduced.

Displacement reactions are usually oxidation-reduction reactions. A typical displacement reaction is that of copper with silver nitrate:

$$\mathrm{Cu(s)} + 2\ \mathrm{AgNO_3(aq)} \longrightarrow 2\ \mathrm{Ag} + \mathrm{Cu(NO_3)_2(aq)}$$

In this reaction, the copper loses electrons (is oxidized):

$$\mathrm{Cu^0} \longrightarrow \mathrm{Cu^{2+}} + 2\ e^-$$

and the silver ion gains electrons (is reduced):

$$\mathrm{Ag^+} + e^- \longrightarrow \mathrm{Ag^0}$$

Oxidation without reduction is impossible. If an element in a reaction loses electrons, another element in the reaction must gain electrons.

Identifying Oxidation-Reduction Reactions

Oxidation numbers have many uses, but the one that concerns us here is their role in determining whether or not a particular reaction involves oxidation-reduction. In an oxidation-reduction reaction, at least two oxidation numbers change. The element that is oxidized increases its oxidation number, and the element that is reduced decreases its oxidation number.

In the reaction of sodium with chlorine, sodium atoms are oxidized to sodium ions; the oxidation number of sodium increases from 0 to +1. At the same time, chlorine is reduced to chloride ions; the oxidation number of chlorine decreases from 0 to -1.

By assigning oxidation numbers to all the elements in the reactants and the products of a reaction, we can determine whether the reaction results in a change in oxidation number.

If a change does occur, the reaction is an oxidation-reduction reaction. For example, consider the reaction between magnesium and oxygen:

$$\underset{0}{2\,Mg} + \underset{0}{O_2} \longrightarrow 2\,\underset{+2,}{Mg}\,\underset{-2}{O}$$

Below each element in each substance in the equation, we have written its oxidation number. The oxidation number of magnesium increases from 0 to +2; magnesium is oxidized. The oxidation number of oxygen decreases from 0 to -2; oxygen is reduced. Thus, the reaction of magnesium with oxygen is an oxidation-reduction reaction.

A reaction that is not an oxidation-reduction reaction will cause no changes in oxidation numbers. Consider the reaction of sodium hydroxide with hydrochloric acid:

$$\underset{+1,}{Na}\,\underset{-2,}{O}\,\underset{+1,}{H} + \underset{+1,}{H}\,\underset{-1}{Cl} \longrightarrow \underset{+1,}{Na}\,\underset{-1}{Cl} + \underset{+1,}{H_2}\,\underset{-2}{O}$$

Below each element in the equation, we have written its oxidation number. Because each element has the same oxidation number in the products as it does in the reactants, we know that this neutralization reaction is not an oxidation-reduction reaction.

Examples

Example One

For the following reactions decide:

(1) Is it an oxidation-reduction?
(2) If so, which element is oxidized and which element is reduced?

a. Bromine can be prepared by bubbling chlorine gas through a solution of sodium bromide. The equation for this reaction is:

$$2\,NaBr(aq) + Cl_2(g) \longrightarrow 2\,NaCl(aq) + Br_2(g)$$

b. If you blow through a straw into limewater, the solution becomes milky. In chemical terms, if carbon dioxide is bubbled through a solution of calcium hydroxide in water a milky white precipitate of calcium carbonate forms:

$$CO_2(g) + Ca(OH)_2(aq) \longrightarrow CaCO_3(\downarrow) + H_2O(l)$$

Solution

Reaction a

Nine-four 1. Write the oxidation number under each element in the equation:

$$\begin{array}{ccccccc} 2\,NaBr(aq) & + & Cl_2(g) & \longrightarrow & 2\,NaCl(aq) & + & Br_2(g) \\ +1\ \ -1 & & 0 & & +1\ \ -1 & & 0 \end{array}$$

2. Do any elements change oxiation number? Yes, both chlorine and bromine do. Therefore, this reaction is oxidation-reduction.

3. The oxidation number of chlorine changes from 0 to -1: chlorine is reduced. The oxidation number of bromine changes from -1 to 0: bromine is oxidized.

Reaction b

$$\begin{array}{ccccccc} CO_2(g) & + & Ca(OH)_2(aq) & \longrightarrow & CaCO_3(\downarrow) & + & H_2O(l) \\ +4\ \ -2 & & +2\ \ -2\ \ +1 & & +2\ \ +4\ \ -2 & & +1\ \ -2 \end{array}$$

Example Two

In the reaction of sodium with chlorine to form sodium chloride, which substance is he oxidizing agent? Which is the reducing agent?

Solution

Write the equation for the reaction and assign oxidation numbers:

$$\begin{array}{ccccc} 2\,Na(s) & + & Cl_2(g) & \longrightarrow & 2\,NaCl(s) \\ 0 & & 0 & & +1\ \ -1 \end{array}$$

Because chlorine changes oxidation number form 0 to -1, it is reduced: it is the oxidizing agent. Because sodium changes oxidation number from 0 to +1, it is oxidized; it is the reducing agent.

Combustion Reactions

Combustion reactions are a special type of oxidation-reduction reaction. We correctly associate combustion reactions with burning. In the usual combustion reaction, the elements in the reacting compound combine with oxygen to form oxides as in the combustion of propane to form carbon dioxide and water:

$$2\,C_3H_8(l) + 10\,O_2(g) \longrightarrow 6\,CO_2(g) + 8\,H_2O(l)$$

Figure below shows the combustion of gasoline in oxygen.

The above reactions take place when an adequate supply of oxygen is present. In the absence of an adequate supply of oxygen, carbon monoxide may be formed instead of carbon dioxide.

$$2\ C_3H_8(l) + 7\ O_2(g) \longrightarrow 6\ CO_2(g) + 8\ H_2O(l)$$

Example

Write the balanced equations for the complete combustion in oxygen of:

a. sulfur to form sulfur dioxide

b. butane, C4H10

c. ethyl alcohol, C2H5OH

Solution

Note that the physical states of these substances are not given. They are therefore omitted from the equations. a. Write the formulas of the reactants, sulfur and oxygen, and of the product, SO2.

$$S_8 + 8\ O_2 \longrightarrow 8SO_2$$

b. Butane contains only carbon and hydrogen and the combustion is complete, so the products are carbon dioxide, and water. The unbalanced equation is:

$$C_4H_{10} + O_2 \not\longrightarrow CO_2 + H_2O$$

Four atoms of carbon on the left give four molecules of carbon dioxid on the right. Ten atoms of hydrogen on the left give 5 molecules of water on the right which requires thirteen atoms of oxygen (6 1/2 molecules) on the left.

$$C_4H_{10} + 6\ 1/2\ O_2 \longrightarrow 4\ CO_2 + 5\ H_2O$$

To write the equation using only whole numbers of molecules, we must multiply through by 2 to get:

$$2\ C_4H_{10} + 13\ O_2 \longrightarrow 8\ CO_2 + 10\ H_2O$$

c. Ethyl alcohol contains carbon, hydrogen, and oxygen. The produces of complete combustion will be carbon dioxide and water.

$$C_2H_5OH + O_2 \not\longrightarrow CO_2 + H_2O$$

Initial balancing gives two atoms of carbon on the left, two molecules of carbon dioxide on the right; six atoms of oxygen on the right, 3 1/2 molecules of oxygen on the left:

$$C_2H_5OH + 3\ 1/2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$$

We multiply by 2 to clear the fraction and give the balanced equation.

$$2\ C_2H_5OH + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$$

Mass Relationships

Simple Problems

A balanced equation is a quantitative statement of a reaction. It relates amounts of reactants to amounts of products. Let us see what this statement means in terms of a particular reaction.

Pentane, C5H12, burns in oxygen to form carbon dioxide and water. The balanced equation for the combustion of pentane is:

$$C_5H_{12} + 8\ O_2 \longrightarrow 5\ CO_2 + 6\ H_2O$$

In qualitative terms, this equation shows that pentane reacts with oxygen to form carbon dioxide and water. In quantitative terms, the equation states that 1 molecule of pentane reacts with 8 molecules of oxygen to form 5 molecules of carbon dioxide and 6 molecules of water.

For 15 molecules of pentane, (8 x 15) or 120 molecules of oxygen would be needed for complete reaction; (5 x 15) molecules of carbon dioxide and (6 x 15) molecules of water would be formed. Whatever number (n) of molecules of pentane were used in the reaction, 5n molecules of carbon dioxide and 6n molecules of water would be formed.

If 6.02 x 1023 molecules (1 mole) of pentane are burned, [8(6.02 x 1023)] molecules (8 moles) of oxygen are needed. The reaction would form [5(6.02 x 1023)] molecules (5 moles) of carbon dioxide and [6(6.02 x 1023] molecules (6 moles) of water.

Any balanced equation gives the ratio between moles of reactants and moles of products. Given the number of moles of one component used or produced in a reaction, the number of moles or grams of any other component used or produced can be calculated. Such calculations are called stoichiometry.

A stoichiometric problem can be stated in many ways, but it always contains the following information:

1. The reaction involved.

2. A stated amount of one component of the reaction.

3. A question asking "how much" of another substance is needed or formed in the reaction.

The quantitative problems in previous chapters were solved by answering a series of questions:

1. What is wanted?

2. What is given?

3. What conversion factors are needed to go from "given" to "wanted"?

4. How should the arithmetic equation be set up so that the units of the "given" are converted to the units of the "wanted"?

Stoichiometric problems can be solved by answering the same set of questions. The only difference is that some of the conversion factors are derived from the balanced chemical equation for the reaction involved. The steps to follow in solving a stoichiometric problem are the following:

1. Write the balanced equation for the reaction.

2. Decide which substance is wanted and in what units.

3. Decide which substance is given and in what units and what amount.

4. Determine the conversion factors required to convert:

a. the amount of given substance into moles

b. the moles of the given substance into moles of the wanted substance

c. the moles of wanted substance into the units wanted in the problem

5. Combine the amount of given substance and its units along with the appropriate conversion factors into an arithmetic equation in such a way that all factors except the wanted substance in

the proper units will cancel.

We will now do some stoichiometry problems. Before we begin, several points should be emphasized.

First, to prevent confusion and errors, the name and units of each item in the equation are always shown.

Second, no arithmetic is done until the whole equation is written out.

Third, all units in the final equation must cancel except for those required in the answer.

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Problems Involving a Limiting Reactant

All the stoichiometry problems encountered thus far have had two reactants, but the amount was given for only one of them. In calculating the solutions, we assumed that enough of the second reactant was present to allow complete reaction of the first. This is not always the case. We will encounter many problems in which we know the amounts of all reactants and must calculate which reactant is present in excess before we can calculate a theoretical yield.

A problem of this type might be encountered if you owned a bicycle shop. Among other parts, each bicycle requires two wheels and one set of handlebars. Suppose that, after a busy season, your stockroom contains only 14 wheels and 6 sets of handlebars, although it contains huge quantities of all the other necessary parts. How many bicycles can you build before a new shipment of wheels and handlebars arrives? You have enough wheels for seven bicycles (14 ÷ 2). You have enough handlebars for six bicycles (6 ÷ 1). Clearly, you can put together only six bicycles and will have two unused wheels. No matter how you juggle the parts, you have only enough handlebars for six bicycles. Even with 100 wheels, you could make only six bicycles. The number of handlebars is the limiting factor in the number of bicycles you can make.

Similarly, in a chemical reaction in which the amount of each reactant is known, one reactant is usually present in excess; the amount of the other limits the amount of product that can be formed. The problem becomes how to decide which is the limiting reactant.

Consider the reaction of hydrogen with chlorine to form hydrogen chloride. The balanced equation for this reaction is:

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

According to the equation, each mole of hydrogen that reacts requires one mole of chlorine to form two moles of hydrogen chloride (Figure 8.7a). If only 0.5 mol hydrogen is present, only 0.5 mol chlorine is needed, and 1.0 mol hydrogen chloride is formed . If 2.0 mol hydrogen are to react, then 2.0 mol chlorine are necessary, and 4.0 mol hydrogen chloride are formed. Suppose you have 2.0 mol hydrogen but only 1.0 mol chlorine .Only 1.0 mol hydrogen can react, because you have only 1.0 mol chlorine. In this instance, chlorine is the limiting reactant; only 2.0 mol hydrogen chloride are formed, and the second mole of hydrogen remains unreacted.

A limiting reactant problem, then, consists of two simpler problems. Suppose we have the reaction

$$A + B \longrightarrow C$$

and we know now much A and B are available. To determine how much C will be formed, we must calculate (1) how much C can be prepared from the given amount of A and (2) how much C can be prepared from the given amount of B. The smaller of these two amounts is the theoretical yield of C.

Energy Changes via Chemical Reactions

All changes, whether chemical or physical, are accompanied by a change in energy. Each reacting molecule possesses a certain amount of energy due to the nature of chemical bonds. So does each product molecule. As the bonds of the reacting molecules break and the new bonds of the products form, energy is released or absorbed, depending on whether the reactants have higher or lower energy than the products.

We can measure energy changes in several ways. The two kinds of energy change of most interest to us are: (1) the change in free energy (G), which is the energy available to do useful work (discussed in Chapter 13), and (2) the change in enthalpy (H), which is the heat energy absorbed or released by the reaction and measured at constant pressure. Most chemical reactions take place under the constant pressure of the atmosphere. The energy released or absorbed by such reactions is the change in enthalpy, H, which can be shown as

$$\Delta H_{reaction} = H_{products} - H_{reactants}$$

In reporting values of H, a superscript is used to show the temperature at which the measurements were made. For example, the symbol H 0°C shows that the change in enthalpy was measured at 0°C. If no temperature is shown, the enthalpy change was measured at 25°C. All changes are measured at one atmosphere pressure.

The value of H given with an equation refers to that particular equation. When the enthalpy change was measured, the physical states of the components were those stated in the equation. If the physical states are different, there will be a different enthalpy change. This difference is illustrated by the next two equations for the formation of water. They differ in enthalpy change. In the first, gaseous water is formed, and in the second, liquid water is formed; the difference between their enthalpy changes reflects the difference in energy content between a gas and a liquid.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -241\ \text{kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286\ \text{kJ}$$

The enthalpy change given for a reaction also depends on the coefficients used in the equation for the reaction. Thus, if the equation for the formation of water is written

$$2\,H_2(g) + \quad O_2(g) \longrightarrow 2\,H_2O(l) \qquad \Delta H = -482\text{ kJ}$$

the enthalpy change is twice what it was in the previous equation for the formation of gaseous water when the coefficient of water was 1. This last problem can be resolved by doing as we do in several equations where we report the enthalpy change per mole of one component of the reaction, thus removing any ambiguity in interpretation.

Endothermic and Exothermic Reactions

A reaction that absorbs energy is an endothermic reaction; its enthalpy change (ΔH) is positive. The enthalpy of the products of the reaction is greater than that of the reactants. Energy is absorbed from the surroundings. The following reactions are endothermic.

1. The formation of hydrogen iodide:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \longrightarrow HI(l) \qquad \Delta H = +25.9\text{ kJ/mol HI} \qquad \text{(equation a)}$$

2. The decomposition of water:

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +285.8\text{ kJ/mol } H_2O \qquad \text{(equation b)}$$

A reaction that releases energy is an exothermic reaction; its enthalpy change is negative. The enthalpy of the products is less than that of the reactants. Energy is released to the surroundings. The following reactions are exothermic.

1. The combustion of methane:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$
$$\Delta H = -891\text{ kJ/mol } CH_4 \qquad \text{(equation c)}$$

2. The formation of water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ/mol } H_2O$$

(equation d)

Notice that the decomposition of water (equation b) is endothermic and requires the input of 285.8 kJ energy per mole of water decomposed. The reverse reaction, the formation of one mole of water from hydrogen and oxygen (equation d), is exothermic and releases 285.8 kJ energy. The amount of energy is the same, but the sign of the energy change is different.

Another example is the relationship between energy change and the direction of a reaction is the formation and decomposition of glucose. Glucose (C6H12O6) is formed from carbon dioxide and oxygen in the cells of green plants in the process called photosynthesis. Photosynthesis is an endothermic reaction. The source of the energy for the formation of glucose is light (radiant energy), usually from the sun.

$$6\ CO_2(g) + 6\ H_2O(l) \xrightarrow{\text{photosynthesis}} C_6H_{12}O_6(s) + 6\ O_2(g)$$

$$\Delta H = +2.80 \times 10^3 \text{ kJ/mol glucose}$$

Thus, green plants have the remarkable ability to trap the energy of sunlight and use that energy to produce glucose from carbon dioxide and water. The energy is stored in the glucose. Animal and plant cells have the equally remarkable ability to metabolize glucose and use the energy released to maintain body temperature or do biological work, such as contracting muscles or thinking.

Endothermic and Exothermic Reactions Examples

Example One

For each of the following reactions: (1) Decide whether the reaction is exothermic or endothermic. (2) Write the equation fo the reverse reaction, and state the accompanying enthalpy change, H.

a. $N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = +181\ kJ$

b. $2\,NO_2(g) \longrightarrow N_2O_4(g) \quad \Delta H = -57.6\ kJ$

c. $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g) \quad \Delta H = -92.5\ kJ$

Solution

a. The enthalpy change is positive; the reaction is endothermic. The reverse reaction is:

$2\,NO(g) \longrightarrow N_2(g) + O_2(g) \quad \Delta H = -181\ kJ$

b. The enthalpy change is negative; the reaction is exothermic. The reverse reaction is:

$N_2O_4(g) \longrightarrow 2NO_2 \quad \Delta H = +57.6\ kJ$

c. The enthalpy change is negative; the reaction is exothermic. The reverse reaction is:
The Stoichiometry of Energy Changes The energy change associated with a reaction is a stoichiometric quantity and can be treated arithmetically, as were mass changes in Section 8.4. For many reactions, enthalpy changes have been determined and tabulated in the chemical literature. The changes listed in such sources apply only to the form of the equation they accompany, as explained previously.

Example Two
Calculate the enthalpy change for the combustion of 35.5 g gaseous propane (C3H8).

$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g) \quad \Delta H = +92.5\ kJ$

Solution

Equation
Given above

Wanted:
? kJ released

Given
35.5 g C3H8;

Conversion factors Propane, C3H8, mass to moles: 44.1 g C3H8 = 1 mol C3H8 The combustion of 1 mol of propane releases 2.22x103 kJ energy.

Arithmetic equation

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O$$

$$\Delta H = -2.22x10^3\ kJ$$