UNIT FOUR

CHEMICAL REACTIONS AND STOICHIOMETRY

Unit Outcomes

After completing this unit, you will be able to:

- *Investigate the fundamental laws of chemical reactions and their application;*
- *explain energy changes in chemical reactions;*
- *develop skills in writing and balancing chemical equations;*
- *discuss types of chemical reactions;*
- *develop skills in solving problems based on chemical equations (mass-mass, volume – volume and mass – volume relationships);*
- *acquire skills to determine limiting reactant, theoretical, actual & percentage yields;*
- *grasp knowledge on oxidation-reduction reactions and analyze them by specifying the oxidizing and the reducing agents, the substance reduced or oxidized;*
- *describe the rate of chemical reaction, the state of a chemical equilibrium and factors affecting them; and*
- *demonstrate scientific enquiry skills: observing, predicting, classifying, measuring, comparing and contrasting, designing experiments, interpreting data, drawing conclusions, applying concepts and problem – solving.*

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4.1 INTRODUCTION

Competencies

***By the end of this unit, you will be able to*:**

- define chemical reaction;
- describe the difference between chemical and physical changes; and
- give some examples of chemical reactions.

The concept of a chemical reaction dates back to about 250 years. It had its origins in early experiments that classified substances as elements and compounds and in theories that explained these processes. The concept of a chemical reaction had a primary role in explaining the science of chemistry as it is known today.

Chemical reaction is a process in which one or more reacting substances, called reactants, are converted to one or more different substances, called products. A chemical reaction rearranges the constituent atoms of the reactants to yield completely new substances as products. The properties of the products are completely different from those of the reactants.

For example, if you burn magnesium in oxygen, the elements are converted to a completely new substance, magnesium oxide. This product is a soft, white, crumbling powder. The characteristics of magnesium oxide are completely different from each magnesium and oxygen. Both the reactants are no longer present in the elemental form.

Magnesium (s) + Oxygen (g) $\longrightarrow$ Magnesium oxide (s)

Chemical reactions result in three types of changes in the original substance (s). These are changes in composition, properties and energy. The changes can be physical or chemical.

A change in which one or more new substances are formed is called a chemical change. It arises because of a chemical reaction. Chemical changes are very important in our lives because the products may determine our day to day activities. Some examples include digestion in our body, photosynthesis, ripening of fruits, fermentation of grapes, synthesizing plastics, combustion of fuels, production of medicines, etc.

Properties such as shape, boiling, freezing, size, color and state of a substance are called physical. A change in such properties of the substance is called physical change. No new substance is formed and it is generally reversible.

Think about the process of chewing food. The food that is crushed by your teeth has the same molecular structure as it did before your first bite, making it a physical change. However, as soon as the saliva in your mouth mixes with these pieces of food, enzymes begin breaking it down to new form, which is a chemical change.

EXERCISE 4.1

Classify the changes in the following processes as physical or chemical.

a. Photosynthesis
b. Heating sulfur in a test tube
c. Making aluminum foil by beating
d. Glowing of an electric bulb
e. Aging
f. Magnetization of iron
g. Fading of dye in cloth
h. Growing of your hair
i. Heating sugar

4.2. FUNDAMENTAL LAWS OF CHEMICAL REACTIONS

Competencies

***By the end of this lesson, you will be able to*:**

- state the law of conservation of mass, the law of definite composition and the law of multiple proportions;
- illustrate each law and solve problems to which the laws apply; and
- demonstrate the law of conservation of mass and the law of definite composition using simple experiments

4.2.1. The Law of Conservation of Mass

"*Nothing comes from nothing*" is a premise in ancient Greek philosophy that argues *what exists now has always existed*. This means that no new matter can come into existence where there was none

before. Antoine Lavoisier (1743 – 1794) redefined this idea as the law of conservation of mass, which states that "matter is neither created nor destroyed in a chemical reaction."

Even though a chemical reaction rearranges atoms into completely different forms, the total mass of the reactants is equal to that of the products because of the law of conservation of mass. More simply, whatever process takes place, you will still have the same mass of stuff before and after the process (however, certain nuclear reactions such as fusion and fission can destroy a small part of the mass into energy).

An argument arising here is that if this law was true, then how could a large piece of wood be reduced to a small pile of ashes? The wood clearly has a greater mass than the ashes. Therefore, one may conclude that mass had been lost. However, the burning of wood does follow the law of conservation of mass if one measures all the gaseous products as well!

$$\text{Wood} + O_2 \rightarrow \text{Pile of ash} + CO_2\,(g) + H_2O\,(g)$$

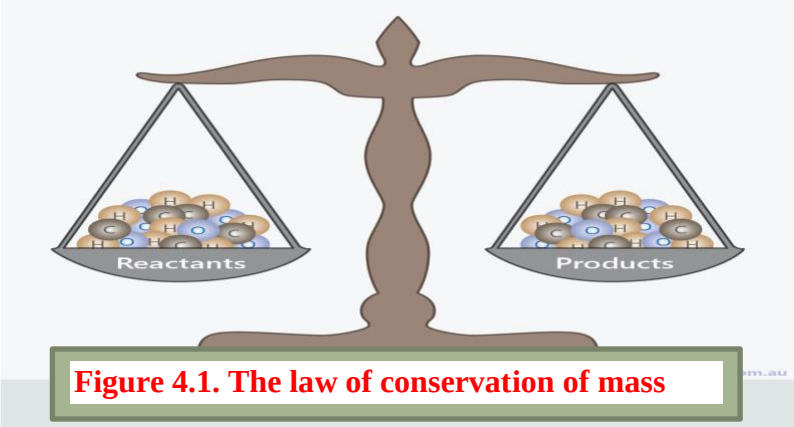


Figure 4.1. The law of conservation of mass

Experiment 4.1

Investigating the Law of Conservation of Mass

Objective: To determine the mass of substances before and after a reaction.

Apparatus: Flask, test tube, thread, rubber stopper, balance.

Chemicals: Sodium chloride, silver nitrate.

Procedure:

1. Take 50 mL of silver nitrate solution in a conical flask.

2. Tie a thread around the top of a test tube. Fill the test tube with a saturated solution of sodium chloride. Suspend the test tube in the flask by means of a thread held by a rubber stopper, as shown in Figure 4.2 below.

3. Weigh the flask (and its contents). Record the result as m_1.

4. Mix the liquids by tilting the conical flask so that the sodium chloride pours into the silver nitrate solution.

5. Reweigh the conical flask and contents and record as m_2. Compare m_1 and m_2.

Observation and analysis

1. What was the color of the solution after the reaction?

2. Is there any difference in mass between m_1 and m_2?

3. What is your conclusion from this experiment?

4. Write the balanced chemical equation for the reaction.

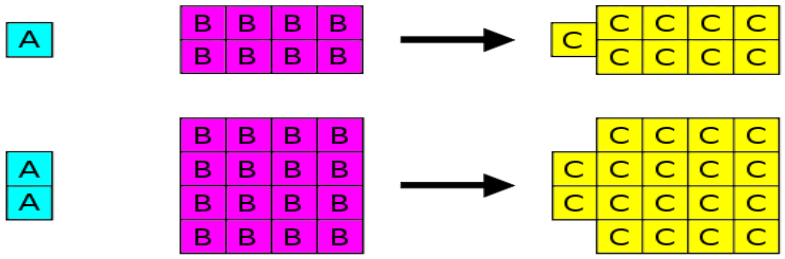


Figure 4.2. The Law of conservation of mass

4.2.2. The Law of Definite Compositions

Joseph Proust (1754 – 1826) formulated the *law of definite proportions* (also called the *Law of Constant Composition* or **Proust's Law**). It states that if a compound is broken down into its

constituent elements, the masses of the constituents will always have the same proportions, regardless of the quantity or source of the substance. The illustration below depicts this law.



If 1.0 g of A reacts with 8.0 g of B, then the law of definite proportions depicts that 2.0 g of A must react with 16.0 g of B. If 1.0 g A reacts with 8.0 g B, then by the law of conservation of mass, they must produce 9.0 g of C. Similarly, when 2.0 g of A react with 16.0 g of B, they must produce 18.0 g of the same substance, C.

In another example, ammonia (NH_3), regardless of where the sample is obtained or how large its volume is, combines in a 3.0 to 14.0 ratio by mass of hydrogen and nitrogen. Similarly, in forming CaO from its elements, 40.0 g of calcium combines with exactly 16.0 g of oxygen, or 10.0 g of calcium with 4.0 g of oxygen, etc. which is in 5.0 to 2.0 ratio by mass of calcium to oxygen.

Experiment 4.2

Investigating the Law of Definite Proportions

Objective: To determine the mass of copper from copper (II) oxide.

Apparatus: Burner, stand, combustion tube, two glass test tubes, two watch glasses.

Chemicals: Copper powder, copper (II) carbonate, hydrogen gas

Procedure:

1. Prepare samples of copper (II) oxide using the following two methods:

   (i). Make copper (II) oxide by heating strongly copper powder in one of the test tubes.

   (ii). Make copper (II) oxide by heating copper (II) carbonate in the second test tube.

2. Take 1.0 g from each of the samples of copper (II) oxide (*from i and ii*). Place each of these samples in a watch glass.

3. Reduce each of these samples: use the combustion tube to heat the samples in a stream of hydrogen as shown in Figure 4.3.

4. Weigh the copper metal that remains in each case. Compare the measurements.

Observation and analysis

1. What is the mass of copper produced in each case?

2. Why is copper metal produced in each case?

3. What can you conclude from the experiment? Write a short report on your observation.

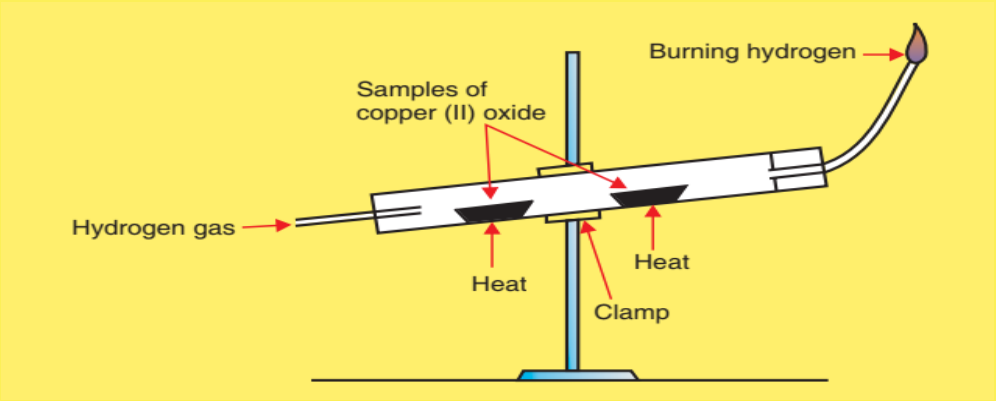


Figure 4.3. Reduction of copper (II) oxide by hydrogen

Example 1

1. A 5.0 – g sample of copper sulfate crystal, $CuSO_4 \cdot X\ H_2O$, lost 1.80 g of water vapor when heated to the anhydrous $CuSO_4$ powder. Apply appropriate law, state the law and find the value of X in one mole of copper sulfate crystal.

2. For a combination reaction, 2.80 g X would exactly react with 5.20 g Y and 7.60 g Z. What mass of product can be obtained when 2.60 g Y react with sufficient amounts of X and Z?

Solutions

1. Applying the law of conservation of mass:

$$CuSO_4 \cdot X\ H_2O \longrightarrow CuSO_4 + X\ H_2O$$

5.0 g 3.2 g + 1.80 g

1.0 mol crystal produces 1.0 mol or 160.0 g of $CuSO_4$. From the law of definite composition (i.e. 3.2 g $CuSO_4$ to 1.80 g H_2O), it follows that 160.0 g $CuSO_4$ corresponds to 90.0 g H_2O, which is 5.0 mol. Therefore, X = 5.0.

2. 2.80 g X + 5.20 g Y + 7.60 g Z = 15.60 g. Applying the law of definite proportions, 2.60 g Y requires 1.40 g of X and 3.80 g of Z, giving 7.80 g of the same product.

4.2.3. The Law of Multiple Proportions

This law states that when two elements combine to form more than one (different) compounds, the masses of one element that combines with a fixed mass of the second element are in the ratio of small whole numbers. In H_2O and H_2O_2, for example, 1.0 g hydrogen combines with 8.0 g oxygen in H_2O and with 16.0 g oxygen in H_2O_2, with a ratio of 8.0 to 16.0 or 1.0 to 2.0. Similarly, nitrogen forms a variety of oxides, five of which are shown here.

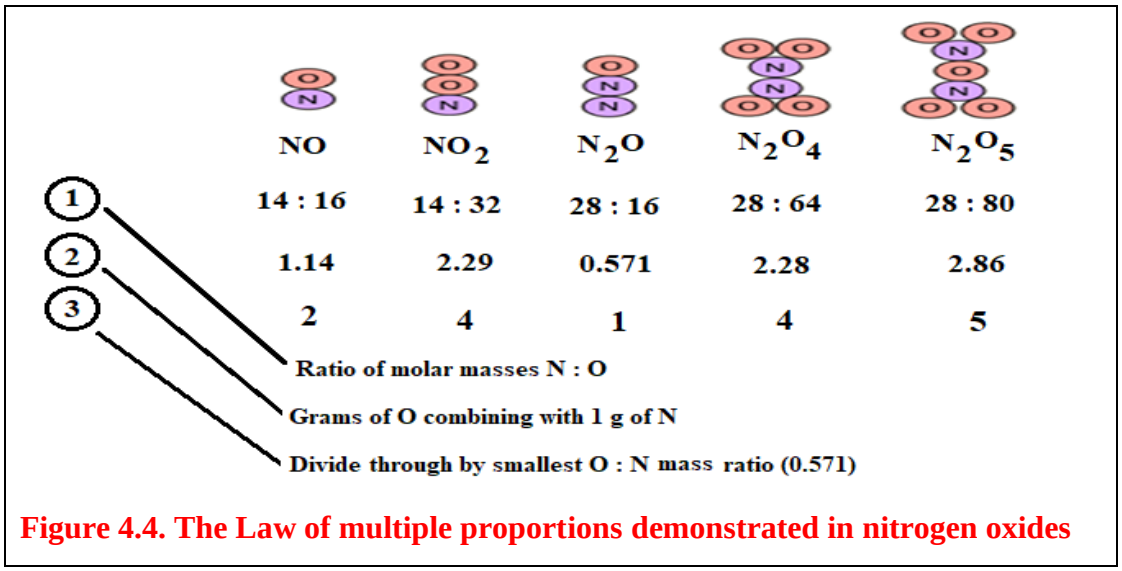


Figure 4.4. The Law of multiple proportions demonstrated in nitrogen oxides

4.3. CHEMICAL EQUATIONS

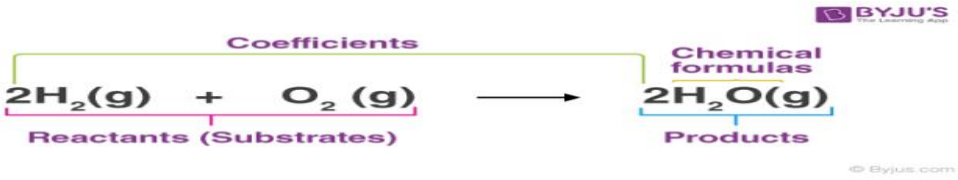
Competencies

By the end of this lesson, you will be able to:

- explain the conventions used to write chemical equations;
- balance chemical equations, using the inspection method;
- balance chemical equations, using the Least-Common-Multiple (LCM) method.
- balance chemical equations using the algebraic method

Chemical equations are symbolic representations of chemical reactions in which the reactants and products are expressed in terms of their respective chemical formulae. Equations also make

use of arrows and symbols to represent the direction of the reaction and the physical states of the substances involved.



It can be observed in the example above that the reacting entities are written on the left – hand side whereas the reaction products are written on the right – hand side of the chemical equation. The reactants and products (which are represented by the respective chemical formulae) can be separated by one of the following symbols.

✓ In order to describe a net forward reaction, the symbol → is used.

✓ In order to describe a reaction that occurs in both forward and backward directions, the symbol ⇄ is used.

Multiple entities on either side of the reaction equation are separated from each other with a + symbol. It can be noted that the → symbol, when used in a chemical equation, is often read as '*gives rise to*' or '*yields*'. To denote physical states of substances:

- The symbol (**s**) is used to describe a solid state
- The symbol (**ℓ**) denotes a liquid or molten state
- The symbol (**g**) implies that the entity is in the gaseous state.
- The (**aq**) symbol describes an aqueous solution.

4.3.1. Writing Chemical Equation

Chemical symbols and formulas are used instead of words to represent a reaction equation.

Steps to write a chemical equation

1. Write a word equation for the reaction. For example, the word equation for the reaction between sodium and chlorine to produce sodium chloride is written as:

Sodium + Chlorine ⟶ Sodium Chloride (*word equation*)

Note that we read the ' + ' sign as 'reacts with' and the arrow can be read as *'to produce', 'to form', 'to give'* or *'to yield'*.

2. Write the symbols and formulas of the reactants and products presented in the word equation.

$Na + Cl_2 \rightarrow NaCl$ (*Chemical equation*)

3. Balance the equation.

$2\ Na + Cl_2 \rightarrow 2\ NaCl$

Generally, a chemical equation must fulfill the following conditions:

i. The equation must represent a true and possible chemical reaction.

ii. The symbols and formulas must be written correctly. The elements hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine and iodine exist as diatomic molecules. These elements should be written as molecules in the equation.

iii. The equation must be balanced. There must be the same number of atoms on both sides of the equation.

A chemical equation has both *qualitative* and *quantitative meanings*.

Qualitatively, a chemical equation indicates the identity and types of the reactants and products in the reaction.
Quantitatively, a chemical equation expresses the relative number (*amount)* of moles, molecules or masses of the reactants and products.

4.3.2. Balancing Chemical Equation

The law of conservation of mass states that no atoms are lost or made during a chemical reaction, so the total mass of the products is equal to the total mass of the reactants. A balanced equation has the same number of atoms of each element on both sides of the arrow.

To balance a chemical equation means to equalize the number of atoms on both sides of the equation by putting appropriate coefficients in front of the formulas. Three methods of balancing chemical equations will be discussed under this topic. These are the inspection, the least common multiple (LCM) and algebraic methods.

I. The Inspection Method

Balancing an equation by inspection means to adjust coefficients by trial and error until the equation is balanced. Simpler chemical equations can be balanced using this method. Apply the

following four steps to balance by this method.

Step 1: Write the word equation.

Step 2: Write the correct symbols and / or formulas for the reactants and products.

Step 3: Place the smallest whole number coefficients in front of the symbols or formulas until the number of atoms of each element is the same on both sides of the equation.

Step 4: Checking: By counting the number of atoms on both sides of the equation, make sure that atoms of all elements are balanced and also the coefficients are expressed as the smallest whole number ratio.

Example 2

Balance the equation for the reaction between hydrogen and nitrogen to produce ammonia.

Solution

Step 1. Nitrogen + Hydrogen → Ammonia (Word equation)

Step 2. $N_2 + H_2 \rightarrow NH_3$ (unbalanced)

Step 3. Check if equal number of atoms of each element are found on both sides. There aren't

There are two nitrogen atoms on the left but only one on the right, so write 2 in front of NH_3.	$N_2 + H_2 \rightarrow 2\ NH_3$
Check again. There are two hydrogen atoms on the left but $(2 \times 3) = 6$ on the right, so write 3 in front of H_2.	$N_2 + 3\ H_2 \rightarrow 2\ NH_3$
Step 4. Check again to see if there are equal numbers of each element on both sides. There are!	(Two nitrogen and six hydrogen atoms)
Add the state symbols if asked to do so.	$N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g)$

Note: Balanced chemical equations only show formulae, not names. A balancing number, written in normal script, multiplies all the atoms in the substance next to it.

EXERCISE 4.2

Balance the following chemical equations, using the inspection method

1. $CaCO_3 \rightarrow CaO + CO_2$
2. $Na + H_2O \rightarrow NaOH + H_2$
3. $H_2O_2 \rightarrow H_2O + O_2$
4. $HNO_3 + H_2S \rightarrow NO + S + H_2O$
5. $Al + H_3PO_4 \rightarrow AlPO_4 + H_2$

II. The LCM Method

In this method, the coefficients for the balanced chemical equation are obtained by taking the LCM of the total valence number of reactants and products and then dividing it by the valence number each of reactants and products. The necessary steps of this method are demonstrated by the following example.

Example 3

1. When aluminum reacts with oxygen, aluminum oxide is formed. Write the balanced chemical equation for the reaction.

Solution

Step 1: Represent the reaction by a word equation.

Aluminum + Oxygen → Aluminum oxide

Step 2: Change the words to symbols and formulas for the reactants and products.

$Al + O_2 \rightarrow Al_2O_3$

Step 3: Place the total valence number of each atom above it.

$$\overset{3}{Al} + \overset{4}{O_2} \rightarrow \overset{6}{Al_2}\overset{6}{O_3}$$

Step 4: Find the LCM of all valence numbers and place it above the arrow.

$$Al + O_2 \xrightarrow[\text{L.C.M}]{12} Al_2O_3$$

Step 5: Divide the LCM by each total valence number to obtain the coefficient for each reactant and product. Place the obtained coefficients in front of the respective formulas.

$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$

Checking: There are 4 Al and 6 oxygen atoms on both sides of the equation. Hence, the chemical equation is correctly balanced.

2. When iron reacts with water, iron (III) oxide and hydrogen are produced. Write the balanced chemical equation.

Solution:

Step 1: Iron + water $\rightarrow$ Iron (III) oxide + hydrogen.

Step 2: $Fe + H_2O \rightarrow Fe_2O_3 + H_2$

Step 3: $\overset{3}{Fe} + \overset{2}{H_2}\overset{2}{O} \rightarrow \overset{6}{Fe_2}\overset{6}{O_3} + \overset{2}{H_2}$

Step 4: $\overset{3}{Fe} + \overset{2}{H_2}\overset{2}{O} \xrightarrow[\text{L.C.M}]{6} \overset{6}{Fe_2}\overset{6}{O_3} + \overset{2}{H_2}$

Step 5: $2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$ (*balanced*)

Checking: There are 2 iron, 6 hydrogen, and 3 oxygen atoms on each side of the equation. Thus, the equation is balanced.

3. The reaction between ammonium sulfate and aluminum nitrate would form aluminum sulfate and ammonium nitrate.

Solution:

Step 1: Ammonium sulphate + Aluminium nitrate $\rightarrow$ Aluminium sulphate + Ammonium nitrate

Step 2: $(NH_4)_2SO_4 + Al(NO_3)_3 \longrightarrow Al_2(SO_4)_3 + NH_4NO_3$

Step 3: $\overset{2}{(N}H_4)_2\overset{2}{SO_4} + \overset{3}{Al}(\overset{3}{NO_3})_3 \longrightarrow \overset{6}{Al_2}(\overset{6}{SO_4})_3 + \overset{1}{NH_4}\overset{1}{NO_3}$

Step 4: $\overset{2}{(NH_4)_2}\overset{2}{SO_4} + \overset{3}{Al}(\overset{3}{NO_3})_3 \xrightarrow[\text{L.C.M}]{6} \overset{6}{Al_2}(\overset{6}{SO_4})_3 + \overset{1}{NH_4}\overset{1}{NO_3}$

Step 5: $3(NH_4)_2SO_4 + 2Al(NO_3)_3 \longrightarrow Al_2(SO_4)_3 + 6NH_4NO_3$ (balanced)

Checking: There are 12 nitrogen, 24 hydrogen, 3 sulphur, 30 oxygen and 2 aluminium atoms on both sides of the equation. Thus, the equation is correctly balanced.

III. Algebraic Method

The strategy for balancing chemical equations algebraically is as follows:

1. Write coefficients using different letters in front of each substance in the equation
2. Write algebraic expressions or rules for each element that equate its atoms on the left-hand side and right-hand side
3. Substitute and simplify to obtain a rule that equates only two letter coefficients that you can solve
4. Substitute the values into the other rules to obtain the balancing coefficients

Example 4

Balance the following equation using algebraic method

$KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + H_2O$

First thing we do is to assign a letter coefficient for each substance:

$a\ KMnO_4 + b\ HCl \rightarrow c\ MnCl_2 + d\ KCl + e\ Cl_2 + f\ H_2O$

Next, apply the law of conservation of mass, which tells us that the total number of atoms of each element must be the same on both sides. Write algebraic rules for each element.

K: $a = d$ Mn: $a = c$ O: $4a = f$

H: $b = 2f$ Cl: $b = 2c + d + 2e$

There are too many unknowns here, but we can substitute the relationships of K and Mn into a relationship of Cl to get rid of c and d: (a = d = c)

$b = 2a + a + 2e = 3a + 2e$

Since b = 2f and 4a = f, it follows that 2f = 8a. Therefore, b = 8a.

Let a = 1. Then, b = 8 and e = 5 / 2. Converting each value to whole number ratio, we get:

a = 2, b = 16, c = 2, d = 2, e = 5 and f = 8.

$2\ KMnO_4 + 16\ HCl \rightarrow 2\ MnCl_2 + 2\ KCl + 5\ Cl_2 + 8\ H_2O$ (balanced)

EXERCISE 4.3

1. Balance the following equations by the **LCM** method.

a. Ammonia burns in oxygen to produce nitrogen monoxide and water.

b. $PCl_5 + H_2O \rightarrow H_3PO_4 + HCl$

c. $Mg + H_2O \rightarrow Mg(OH)_2 + H_2$

d. $Zn(NO_3)_2 \rightarrow ZnO + NO_2 + O_2$

e. There is complete neutralization between sulfuric acid and sodium hydroxide solutions.

2. Balance the equations by **algebraic** method.

f. $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

g. $HNO_3 + H_2S \rightarrow NO + S + H_2O$

4.4. ENERGY CHANGES IN CHEMICAL REACTIONS

Competencies

***By the end of this section, you will be able to*:**

- explain energy changes in chemical reactions;
- describe and illustrate endothermic and exothermic reactions using diagrams;
- conduct simple experiments to demonstrate exothermic and endothermic reactions;
- describe the importance of chemical changes.

Almost all chemical reactions are accompanied by energy changes. These could be in the form of heat, light, electrical, and so on. On the basis of energy changes, chemical reactions can be divided into exothermic and endothermic reactions. (Note that physical processes can also be exothermic or endothermic.)

4.4.1. Exothermic and Endothermic Reactions

Can heat energy be considered as a reactant or a product?

Endothermic Reaction

A chemical reaction which absorbs heat energy from the surroundings is known as endothermic. During this process, heat flows **into** the system from its surroundings and thus, is written on the left side of the equation.

Reactants + Heat → Products

Here are some examples of endothermic reactions.

A. When solutions of barium hydroxide and ammonium chloride react, the temperature falls so sharply that water *under* the beaker will freeze!

B. When a crucible containing calcium carbonate is strongly heated, the carbonate will decompose to solid calcium oxide and gaseous carbon dioxide.

Reaction **A** above is *spontaneous*, meaning it proceeds by its own without any external influence. However, many endothermic reactions like **B** above require continuous supply of energy to start and keep them going. Cooking food, respiration, boiling, etc. are additional examples of endothermic reactions.

Exothermic Reaction

A chemical reaction that releases heat energy to the surroundings is known as exothermic. During this process, heat is **given – off** from the system to its surroundings and this energy is written on the right side of the equation.

Reactants → Products + Heat

At the end of each process, there is temperature rise which can be measured. Here are examples.

A. To start the reaction between iron and sulfur, you must heat the mixture. But soon it glows red hot - *without* the Bunsen burner!

B. Mixing silver nitrate and sodium chloride solutions produces a white precipitate of silver chloride which is accompanied with a rise in temperature.

C. When water is added to lime (calcium oxide), heat is given out, so the temperature rises.

The burning of fuels in oxygen is a common example which releases heat during the reaction.

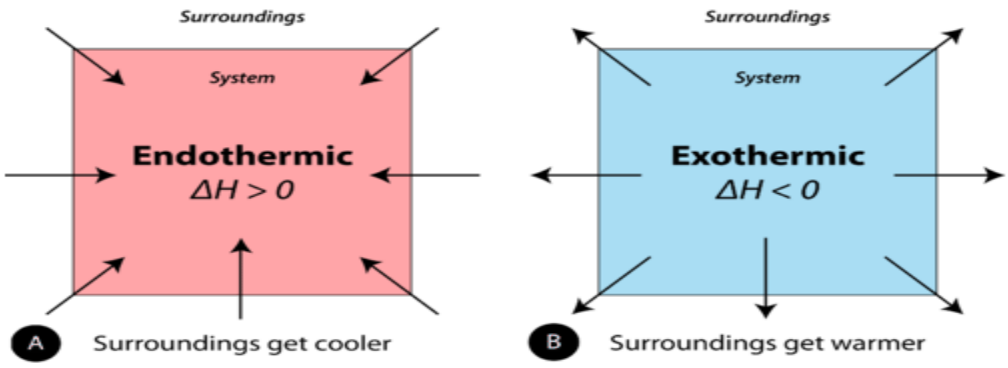


Figure 4.5. Energy transfer during endothermic and exothermic reactions

The amount of heat energy liberated or absorbed by a chemical reaction is called heat of reaction or change in enthalpy. It is symbolized as ΔH and expressed in unit of kilo joules per mol (kJ /

mol). The change in enthalpy (ΔH) is the difference between the energy of the products and the energy of the reactants.

$$\Delta H = Hp - Hr$$

where Hp is the heat content (energy) of the product and Hr is the heat content of the reactant.

4.4.2. Energy Diagrams

For an endothermic reaction, ΔH is positive because the energy of the product is higher than the energy of the reactant as shown in Figure 4.6.

$H_p > H_r$, ΔH is positive ($\Delta H > 0$)

For example, when nitrogen reacts with oxygen to form nitrogen dioxide, 66.4 kJ of heat energy is absorbed (*i.e.*, ΔH = + 66.4 kJ) and thus the reaction is endothermic.

$N_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,NO_2\,(g)$; $\Delta H = +66.4$ kJ

For exothermic reactions, ΔH is negative because the energy of the reactants is higher than the energy of the products. As a result, the enthalpy of the system decreases (Fig. 4.6)

$H_p < H_r$; ΔH is negative ($\Delta H < 0$)

For example, when carbon burns in oxygen to produce carbon dioxide, 393.5 kJ of heat energy is liberated and hence the reaction is exothermic ($\Delta H = -393.5$ kJ /mol).

$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$: $\Delta H = -393.5$ kJ /mol

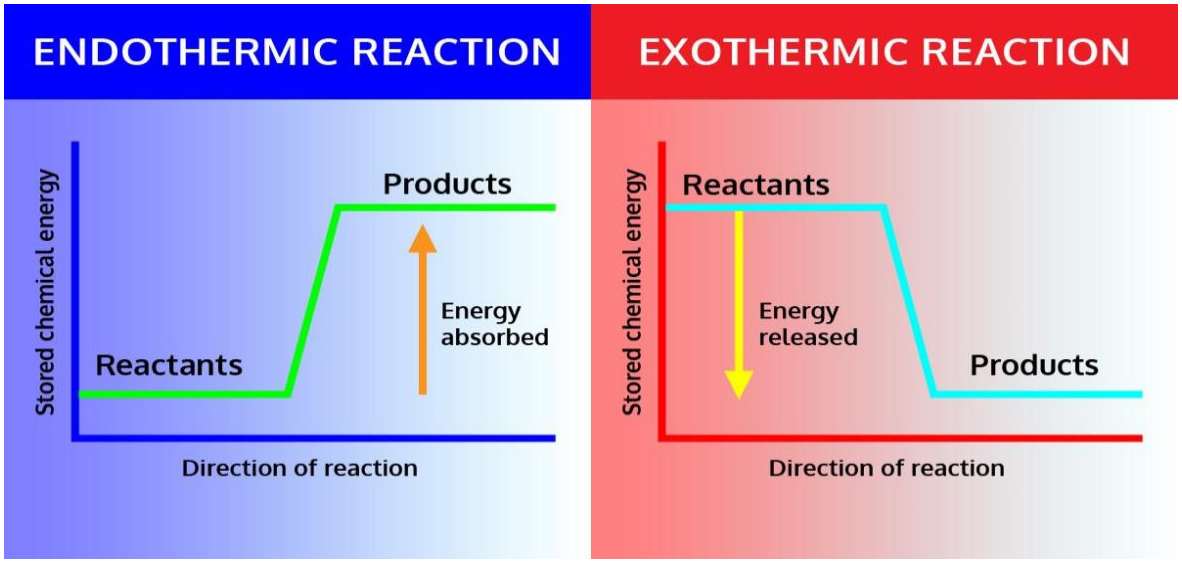


Figure 4.6. Energy diagrams for endothermic and exothermic reactions

Experiment 4.3

Investigating the Heat Involved in a Chemical Reaction

Objective: To determine the exothermic/endothermic nature of the reaction between sulfuric acid and sugar.

Apparatus: beaker and reagent bottle.

Chemicals: Concentrated H_2SO_4 and sugar.

Procedure:

1. Take small amount of sugar in a beaker.

2. Add a little concentrated sulfuric acid to the sugar.

3. Touch the outer surface of the beaker and record your observation.



Figure 4.7. Reaction between sulfuric acid and sugar

Observation and analysis

1. Does the beaker feel hot or cold when you touch it?
2. Did you see any steam in the beaker?
3. What is the color of the product formed?
4. Write a balanced chemical equation.
5. What can you conclude from the experiment? [Caution-When mixing concentrated acid and water, always add the acid to the water; never add water to concentrated acid.]

Experiment 4.4

Investigating the Heat Involved in a Process

Objective: To investigate the exothermic/endothermic nature of the process when ammonium nitrate is dissolved in water.

Apparatus: Beaker, thermometer, stirrer.

Chemicals: Ammonium nitrate and water.

Procedure:

1. Take 100 mL of water in a beaker and record its temperature.

2. Dissolve 15 g of solid ammonium nitrate (NH_4NO_3) in the 100 mL of water.

3. Touch the outer surface of the beaker and record the temperature of the solution with the help of a thermometer.

Observation and analysis:

1. Does the beaker feel hot or cold when you touch it?

2. Is the temperature increased or decreased after the addition of NH_4NO_3?

3. What do you conclude from this experiment?

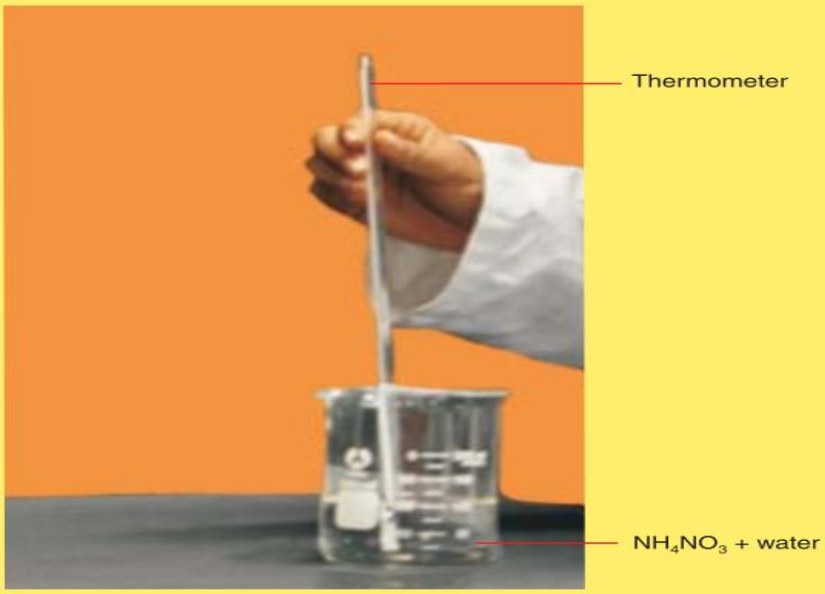


Figure 4.8. Dissolution of ammonium nitrate in water

EXERCISE 4.4

In each of the following cases, determine the sign of ΔH. State whether the reaction is exothermic or endothermic, and sketch an enthalpy diagram.

1. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + \text{heat}$
2. $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g),\ \Delta H = +241.7\ kJ$
3. $N_2(g) + 2H_2O(g) + \text{heat} \rightleftharpoons 2NO(g) + 2H_2(g)$
4. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$
5. $N_2O_4(g) + \text{heat} \rightleftharpoons 2NO_2(g)$
6. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) + 21\ kJ$

Energy produced by chemical reactions have many practical applications (*uses*). For example, energy lifts rockets and airplanes, runs cars, extracts metal from their ores. The energy from fuel combustion can convert water to steam. The steam can run a turbine and generates electricity.

Respiration releases the energy our cells need by oxidizing glucose. This energy helps to maintain our body temperature and body exercises.

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + \text{Energy}$$

4.5 TYPES OF REACTIONS

Competencies

***By the end of this section, you will be able to*:**

- list and define the four types of chemical reactions;
- give examples for each type of reaction; and
- conduct some experiments that demonstrate each type of reaction.

Thousands of known chemical reactions occur in living systems, in industrial processes and in chemical laboratories. Memorizing the equations for so many chemical reactions would be a difficult task. It is therefore more useful and realistic to classify reactions according to various similarities and regularities. This general information about reaction types can then be used to predict the products of specific reactions.

There are several ways to classify chemical reactions and none are entirely satisfactory. The classification scheme described in this section provides an introduction to five basic types of reactions: synthesis, decomposition, single displacement, double displacement, and combustion.

4.5.1 Combination Reaction (Synthesis or Composition)

A reaction in which two or more substances combine to form a single substance is called combination or synthesis. In such a reaction, two elements, two compounds, or an element and a compound may react to form a single compound. Combination reactions can be represented by the following general form of equation.



where the reactants A and B are elements or compounds, the product AB is a compound.

(i) Reaction of elements with oxygen

One simple type of synthesis reaction is the combination of an element with oxygen to produce *oxide* of the element. Almost all metals react with oxygen to form oxides. For example, when a thin strip of magnesium metal is placed in an open flame, it burns with bright white flame, leaving behind a white powder of magnesium oxide.

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

Nonmetals also undergo synthesis reaction with oxygen to form oxides. Sulfur, for example, reacts with oxygen to form sulfur dioxide while carbon forms carbon dioxide.

$$S_8\ (s) + 8\ O_2\ (g) \longrightarrow 8\ SO_2\ (g)$$

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g)$$

Hydrogen reacts with oxygen to form dihydrogen monoxide, better known as water.

$$2\ H_2\ (g) + O_2\ (g) \longrightarrow 2\ H_2O\ (g)$$

(ii) Reaction of metals with halogens

Most metals react with the Group 17 (VIIA) elements or halogens, to form either ionic or covalent compounds. For example, Group 1 (IA) metals react with halogens to form ionic compounds with the formula MX, where M is the metal and X is the halogen. Examples include the reactions of sodium with chlorine and potassium with iodine.

$$2\ Na\ (s) + Cl_2\ (g) \longrightarrow 2\ NaCl\ (s)$$

$$2\ K\ (s) + I_2\ (g) \longrightarrow 2\ KI\ (s)$$

Group 2 (IIA) metals react with the halogens to form ionic compounds with the formula MX_2.

$$Mg\ (s) + F_2\ (g) \longrightarrow MgF_2\ (s)$$

$$Sr\ (s) + Br_2\ (\ell) \longrightarrow SrBr_2\ (s)$$

The halogens undergo synthesis reaction with many different metals. Fluorine in particular is so reactive that it combines with almost all metals. For example, it reacts with cobalt to form cobalt (III) fluoride and with uranium to form uranium (VI) fluoride.

$$2\,Co\,(s) + 3\,F_2\,(g) \longrightarrow 2\,CoF_3\,(s)$$

$$U\,(s) + 3\,F_2\,(g) \longrightarrow UF_6\,(g)$$

(iii) Synthesis reaction with oxides (Reaction between compounds)

Oxides of active metals react with water to produce metal hydroxides. Examples include:

$$Na_2O\,(s) + H_2O\,(\ell) \longrightarrow 2\,NaOH\,(s)$$

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

Oxides of nonmetals react with water to produce oxy-acids. For example, sulfur dioxide, SO_2, with water produces sulfurous acid.

$$SO_2\,(g) + H_2O\,(\ell) \longrightarrow H_2SO_3\,(aq)$$

Certain metal oxides and nonmetal oxides combine with each other to synthesize salts. For example, calcium sulfite is formed by the reaction between calcium oxide and sulfur dioxide.

$$CaO\,(s) + SO_2\,(g) \longrightarrow CaSO_3\,(s)$$

Experiment 4.5

Investigating Combination (Synthesis) Reaction

Objective: To investigate the reaction between sulfur and iron.

Apparatus: Test tube, stand, burner, watch glass

Chemicals: Sulfur powder, iron filings

Procedure:

1. Mix about 3.0 g of iron filings and 2.0 g of powdered sulfur in a watch glass.
2. Transfer the mixture in a glass test tube.
3. Mount the test tube in a sloping position on a stand as shown in Figure 4.9
4. Heat the test tube until the mixture in the glass glows red hot.
5. Remove the test tube from the flame and observe the result.

Observation and analysis:

1. What were the colors of iron filings and sulfur before the reaction?
2. What was the color of the resulting compound after the reaction?
3. Write a balanced chemical equation for the reaction.

4. Identify the type of reaction.

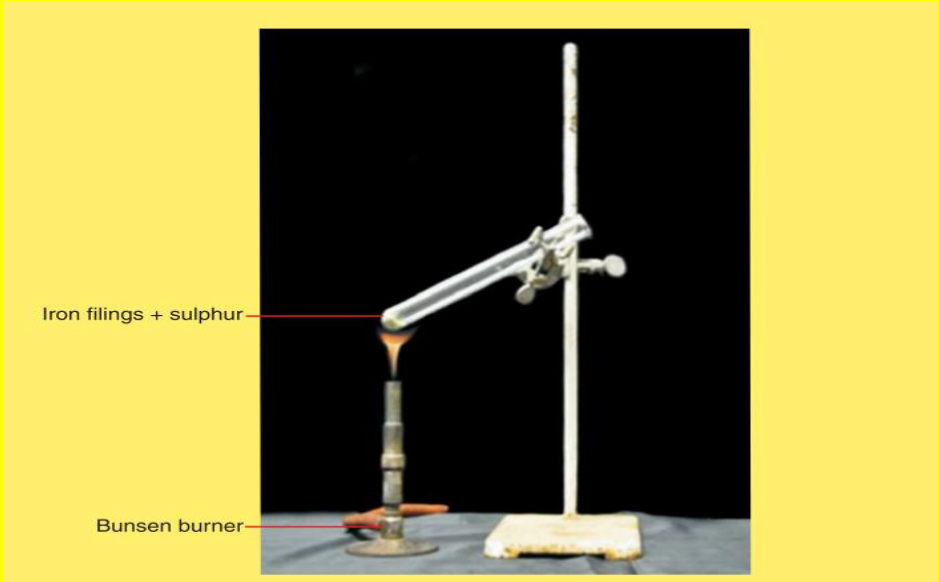


Figure 4.9. The Reaction between iron and sulfur

4.5.2 Decomposition Reaction

Decomposition is a reaction in which a compound breaks down into two or more simpler substances. Decomposition reactions are the opposite of synthesis reactions and are represented by the following general equation.



AB is a compound, A and B can be elements or simpler compounds. Most decomposition reactions take place only when energy in the form of electricity or heat is added. The heat supplied is usually indicated by a "*delta*" (Δ) symbol above the arrow. Here are some examples.

(i) Decomposition of binary compounds

The simplest kind of reaction in this class is the decomposition of a binary compound into its elements. One example is the decomposition of water into hydrogen and oxygen by passing an electric current through the liquid. The decomposition of a substance by an electric current is called ***electrolysis*.**

$$2\,H_2O\,(\ell) \xrightarrow{\text{electric current}} 2\,H_2\,(g) + O_2\,(g).$$

Oxides of the less active metals decompose into their elements when heated. Joseph Priestley, one of the founders of modern chemistry, discovered oxygen when he heated mercury (II) oxide, producing mercury and oxygen.

$$2\,HgO\,(s) + Heat \longrightarrow 2\,Hg\,(\ell) + O_2\,(g)$$

(ii) Decomposition of metal carbonates

All metal carbonates, except sodium and potassium, decompose when heated to form the metal oxide and carbon dioxide.

$$CaCO_3\,(s) + \text{Heat} \longrightarrow CaO\,(s) + CO_2\,(g)$$

$$CuCO_3\,(s) + \text{Heat} \longrightarrow CuO\,(s) + CO_2\,(g)$$

Sodium hydrogen carbonate decomposes into sodium carbonate, carbon dioxide and water.

$$2\ NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

(iii) Decomposition of metallic nitrates

a) Decomposition of Group IA metal nitrates produces nitrites and oxygen.

$$2\ NaNO_3\,(s) + \text{Heat} \longrightarrow 2\ NaNO_2\,(s) + O_2\,(g)$$

b) Decomposition of all nitrates, except Group IA metals, gives nitrogen dioxide, metal oxide and oxygen gas.

$$2\ Ca\,(NO_3)_2\,(s) + \text{Heat} \longrightarrow 2\ CaO\,(s) + 4\ NO_2\,(g) + O_2\,(g)$$

$$2\ Pb\,(NO_3)_2\,(s) + \text{Heat} \longrightarrow 2\ PbO\,(s) + 4\ NO_2\,(g) + O_2\,(g)$$

(iv) Decomposition of metal hydroxides

All metal hydroxides except those of Group IA, decompose when heated to yield metal oxides and water. For example, calcium hydroxide decomposes to calcium oxide and water.

$$Ca\,(OH)_2\,(s) + \text{Heat} \longrightarrow CaO\,(s) + H_2O\,(g)$$

(v) Decomposition of metal chlorates

When a metal chlorate is heated, it decomposes to a metal chloride and oxygen. For example, potassium chlorate, $KClO_3$, decomposes in the presence of a catalyst to potassium chloride and oxygen.

$$2\ KClO_3\,(s) + \text{Heat [+ Catalyst]} \longrightarrow 2\ KCl\,(s) + 3\ O_2\,(g)$$

(vi) Decomposition of acids

Certain acids decompose into nonmetal oxides and water. Carbonic acid is unstable and decomposes readily at room temperature to produce carbon dioxide and water.

$$H_2CO_3\,(aq) \longrightarrow CO_2\,(g) + H_2O\,(\ell)$$

When heated, sulfuric acid decomposes into sulfur trioxide and water.

$$H_2SO_4\,(aq) + \text{Heat} \longrightarrow SO_3\,(g) + H_2O\,(\ell)$$

Experiment 4.6

Investigating Decomposition Reactions

Objective: To investigate the decomposition of copper (II) carbonate.

Apparatus: Test tube, stand, burner, cork, delivery tube.

Chemicals: Copper (II) carbonate and lime water.

Procedure:

Put copper (II) carbonate powder in a glass test-tube. Mount the test tube in a sloping position on a stand as shown in Figure 4.10. Fit a cork and a delivery tube to the test tube. Put another test tube containing lime water at the end of the delivery tube. Heat the copper (II) carbonate with a burner.

Observation and analysis:

1. What was the color of copper (II) carbonate before heating?
2. What was the color during heating and after cooling?
3. What change did you observe in the lime water?
4. Write a balanced chemical equation for the reaction.

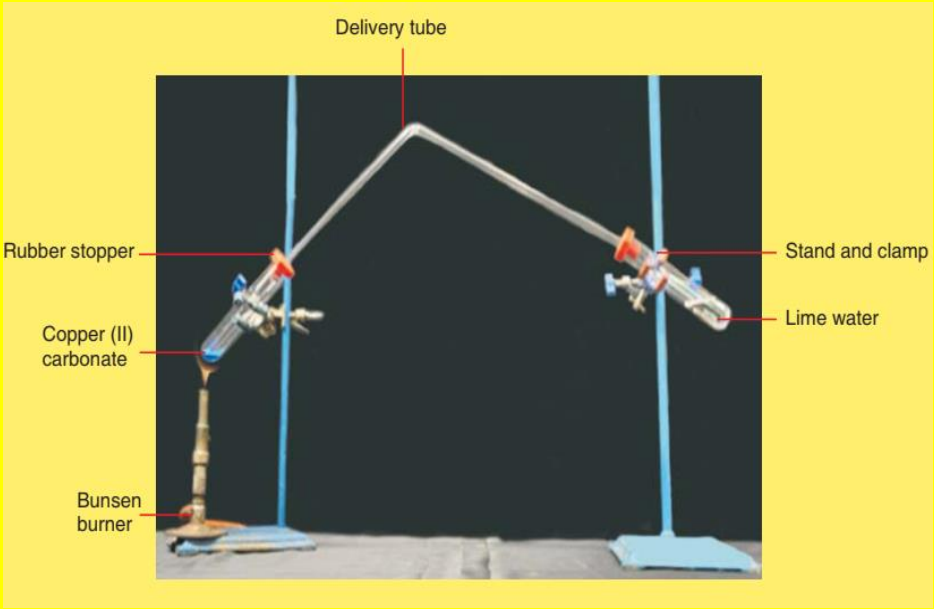


Figure 4.10. Decomposition of copper (II) carbonate

4.5.3 Single Displacement Reaction

A reaction in which one element displaces another element from its compound is known as single displacement or replacement reaction. Many single displacement reactions take place in aqueous solution. The amount of energy involved in this type of reaction is usually smaller than the

amount involved in synthesis or decomposition reactions. Such a reaction is represented by the following two general forms.

If A is a metal, it will displace B to form AC, provided A is a more active than B.



If A is a nonmetal, it will displace C to form BA, provided A is a more active nonmetal than C.



In general, a more reactive element displaces the less reactive element from its compound. Examples of single displacement reactions are given below.

(i) Displacement of a metal from its compound by another metal

$2\ Al\ (s) + 3Pb\ (NO_3)_2\ (aq) \longrightarrow 3\ Pb\ (s) + 2\ Al\ (NO_3)_3\ (aq)$

$Zn\ (s) + CuSO_4\ (aq) \rightarrow Cu\ (s) + ZnSO_4\ (aq)$

The above two reactions are possible because aluminum is more reactive than lead and zinc is more reactive than copper.

(ii) Displacement of hydrogen from water and acids by active metals

$2\ Na\ (s) + 2\ H_2O\ (\ell) \longrightarrow 2\ NaOH\ (aq) + H_2\ (g)$

$3\ Fe\ (s) + 4\ H_2O\ (\boldsymbol{g}) \longrightarrow Fe_3O_4\ (s) + 4\ H_2\ (g)$

$Mg\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$

(iii) Displacement of halogens

Another displacement reaction is when a halogen replaces another halogen from its compound. Fluorine is the most active halogen and hence can replace any of the other halogens from their compounds. Each halogen is less active than the one above it in the Periodic Table. Therefore, a halogen can replace any of its group members below it. Here are some examples.

$Cl_2(g) + 2\ KBr\ (aq) \longrightarrow 2\ KCl\ (aq) + Br_2\ (\ell)$

$F_2\ (g) + 2\ NaCl\ (aq) \longrightarrow 2\ NaF\ (aq) + Cl_2\ (g)$

$Br_2\ (\ell) + KCl\ (aq) \longrightarrow$ **no reaction**

Experiment 4.7

Investigating Single Displacement Reaction

Objective: To investigate the displacement reaction between iron and copper (II) sulfate.

Apparatus: Iron rod and beaker.

Chemicals: Copper (II) sulfate (blue) solution

Procedure:

1. Clean a piece of iron rod or iron knife with emery paper to remove any rust.

2. Take copper sulfate solution in a beaker.

3. Dip the iron rod into the copper (II) sulfate solution as shown in **Figure 4.11** and wait for a few minutes. What did you observe on the iron rod?

4. Allow the reactants to stand for one day and observe any change on the iron rod.

Observation and analysis:

1. What did you observe on the iron rod after one day?

2. Write a balanced chemical equation for the reaction.

3. Write the conclusion for the experiment.

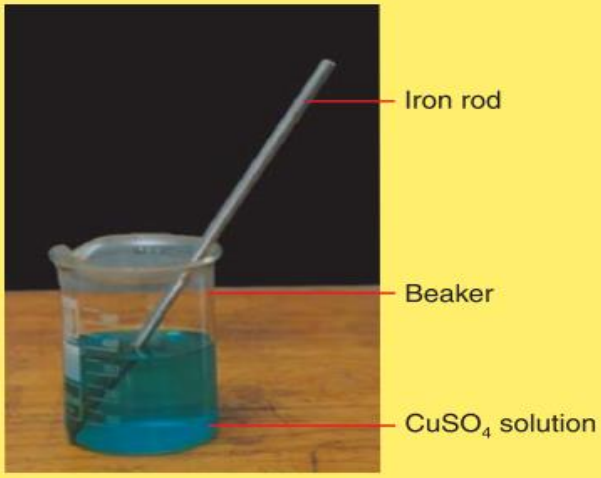


Figure 4.11 Reaction between iron and copper (II) sulfate solution

4.5.4. Double Displacement Reactions

Double displacement is a reaction in which two compounds in solution react with each other to form two new compounds by exchange of the positive and negative ions of each reactant. It is also known as double replacement reaction or metathesis. One of the products is usually a *precipitate*, an *insoluble gas* that bubbles out of the solution, or a *molecular compound*, usually

water. The other product is often soluble and remains in the solution.

This type of reaction can be depicted by the following general equation followed by examples.



(i) Formation of a precipitate

This occurs when the cation of one reactant combines with the anion of another reactant to form an insoluble or slightly soluble product. The symbol (↓) denotes a precipitate or a solid product. For example, when aqueous solutions of potassium iodide and lead (II) nitrate are mixed, a yellow precipitate of lead (II) iodide is formed.

$$2\ KI\ (aq) + Pb\ (NO_3)_2\ (aq) \longrightarrow PbI_2\ (\downarrow) + 2\ KNO_3\ (aq)$$

Similarly, solutions of barium nitrate and sodium sulfate produce a precipitate of barium sulfate and a solution of sodium nitrate.

$$Ba\ (NO_3)_2\ (aq) + Na_2SO_4\ (aq) \rightarrow BaSO_4\ (\downarrow) + 2\ NaNO_3\ (aq)$$

The potassium, sodium and nitrate ions do not take part in each reaction. They remain in solution as aqueous ions and therefore are often referred to as *spectator ions*.

(ii) Formation of a gas

In some double displacement reactions, one of the products is an *insoluble gas* that bubbles out of the mixture. Examples:

$$FeS\ (s) + 2\ HCl\ (aq) \longrightarrow FeCl_2\ (aq) + H_2S\ (\mathbf{g})$$

$$Na_2CO_3\ (aq) + 2\ HCl\ (aq) \rightarrow 2\ NaCl\ (aq) + H_2O\ (\boldsymbol{\ell}) + CO_2\ (\mathbf{g})$$

(iii) Formation of a molecular product

Some double displacement reactions produce very stable molecular compounds, such as water and ammonia. For example, the neutralization reaction between aqueous solutions of hydrochloric acid and sodium hydroxide produces a solution of sodium chloride and water.

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

Experiment 4.8

Investigating Double Displacement Reactions

Objective: To observe the displacement reaction between Na_2SO_4 and $Ba\ (NO_3)_2$.

Apparatus: Beaker, stirrer, filter paper, filter funnel.

Chemicals: Na_2SO_4 and $Ba\ (NO_3)_2$.

Procedure:

1. Take solution of $Ba(NO_3)_2$ into a beaker and add dropwise Na_2SO_4 solution. Then stir it continuously.

2. Filter the precipitate using a filter paper and funnel. Collect the filtrate or the solution in a clean beaker.

Observation and analysis:

3. Write the names of the compounds that are formed as a precipitate and as solution at the end of the reaction.

4. What was the color of the precipitate?

5. Write the balanced chemical equation for the reaction.



Figure 4.12. Double displacement reaction between Na_2SO_4 and $Ba(NO_3)_2$

4.5.5. Combustion Reaction

In a combustion reaction, a substance burns with oxygen releasing a large amount of energy in the form of light and heat. The burning of natural gas, propane, gasoline, and wood are examples of combustion reaction. For example, the combustion of propane, C_3H_8 produces carbon dioxide and water vapor, with the evolution of energy.

$$C_3H_8\,(g) \;+\; 5\,O_2\,(g) \;\longrightarrow\; 3\,CO_2\,(g) \;+\; 4\,H_2O\,(g) \;+\; \text{Heat}$$

Respiration is a combustion reaction between glucose and oxygen.

EXERCISE 4.5

1. Chemical reactions in aqueous solution occur if one or more of the following is / are observed, which are called *driving forces* of the reaction.

(i) formation of a solid product or a precipitate,

(ii) a gas bubbles out of the solution; and / or

(iii) a molecular substance is observed as a product.

Predict and write the driving force (if present) for each of the following reactions in solution.

a. $BaCl_2$ (aq) + K_2SO_4 (aq) → $BaSO_4$ + 2 KCl (aq)

b. Na_2CO_3 (aq) + 2 HCl (aq) → 2 NaCl (aq) + CO_2 + H_2O

c. Acid + Base → Salt + Water

d. $CaCl_2$ (aq) + 2 $NaNO_3$ (aq) → Ca $(NO_3)_2$ (aq) + 2 NaCl (aq)

2. Write a balanced equation for those you agree there is a chemical reaction. Give your reason why you disagree with the others.

a. Magnesium metal is added to an aqueous solution of copper sulfate

b. Bromine is added to a solution that contains sodium iodide

c. Magnesium nitrate is heated in a closed vessel

d. Lead carbonate is heated to high temperature

e. Chlorine gas is bubbled through an aqueous solution of sodium fluoride

f. Sulfurous acid is heated to appropriate temperature

g. Aqueous solutions of sodium chloride and potassium nitrate are mixed

4.6 STOICHIOMETRY

Competencies

***By the end of this section, you will be able to*:**

- describe mole ratios from balanced chemical equations;
- solve mass – mass problems based on given chemical equations;
- define molar volume and state Avogadro's principle;
- solve volume – volume and mass – volume problems based on given chemical equations;
- define and determine limiting and excess reactants; and
- define and calculate theoretical, actual and percentage yields.

Stoichiometry is the quantitative relationship between reactants and products in a balanced chemical equation. In other words, stoichiometry is the study of amount or ratio of moles, mass, energy and volumes (for gases) of reactants and products. Stoichiometric calculations are based on the following two major principles.

i. The composition of any substance in the chemical equation should be expressed by a definite formula.

ii. The law of conservation of mass must be obeyed

4.6.1 Molar Ratios in Balanced Chemical Equation

From a balanced chemical equation, it is possible to determine the:

- number of moles of each reactant and product; and
- relative mass of each of the reactants and products

For example, in the reaction between hydrogen and oxygen to produce water, 2 mol of H_2 combines with 1 mol of O_2 to yield 2 mol of H_2O.

	$2H_2(g)$	+	$O_2(g)$	→	$2H_2O(l)$
Mole →	2 mole		1 mole		2 mole
Molecule →	2 molecule		1 molecule		2 molecule

The equation also tells us that 4.0 g of hydrogen reacts with exactly 32.0 g of oxygen to produce 36.0 g of water.

Calculations based on chemical equations (*stoichiometric problems*) are classified into mass – mass, volume – volume and mass – volume problems.

4.6.2 Mass–Mass Relationships

In mass – mass problems, there are two methods for solving such types of problems:

(i) Mass – ratio method

(ii) Mole – ratio method

(i) The mass – ratio method

In this type of stoichiometric calculation, the mass of one substance is determined from a given mass of the other substance using the following steps.

Step 1: Write the balanced chemical equation.

Step 2: Place the given mass above the corresponding formula, and *x* above the formula of the substance whose mass is to be determined.

Step 3: Write the total mass of the substances below the formula of each substance.

(*Total mass is the molar mass of the substance multiplied by its coefficient*).

Step 4: Set up the proportion.

Step 5: Solve for the unknown mass, *x*.

Example 5

1. How many grams of oxygen are produced by the decomposition of 145.0 g of potassium chlorate?

Solution:

Step 1: $2KClO_3 \rightarrow 2KCl + 3O_2$

Step 2: $\overset{145\,g}{2\,KClO_3} \rightarrow 2KCl + 3\overset{x}{O_2}$

Step 3: $\underset{(2\times122.5)\,g}{\overset{145\,g}{2\,KClO_3}} \rightarrow 2KCl + \underset{(3\times32)\,g}{\overset{x}{3\,O_2}}$

Step 4: $\frac{145\,g}{245\,g} = \frac{x}{96\,g}$

Step 5: $x = 56.8\ g$

2. How many grams of calcium chloride are formed when 15.0 g of calcium metal reacts with hydrochloric acid?

Solution:

Step 1: $Ca + 2HCl \rightarrow CaCl_2 + H_2$

Step 2: $\overset{15\,g}{Ca} + 2HCl \rightarrow \overset{x}{CaCl_2} + H_2$

Step 3: $\underset{40\,g}{\overset{15\,g}{Ca}} + 2HCl \rightarrow \underset{111g}{\overset{x}{CaCl_2}} + H_2$

Step 4: $\frac{15\,g}{40\,g} = \frac{x}{111\,g}$

Step 5: $x = 41.63\ g$

Therefore, 41.63 g of $CaCl_2$ is produced.

(ii) The mole – ratio method

This is the ratio between the number of moles of any two substances in a given reaction. In this method, the given mass is converted into moles, and the number of moles for the required substance is calculated. If needed, the moles can be converted back to the respective masses. Follow the steps applied for mass – mass ratio to solve mole – ratio problems.

Step 1: Write the balanced chemical equation.

Step 2: Convert the given mass to mole and write the obtained mole and the required quantity, *x*, above the formulas of the respective substances.

Step 3: Place the coefficients as number of moles under the formula of each substance involved.

Step 4: Set up the proportion.

Step 5: Solve for the unknown value, *x*; and convert the mole obtained into mass.

Example 6

1. How many grams of sodium metal are needed to react with 10.0 g of water?

Solutions

Step 1: $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

Step 2: *moles of* H_2O = given mass / molar mass = 10.0 g / (18 g/mol) = 0.56 mol

Step 3: $\overset{x}{2\ Na} + \overset{0.56mol}{2H_2O} \rightarrow 2\ NaOH + H_2$

Step 4: $\frac{x}{2\ mol} + \frac{0.56mol}{2\ mol} \rightarrow 2\ NaOH + H_2$

Step 5: x = 0.56 mol of Na

Now, convert 0.56 mol of Na to grams

Mass of Na = mole × atomic mass = 0.56 mol × 23 g/mol = 12.88 g

Therefore, 12.88 g of sodium metal is needed to react with 10 g of water.

2. What mass of nitrogen dioxide is produced by the decomposition of 182.0 g of magnesium nitrate?

Solution:

Step 1: $2\ Mg(NO_3)_2 \rightarrow 2MgO + 4\ NO_2 + O_2$

Step 2: moles of $Mg(NO_3)_2$ = 182 g / (148 g/mol) = 1.23 mol

$$\overset{1.23mol}{2Mg(NO_3)_2} \rightarrow 2MgO + \overset{X}{4NO_2} + O_2$$

Step 3: $\underset{2\ mol}{\overset{1.23\ mol}{2Mg(NO_3)_2}} \rightarrow 2MgO + \underset{4\ mol}{\overset{X}{4NO_2}} + O_2$

Step 4: $\frac{1.23\ mol}{2\ mol} = \frac{X\ mol}{4\ mol}$

Step 5: x = 2.46 mol of NO_2; mass of NO_2 produced = 2.46 mol × 46 g/mol = 113.2 g

EXERCISE 4.6

1. How many grams of NaOH are needed to neutralize 50.0 g of H_2SO_4?

2. How many grams of $CaCO_3$ are needed to react with 15.2 g of HCl according to the following equation? (unbalanced)

$$CaCO_3 + HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

3. Calculate the mass of $CaCl_2$ formed when 5.0 mol of chlorine gas reacts with calcium metal.

4. How many moles of H_2O are required to produce 4.5 mol of HNO_3 according to the following reaction? (unbalanced)

$$NO_2 + H_2O \rightarrow HNO_3 + NO$$

5. In the decomposition of $KClO_3$, how many moles of KCl are formed in the reaction that produces 0.05 mol of O_2?

6. How many moles of CaO are needed to react with excess water to produce 370.0 g of calcium hydroxide?

4.6.3 Volume -Volume Relationships

In reactions involving gases, the volume of gases can be determined on the principle that 1.0 mol of any gas occupies a volume of 22.4 L at STP (*standard temperature* and *pressure* = 0°C and *1.0 atm*). It is also known that 22.4 L at STP of any gas weighs exactly its molecular mass. This volume, 22.4 L, of a gas is known as molar volume.

The relationship between the volume of a gas and its number of molecules was explained by Avogadro, hence forth known as Avogadro's law. It is stated as "*equal volumes of different gases under the same temperature and pressure contain equal number of molecules*." This equally means the volume of a gas is proportional to its number of molecules at STP.

Mathematically: **$V \alpha n$;** where V is the volume and n is the number of mole.

In volume – volume problems, based on the given volume of one substance, the volume of the other is found mathematically. The steps to solve volume-volume problems are shown by the following examples.

Example 7

What volume of oxygen will react with carbon monoxide to produce 20.0 L of carbon di oxide, all gases measured at STP?

Solution:

Step 1: Write the balanced chemical equation

$$2CO\ (g) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$$

Step 2: Place the given volume and the required volume, *x*, above the corresponding formulas.

$$\overset{}{2CO} + \overset{x}{O_2} \rightarrow \overset{20\ L}{2CO_2}$$

Step 3: Write the total molar volume (22.4 L multiplied by any coefficient) below the formulas

$$\overset{}{2CO} + \overset{x}{O_2} \rightarrow \overset{20\ L}{2CO_2}$$
$$\underset{}{} \quad \underset{22.4L}{} \quad \underset{2(22.4)L}{}$$

Step 4: Set up the proportion.

$$\frac{x}{22.4L} = \frac{20L}{2(22.4)L}$$

Step 5: Solve for the unknown volume, *x*.

x = 10 L of O_2 are needed.

EXERCISE 4.7

1. What volume of nitrogen reacts with 33.6 L of oxygen to produce nitrogen dioxide?

2. How much sulfur trioxide in liters is formed if 560.0 cc of sulfur dioxide is burned in O_2?

3. How many liters of ammonia are required to react with 145.60 L of oxygen according to the following reaction? (unbalanced)

$$NH_3\ (g) + O_2\ (g) \rightarrow NO\ (g) + H_2O$$

4. Find the volume & mass of O_2 produced by the decomposition of 5 mol of $KClO_3$ at STP?

5. How many moles and grams of water vapor are formed when 56.0 L of butane gas, C_4H_{10}, burns completely in oxygen at STP?

4.6.4 Mass – Volume Relationships

In mass – volume problems, either the mass of one substance is given and the volume of the other is calculated or the volume of one substance is given and the mass of the other one is evaluated. The steps to solve such type of problems are the same as the previous steps except putting the masses on one side and the volumes on the other side of the equality sign.

Example 8

1. How many grams of calcium carbonate should decompose to produce 11.2 L of carbon dioxide at STP?

Solution:

Step 1: $CaCO_3 \rightarrow CaO + CO_2$

Step 2: $\overset{x}{CaCO_3} \rightarrow CaO + \overset{11.2\,L}{CO_2}$

Step 3: $\underset{100\,g}{\overset{x}{CaCO_3}} \rightarrow CaO + \underset{22.4\,L}{\overset{11.2\,L}{CO_2}}$

Step 4: $\frac{x}{100\,g} = \frac{11.2\,L}{22.4\,L}$

Step 5: $x = 50$ g of $CaCO_3$ is decomposed.

2. How many liters of oxygen at STP react with 72 g of aluminum to produce aluminum oxide?

Solution:

Step 1: $4Al + 3O_2 \rightarrow 2Al_2O_3$

Step 2: $\overset{72\,g}{4Al} + \overset{x}{3O_2} \rightarrow 2Al_2O_3$

Step 3: $\underset{(4\times27)\,g}{\overset{72\,g}{4Al}} + \underset{(3\times22.4)\,L}{\overset{x}{3O_2}} \rightarrow 2Al_2O_3$

Step 4: $\frac{72\,g}{108\,g} = \frac{x}{67.2\,L}$

Step 5: $x = 44.8$ L of O_2

Hence, 44.8 litres of oxygen is required at STP to react with 72 g of aluminium

EXERCISE 4.8

1. How many liters of oxygen are required to react with 23.0 g of methane according to the following equation? (Unbalanced)

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

2. Calculate the mass of calcium carbide that is needed to produce 112.0 cm^3 of acetylene, measured at STP, according to the following equation.

$$CaC_2 + 2\,H_2O \rightarrow C_2H_2\,(g) + Ca\,(OH)_2$$

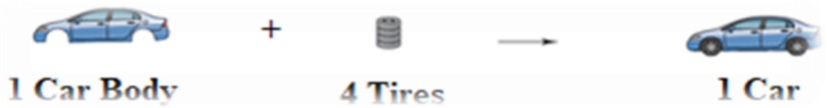
3. How many milliliters of sulfur dioxide are formed when 12.0 g of iron sulfide ore (pyrite) reacts with oxygen according to the following equation at STP? (Unbalanced)

$$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2\ (g)$$

4.6.5 Limiting and Excess Reactants

Reactants are often added to a reaction vessel in amounts different from the molar proportions given by the chemical equation. In such cases, only one of the reactants may be completely consumed at the end of the reaction, whereas some amount of other reactant will remain unreacted. The ***limiting reactant*** (or ***limiting reagent***) is the reactant that is entirely consumed when a reaction goes to completion. A reactant that in part remains unreacted is often referred to as the **excess reactant**. Once one of the reactants is used up, the reaction stops. This means that *the amount a product is always determined by the limiting reactant.*

To clarify the idea of a limiting reactant, let's consider a situation from real life. A car assembly factory has 1500 car – bodies and 4000 tires. How many cars can be made with the supplies on hand? Does the plant manager need to order more car – bodies or more tires? Obviously, 4 tires are required for each car – body, so the "balanced equation" is



How much "product" (cars) can be made from the amount of each "reactant"?

$$\frac{1500\ car\ bodies\ x\ 1\ car}{1\ car\ body} = 1500\ cars$$

$$\frac{4000\ tires\ x\ 1\ car}{4\ tires} = 1000\ cars$$

The number of tires limits the number of cars because less "product" (fewer cars) can be produced from the available tires. There will be 1500 - 1000 = 500 car – bodies in excess, and they cannot be turned into cars until more tires are delivered.

As another example, let us consider the following reaction:

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

Assume you mixed 1.0 mol H_2 with 3.0 mol Cl_2. There is insufficient H_2 to react with all of the Cl_2 because 3.0 mol Cl_2 requires 3.0 mol H_2 for complete reaction. Therefore, Cl_2 is the **excess** reactant while H_2 is deficient. The available H_2 determines the amount of product from the reaction. Thus, H_2 is the **limiting reactant** and the amount of HCl produced will be only 2.0 mol, leaving an excess of 2.0 mol Cl_2 unreacted.

Example 9

How much ammonia is produced if 10 g of hydrogen reacts with 18 g of nitrogen?

Solution :

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

First determine the number of moles;

$$\text{Moles of } H_2 = \frac{10\text{ g}}{2\text{ g/mol}} = 5\text{ mol}$$

$$\text{Moles of } N_2 = \frac{18\text{ g}}{28\text{ g/mol}} = 0.64\text{ mol}$$

Now, calculate the number of moles or masses of the product that would be formed by each reactant.

The reactant that gives the smallest amount of product is the limiting reactant.

i. **Using the quantity of H_2**

$$\overset{5\text{ mol}}{3H_2} + N_2 \rightarrow \overset{x}{2NH_3}$$
$$\overset{3\text{ mol}}{\quad} \qquad \overset{2\text{ mol}}{\quad}$$

$$\frac{5\text{ mol}}{3\text{ mol}} = \frac{x}{2\text{ mol}}$$

$x = 3.33$ mol NH_3

$$\text{Mass of } NH_3 = 3.33\text{ mol} \times 17\text{ g/mol}$$
$$= 56.6\text{ g}$$

ii. **Using the quantity of N_2**

$$3H_2 + \overset{0.64\text{ mol}}{N_2} \rightarrow \overset{x}{2NH_3}$$
$$\qquad \overset{1\text{ mol}}{\quad} \qquad \overset{2\text{ mol}}{\quad}$$

$$\frac{0.64\text{ mol}}{1\text{ mol}} = \frac{x}{2\text{ mol}}$$

$x = 1.28$ mol NH_3

$$\text{Mass of } NH_3 = 1.28\text{ mol} \times 17\text{ g/mol}$$
$$= 21.8\text{ g}$$

Therefore, the limiting reactant is nitrogen, because it gives less amount of NH_3, *i.e.*, 21.8 g NH_3. In the reaction, 0.64 mole (18 g) of N_2 is consumed. Hydrogen is in excess. The amount of hydrogen consumed will be:

$$\overset{x}{3H_2} + \overset{18\text{g}}{N_2} \rightarrow 2NH_3$$
$$\overset{6\text{g}}{\quad} \qquad \overset{28\text{ g}}{\quad}$$

or

$$\overset{x}{3H_2} + \overset{0.64\text{ mol}}{N_2} \rightarrow 2NH_3$$
$$\overset{3\text{ moles}}{\quad} \qquad \overset{1\text{ mole}}{\quad}$$

$$\frac{x}{6} = \frac{18}{28}$$

$x = 3.86$ g of H_2

$$\frac{x}{3\text{ mol}} = \frac{0.64\text{ mol}}{1\text{ mol}}$$

$x = 1.92$ mol of H_2

Therefore, 3.86 g or 1.92 moles of H_2 is used in the reaction, and 6.14 g or 3.08 moles of H_2 is left unreacted.

EXERCISE 4.9

1. If 6.5 g zinc reacts with 5.0 g HCl according to the following equation, (unbalanced)

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

(a) Which substance is the limiting reactant?

(b) What mass of a reactant is in excess?

(c) How many grams of hydrogen would be produced?

2. What mass of Na_2SO_4 is produced if 49.0 g of H_2SO_4 reacted with 80.0 g of NaOH?

3. If 20.0 g of $CaCO_3$ and 25.0 g of HCl were mixed, what mass of CO_2 is produced?

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

4. If 3.0 mol of calcium were mixed with 3.0 mol of oxygen to produce calcium oxide, then

(a) Which substance is the limiting reactant?

(b) How many moles of calcium oxide will be obtained?

5. Consider the following reaction:

$$2Al + 3H_2SO_4\,(aq) \rightarrow Al_2(SO_4)_3 + 3H_2\,(g)$$

How many grams of hydrogen gas will be produced if 0.8 mol of aluminum is allowed to react with 1.0 mol of sulfuric acid?

4.6.6 Theoretical, Actual and Percentage Yields

Practically, 100 % yield is rare in a chemical reaction. The theoretical yield of a chemical reaction is the calculated amount of the product that can be obtained from a given amount of reactant, according to the balanced chemical equation. The quantity calculated represents the maximum yield (100 %) of the product.

The measured (experimentally obtained) amount of product in any chemical reaction is known as the actual yield. This is usually less than the theoretical yield (*calculated amount*). The percentage yield is the ratio of the actual yield to the theoretical yield multiplied by 100.

$$\text{Percentage yield} = \frac{\text{Acutal yield}}{\text{Theoretical yield}} \times 100$$

Example 10

25.0 g of methane gas (CH_4) burns in oxygen to produce carbon dioxide and water. If 60.3 g of carbon dioxide were obtained from the reaction, what is the percent yield of the reaction? How much water will be obtained at the same time?

Solution :

The actual yield is 60.3 g of CO_2.

Determine the theoretical yield using mass-mass relationship

$$\underset{16\,g}{\overset{25\,g}{CH_4}} + 2O_2 \rightarrow \underset{44\,g}{\overset{x}{CO_2}} + 2H_2O$$

$$\frac{25\,g}{16\,g} = \frac{x}{44}$$

x = 68.75 g of CO_2 (*theoretical yield*)

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

$$= \frac{60.3\,g}{68.75\,g} \times 100\% = 87.7\ \%$$

Amount of water obtained will be: $\frac{25\,g}{16\,g} = \frac{Y}{36\,g}$; therefore, y = 56.25 g.

EXERCISE 4.10

1. When 20.0 g of sulfur dioxide gas burns in sufficient oxygen, it produced 15.0 g of sulfur tri oxide gas at STP.

(a) What is the percentage yield?

(b) What mass and volume of oxygen were consumed by the reaction?

(c) What volume of sulfur trioxide were obtained?

2. When 16.0 g SO_2 were allowed to burn with 7.0 g O_2, it produced 12.0 g sulfur trioxide.

(a) In addition to the product, what and how much substance is found in the reaction vessel?

(b) What is the percentage yield of the reaction?

3. The burning of octane (C_8H_{18}) in oxygen produces carbon dioxide and water as the only products. When 28.5 g of octane burned in sufficient oxygen, it gave 82.5 % yield by mass of each product. What is the actual yield of each of carbon dioxide and water?

4. (***Challenge)*** A sample of a certain compound contains 2.80 g X, 5.20 g Y and 7.60 g Z. What mass of this compound would be formed theoretically from the following combinations?

(a) 1.0 g each of X, Y and Z

(b) 1.0 g of X, 2.0 g of Y and 3.0 g of Z

5. Butane gas (C_4H_{10}) burns in oxygen to produce carbon dioxide and water. If 10.0 L of butane was allowed to burn completely in sufficient oxygen at 110 ^{0}C:

(a) What volume (in L) of oxygen were consumed by the reaction?

(b) What are the volumes of carbon dioxide and water vapor produced by the reaction?

4.7 OXIDATION AND REDUCTION REACTIONS

Competencies

***By the end of this section, you will be able to*:**

- define the terms oxidation and reduction in terms of electron transfer;
- assign oxidation number (oxidation state);
- analyze a given redox reaction by specifying the substance reduced and the substance oxidized, and also the oxidizing and reducing agents; and
- Distinguish between redox and non – redox reactions.

We are familiar with chemical processes like rusting, burning, respiration, photosynthesis and so on. All these processes involve oxidation – reduction (redox) reactions.

4.7.1 Oxidation – Reduction

Oxidation is a process in which a substance loses electrons in a chemical reaction. Consider the following synthesis reaction.

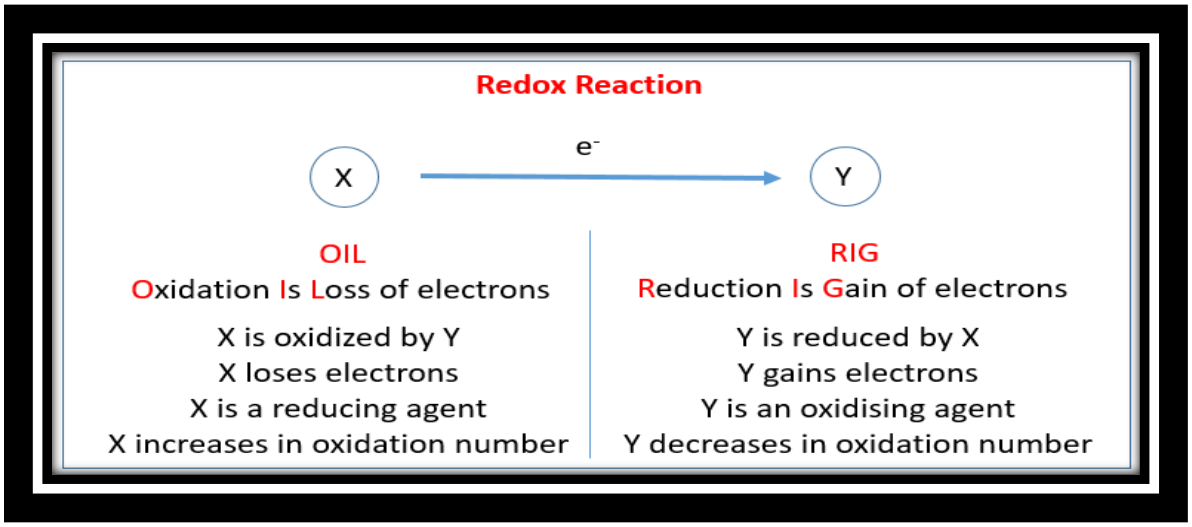
$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

Each sodium atom lost one electron and has turned to a sodium ion. Hence, sodium is oxidized.

$$Na \rightarrow Na^+ + e^-$$

Reduction is a process in which a substance gains electron in a chemical reaction. In the above reaction, each chlorine atom gained an electron and has changed to chloride ion. Thus, chlorine is reduced. $Cl_2 + 2e^- \rightarrow 2\ Cl^-$

The processes of oxidation and reduction always occur simultaneously because if one substance loses electrons, the other substance must accept these electrons. Since the process of oxidation and reduction involve transfer of electrons, it also results in changes of oxidation number. Thus, oxidation and reduction reactions can also be defined in terms of oxidation number. Oxidation involves ***increase*** in oxidation number while reduction involves ***decrease*** in oxidation number of a substance.



4.7.2 Oxidation Number or Oxidation State

Oxidation number or oxidation state is the number of electrons that an atom appears to have gained or lost when it is combined with other atoms.

Rules for assigning oxidation number

Rule 1: The oxidation number of all elements in free state is zero. This rule also applies for diatomic or polyatomic elements.

Example: The oxidation number of Na = 0, Cl in Cl_2 = 0, O in O_3 = 0, S in S_8 = 0.

Rule 2: The oxidation number of a mono atomic ion is equal to the charge on the ion.

Example: $Na^+ = +1$, $Mg^{2+} = +2$, $S^{2-} = -2$, $Al^{+3} = +3$, etc.

Rule 3: The oxidation number of oxygen in a compound is – 2 except in the following cases.

The oxidation number of oxygen in:

Peroxides is –1. Example: Na_2O_2 Superoxide is –1/2. Example: KO_2

Oxygen difluoride (OF_2) is +2.

Rule 4: The oxidation number of hydrogen in its entire compounds is +1 except in metal hydrides, (like NaH, CaH_2 and AlH_3), where its oxidation number is –1.

Rule 5: The sum of the oxidation number of all the atoms in a neutral compound is zero.

Example: $\overset{+1\ +6\ -2}{H_2SO_4}$ $((+2) + (+6) + (-8) = 0)$

Rule 6: In a polyatomic ion, the sum of the oxidation numbers of the constituent atoms equals the charge on the ion.

Example: $(\overset{+6\ -2}{SO_4})^{-2}$ $((+6) + (-8) = -2)$

Rule 7: Elements of Group IA have +1 and Group IIA have +2 oxidation states in all their compounds.

Rule 8: In a compound, the more electronegative element is assigned a negative oxidation number and the less electronegative element is assigned a positive oxidation number, example:

$\overset{+2}{N}\quad\overset{-2}{O}$ (Oxygen is more electronegative than nitrogen).

Example 11

1. Determine the oxidation number of phosphorus in $Ca(H_2PO_4)_2$

Solution:

The oxidation number of Ca is +2 (Rule 7).

Let, the oxidation number of P be *x*.

$$\overset{+2}{Ca}\quad\overset{(+1}{H_2}\quad\overset{X-2)}{PO_4}$$

$$+2 + (4 \times (1)) + (2 \times x) + (8 \times (-2)) = 0$$

$$2 + 4 + 2x - 16 = 0$$

$$2x - 10 = 0 \text{ or } x = +5$$

Hence, the oxidation number of P in $Ca(H_2PO_4)_2$ is + 5

2. What is the oxidation number of chromium in $Na_2Cr_2O_7$?

Solution:

The oxidation number of O is –2 (Rule 3)

The oxidation number of Na is +1 (Rule 7)

Let the oxidation number of Cr be *x*.

$$\begin{matrix} +1 & X & -2 \\ Na & Cr & O \end{matrix}$$

Since the sum of the oxidation numbers of Na, Cr and O in $Na_2Cr_2O_7$ is 0 (Rule 5), it follows that:

$$\begin{matrix} +1 & X & -2 \\ 2\,Na & 2\,Cr & 7\,O \end{matrix}$$

$$(1 \times 2) + (x \times 2) + (-2 \times 7) = 0$$

$$2 + 2x - 14 = 0$$

$$x = +6$$

Therefore, the oxidation number of Cr in $Na_2Cr_2O_7$ is +6.

EXERCISE 4.11

1. Determine the oxidation number of the specified element in each case.

a. S in S^{-2}

b. N in NH_4^+

c. Fe in $K_4[Fe(CN)_6]$

d Cl in ClO_3^-

e. P in PO_4^{-3}

f. S in $S_2O_8^{-2}$

2. Determine whether each process is oxidation or reduction. (unbalanced)

a. $Cu^{2+} \rightarrow Cu$

b. $O \rightarrow O^{2-}$

c. $Fe^{2+} \rightarrow Fe^{3+}$

d. $SO_4^{2-} \rightarrow S_2O_8^{2-}$

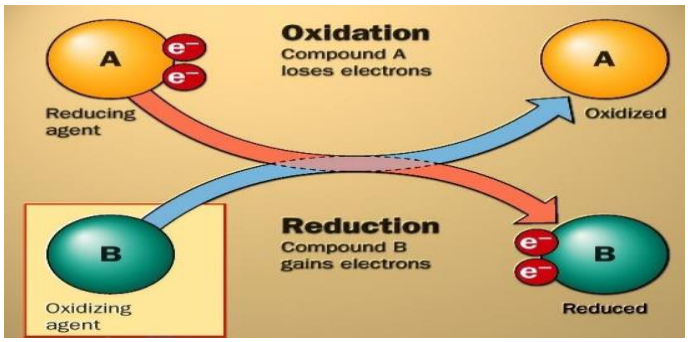
e. $NO \rightarrow NO_2$

f. $C_2O_4^{2-} \rightarrow CO_2$

4.7.3. Oxidizing and Reducing Agents

A substance that causes another substance to be oxidized, while itself undergoing reduction, is known as an oxidizing agent or oxidant. The substance that causes the other substance to get reduced while itself being oxidized, is referred to as a reducing agent or reductant.

Oxidizing agents are reduced (*gain electrons*) and there is a decrease in oxidation number in the process. Reducing agents are oxidized (*lose electrons*), hence there is an increase in oxidation number.



Certain oxidizing agents show visible color changes during the reaction. For example, permanganate ion, (MnO_4^{--}) changes from purple to colorless as it is reduced in acidic medium.

MnO_4^- (purple) → Mn^{2+} (colorless)

Similarly, when a substance is oxidized by dichromate ion in acidic medium, the dichromate ion turns from orange to green. $Cr_2O_7^{2-}$ (orange) → Cr^{3+} (green)

Such color changes are useful in checking the oxidation of a substance during the reaction. Other common oxidizing agents include chlorine, potassium chromate, sodium chlorate and manganese (IV) oxide.

Similarly, certain reducing agents undergo visible color change during oxidation. For example, a moist starch solution changes potassium iodide paper to blue – black to show that iodine is formed: Starch + $2\ I^- \rightarrow I_2$ (blue – black). Since the iodide is oxidized to iodine, it is the reducing agent. Bubbling hydrogen sulfide through a solution of an oxidizing agent forms a yellow precipitate (sulfur): S^{2-} + oxidizing agent → S (yellow). H_2S acts as a reducing agent. Other common reducing agents include carbon, carbon monoxide, sodium thiosulphate, sodium sulfite and iron (II) salts.

The oxidizing/ reducing ability of substances depends on many factors. Some of these are:

Electronegativity: Elements with high electronegativity value such as F_2, O_2 and Cl_2 are good oxidizing agents. Elements with higher electro positivity, for example, metallic elements like Na, K, Mg and Al are good reducing agents.

Oxidation states: Some elements exhibit more than one oxidation states. In a compound or ion, if one element is in its higher oxidation state, then the compound or the ion is an oxidizing agent. Similarly, if an element of a compound or ion is in its lower oxidation state, then the compound or ion is a reducing agent. Here are some examples.

$\overset{+7}{K}\overset{+7}{Mn}O_4, \overset{+7}{Na}\overset{+7}{Cl}O_4, K_2\overset{+6}{Cr}_2O_7$ ... are oxidizing agents

$\overset{+2}{Fe}S, \overset{+2}{C}O, Na_2\overset{+4}{S}O_3$ ... are reducing agents

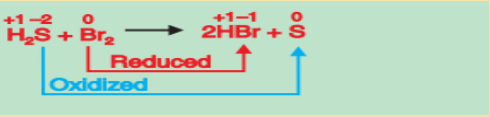
Example 12

Identify the oxidizing and reducing agents, the substance oxidized and reduced in the following reaction.

$$H_2S + Br_2 \rightarrow 2\,HBr + S$$

Solution:

Let us assign oxidation numbers to all the elements of the reactants and products.



In the reaction, the S ion in H_2S increases its oxidation number from –2 to 0. Hence, S is oxidized and H_2S is the reducing agent. The oxidation number of Br decreases from 0 to –1. Thus, Br_2 is reduced and is the oxidizing agent.

So far, we discussed about oxidation and reduction (Redox) reactions. However, there are also non-redox reactions, in which no electron is exchanged between the reacting substances. As a result, the oxidation numbers of the atoms do not change during the reaction. Usually, such types of reactions involve the exchange of positive and negative ions. Most of the double displacement reactions, like acid base neutralization reactions are non – redox. Example:

$$\overset{+2\ -1}{BaCl_2} + \overset{+1\ +6\ -2}{Na_2SO_4} \rightarrow \overset{+2\ +6\ -2}{BaSO_4}\downarrow + \overset{+1\ -1}{2NaCl}$$

$$\overset{+1\ -1}{HCl} + \overset{+1\ -2\ +1}{NaOH} \rightarrow \overset{+1\ -1}{NaCl} + \overset{+1\ -2}{H_2O}$$

EXERCISE 4.12

1. Consider drying a wet dish using a towel.

A. Which substance acts as a drying agent?

B. What name can be given to the dish (dried substance)?

C. Which substance gets wet during the process?

2. Label each reaction as oxidation, reduction or non – redox.

a $Cl_2 \rightarrow Cl^-$ b $MnO_4^- \rightarrow MnO_2$

c $CrO_2 \rightarrow CrO_4^{2-}$ d $SO_4^{2-} \rightarrow SO_3^{2-}$

e $Cr_2O_7^{2-} \rightarrow CrO_4^{2-}$

f. $H_2CO_3 \rightarrow H_2O + CO_2$

3. In each of the following equations, identify the substances oxidized and reduced, the oxidizing and reducing agents (unbalanced). Also balance each equation.

a. $Fe_2O_3 + CO \rightarrow Fe + CO_2$

b. $CuO + H_2 \rightarrow Cu + H_2O$

c. $NO_2 + H_2O \rightarrow HNO_3 + NO$

d. $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

4.8. RATES OF CHEMICAL REACTIONS & CHEMICAL EQUILIBRIUM

Competencies

By the end of this section, you will be able to:

- define and explain what is meant by reaction rate and describe it using a graph;
- carry out an experiment to illustrate the relative rate of reactions;
- assess how collision, activation energy and proper orientation of reactants play a role in chemical reactions;
- explain and perform activities on the effects of changes in temperature, concentration or pressure, catalyst and surface area on the rates of a chemical reaction;
- define and compare & contrast reversible and irreversible reactions;
- define and describe the characteristics of chemical equilibrium;
- state Le Châtelier's principle and use it to explain the effect of changes in temperature, pressure and concentration of reactants at equilibrium.

4.8.1 Reaction Rate

Some chemical reactions proceed quickly, whereas others require days, months or even years to give products. For example, rusting of iron, fermentation, oxidation – reduction, etc. are slow reactions. On the other hand, combustion of fuel, reaction of active metals with acids, firing of a gun, explosion, neutralization between acid and base, etc. are fast reactions. These differences depend primarily on the differences in the chemical nature of the reacting substances.

Experiment 4.9

Measuring Rate of a Reaction

Objective: To measure the rate of the reaction between HCl and $CaCO_3$.

Apparatus: Balance, conical flask, cotton wool, stop watch.

Chemicals: HCl, $CaCO_3$

Procedure:

1. Pour 50 mL of dilute hydrochloric acid into a conical flask.

2. Place the conical flask on a laboratory balance.

3. Add 25.0 g of calcium carbonate (*marble chips*) into the flask. Plug the cotton wool immediately as shown in Figure 4.13. This will help to prevent escape of the acid spray.

4. Read and record the mass of the flask and its content at one-minute intervals until the reaction is over. (*Use a stop watch*).

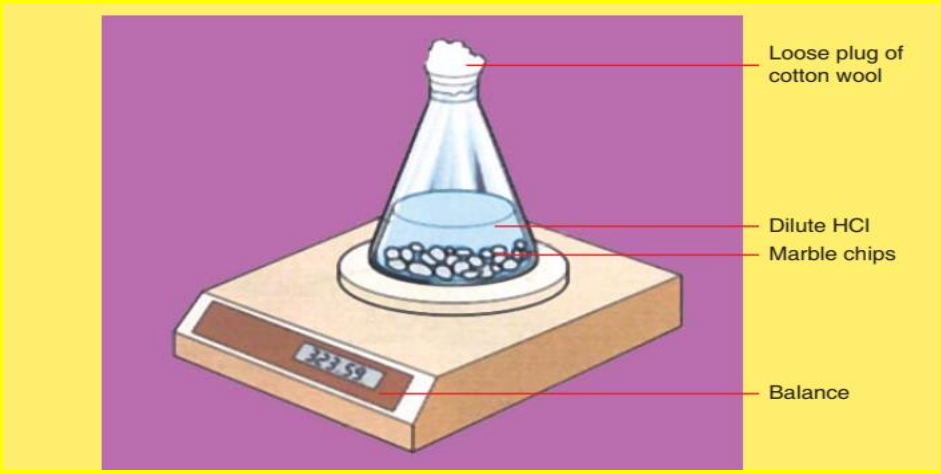


Figure 4. 13. Measuring the rate of reaction between HCl and $CaCO_3$

Observation and analysis:

1. What happens to the mass during the reaction?

2. Write the balanced chemical equation.

Use the following table to record your results.

Time (min)	0	1	2	3	4	5	6	7
Mass (g)								
Change in mass (g)								

3. Plot a graph between time (*x*-axis) and change in mass (*y*-axis) and draw a smooth curve through maximum points.

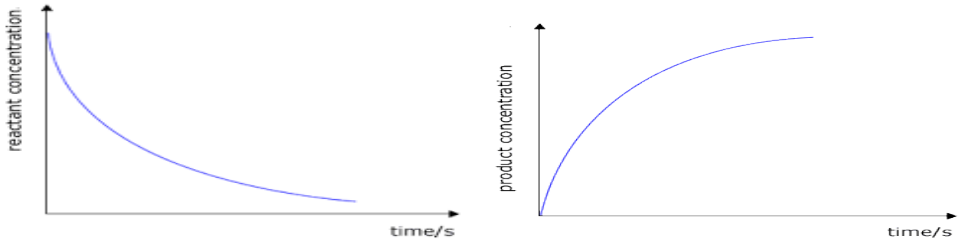
4. Why is the graph steep at the beginning but horizontal at the end of the reaction?

5. At what time does the reaction stop?

The rate (speed) of a chemical reaction measures the decrease in concentration of a reactant or the increase in concentration of a product per unit time. This means that the rate of a reaction determines how fast the concentration of a reactant or product changes with time. It is obtained by measuring the concentration of reactants or products during the reaction time. Methods for determining the concentration of reactants or products depend on the type of the reaction. Some of the methods are:

a. Color (*change in color*);
b. Pressure (*increase or decrease in pressure, particularly in gases*);
c. Volume (*increase or decrease in size, particularly in gases*);
d. Mass (*gain or loss in weight*); and
e. Amount of precipitate formed

During the course of a reaction, the concentration of reactants decreases while that of products increases with time. The following sketch depicts rate expressions in terms of the disappearance of reactants and the appearance of products.



Thus, the rate of a reaction is calculated by dividing the change in concentration of reactant or product by the time taken for the change to occur.

$$\textbf{Rate of reaction} = \frac{\text{Change in concentration of a substance}}{\text{Change in time}} = \frac{\Delta C}{\Delta t}$$

From this expression, it follows that the rate of a reaction is inversely proportional to the time taken by the reaction.

$$\textbf{Rate } \alpha \frac{1}{\textbf{Time}}$$

For the simple reaction, X → Y, the rate of reaction is expressed in terms of a reactant concentration as

$$r = -\frac{\Delta [X]}{\Delta t} = \frac{[X]_f - [X]_i}{\Delta t}$$

where r is the rate of the reaction and X is the reactant. $[X]_i$ and $[X]_f$ are initial and final concentrations, respectively. $\Delta [X]$ denotes change in concentration of X and Δt is the change in time. The negative sign indicates the decrease in concentration of the reactant. Note that concentration is usually expressed in mole per liter. In terms of product concentration, the rate of a reaction is given by:

$$\mathbf{r} = \frac{\Delta [\mathbf{Y}]}{\Delta \mathbf{t}} = \frac{[\mathbf{Y}]_f - [\mathbf{Y}]_i}{\Delta \mathbf{t}}$$

where [Y] is the concentration of the product in moles per liter, mol / L. For a given product, the final concentration $[Y]_f$ is greater than the initial concentration, $[Y]_i$. Thus, the difference, $\Delta Y = [Y]_f - [Y]_i$ is positive and the rate of a reaction is also positive. Figure 4.14 below illustrates the change of the rate of a chemical reaction with time. A reaction becomes slower after a certain time because the concentration of reactants decreases with time. The rate curve turns less and less steep until it becomes a horizontal line. No more reactant is used up at this point. Note that the rate of a reaction is the slope of the tangent to the curve at any particular time.

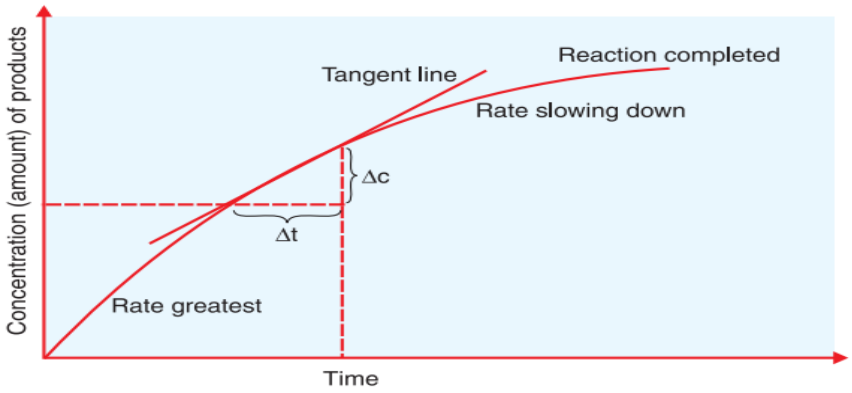


Figure 4.14 The change in concentration of product with time

(A) Pre-conditions for a Chemical Reaction

Chemical reactions are usually explained by the collision theory. The assumptions of this theory are that:

(i) The particles of the reacting substances must collide.

(ii) The reactants must have energy greater than or equal to activation energy, and

(iii) The particles must have proper orientation.

(i) Collisions between reactants

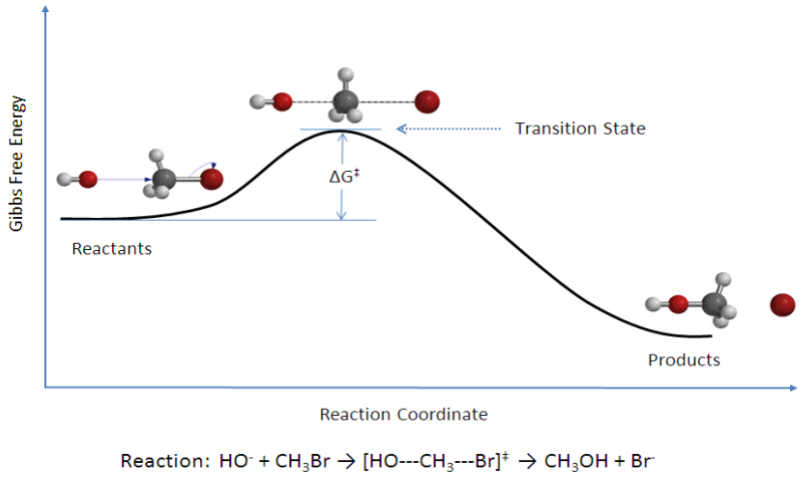
The first pre condition for a reaction is the direct contact of the reacting substances with each other. However, all collisions between molecules may not effective in bringing a reaction.



a Linear b Bent

(ii) Activation energy

If collisions between the reactant molecules do not have sufficient energy, then no reaction will take place. Therefore, a reaction collision must have sufficient energy to break the bonds in the reactants. The minimum amount of energy needed for a reaction is known as activation energy. In the following diagram, activation energy is denoted by $\Delta G^{\#}$.



(iii) Proper orientation

Collision of molecules with sufficient activation energy will not bring a reaction if the reacting molecules are poorly oriented. Thus, the collision between molecules should have the proper orientation.

Note: *Linear collision is more effective than non- linear collision*

Consider the reaction between H_2 and Cl_2 molecules: $H_2 + Cl_2 \rightarrow 2\ HCl$

For the reaction to occur, first H_2 and Cl_2 molecules must collide with each other. In addition, for the collision to be effective, the colliding molecules must have sufficient energy to break the H – H and Cl – Cl bonds.

Unless, the molecules are oriented in proper positions, there is no product formation. Therefore, as shown in Figure 15 below, the H_2 and Cl_2 molecules rearrange themselves so as to form a new

H – Cl molecule.

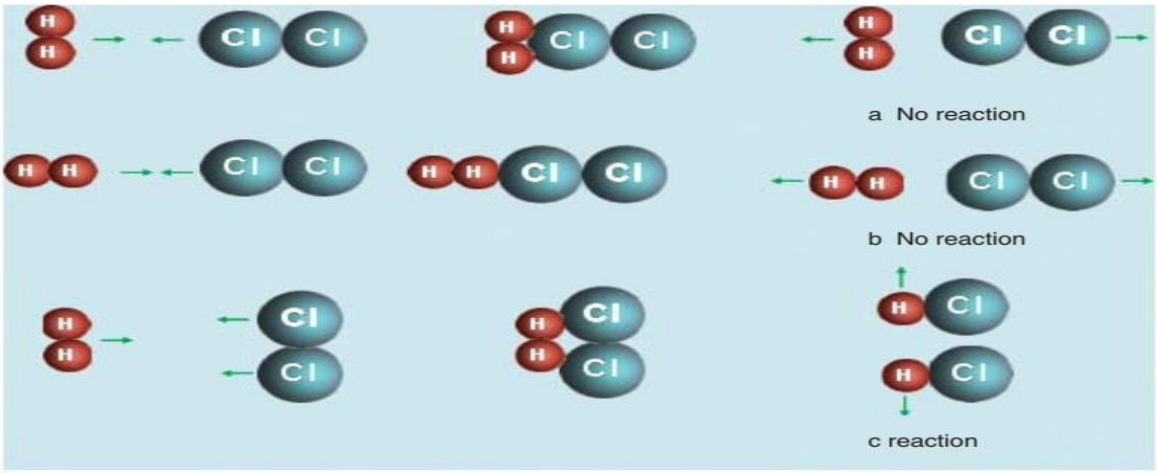


Figure 4.15 Molecular collisions and chemical reactions

(B) Factors Affecting the Rate of a Chemical Reaction

The rate of a chemical reaction depends on nature of the reactants, temperature, concentration, surface area and catalyst.

(i) Nature of the reactants

The rate of a reaction is influenced by the type and nature of the reacting substances. For example, the following reactions have different rates due to the nature of the metals (reactants).

$Mg + 2\,HCl \rightarrow MgCl_2 + H_2$ (fast reaction)

$Fe + 2\,HCl \rightarrow FeCl_2 + H_2$ (slow reaction)

$2\,K + 2\,H_2O \rightarrow 2\,KOH + H_2$ (very fast, catches fire)

$Cu + HCl \text{ or } H_2O \rightarrow$ No reaction

(ii) Temperature

An increase in temperature increases the rate of a reaction. This is because as the temperature increases, the average kinetic energy of the particles increases which in turn increases the number of effective collisions. For many chemical reactions, the rate of a reaction generally doubles for every 10°C rise in temperature.

(iii) Concentration of reactants

The number of collisions is proportional to the concentration of the reactants. Increasing the concentration allows more contacts between the reacting particles, which results in increasing the rate of reaction. In case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect if the reactants are either solids or liquids.

For example, if you heat a piece of steel wool in air (21% oxygen by volume) it burns slowly, but in pure oxygen (100% oxygen by volume) it bursts into a dazzling white flame. This indicates that the rate of burning increases as the concentration of oxygen becomes higher.

Experiment 4.10

Investigating the effect of concentration on reaction rate

Objective: To determine the rate of the reaction between magnesium with each of 0.1 M and 5.0 M sulfuric acid solutions

Apparatus: Beakers and tongs

Chemicals: H_2SO_4 and magnesium ribbon

Procedure:

1. Pour 20 mL of 0.1 M H_2SO_4 into the first beaker.

2. Holding with a tong, deep 1.0 cm long magnesium ribbon into the beaker.

3. Note how fast the reaction proceeds

4. Now, pour 20 mL of 5.0 M H_2SO_4 into the second beaker.

5. Hold 1.0 cm long magnesium with a tong and deep it to the second beaker.

6. Observe how fast the reaction proceeds.

Observation and Analysis:

(i) In which of the two beakers does a gas bubble faster?

(ii) Write a balanced chemical equation for the reaction.

(iii) What do you conclude from this experiment?

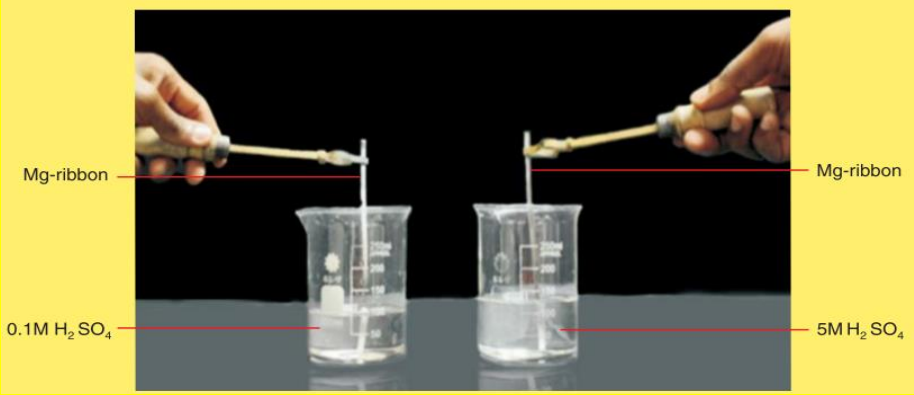


Figure 4.16 The effect of concentration on rate of a reaction

(iv) Surface area of reactants

When the reactants are in different phases, be it solid, liquid or gas, then the surface area of the substances affects the rate of the reaction. The higher the surface area, the faster is the rate of the reaction. This is because the increase in contact results in more collision between each small particle of reactants. Wood shavings burn faster than solid wood, for example, because they have greater surface area in contact with the oxygen with which they are combining.

Experiment 4.11

Investigating the Effect of Surface Area on Reaction Rate

Objective: To determine the rate of reaction of a lump and powdered calcium carbonate with hydrochloric acid.

Apparatus: Beakers, mortar and pestle (grinder).

Chemicals: Calcium carbonate and dilute hydrochloric acid.

Procedure:

(a) 1. Take 5.0 g of calcium carbonate and put it in the first beaker.

2. Add 100 mL of dilute hydrochloric acid into the beaker carefully.

3. Observe how fast the reaction proceeds.

(b) 1. Put 5.0 g of calcium carbonate into a mortar and grind it with the pestle until it becomes powder.

2. Transfer this powdered calcium carbonate into the second beaker.

3. Add 100 mL of dilute hydrochloric acid carefully.

4. Observe how fast the reaction proceeds.

Observation and Analysis:

(i) Which of the reactions is faster; (*a*) or (*b*)?

(ii) What do you conclude from the experiment?

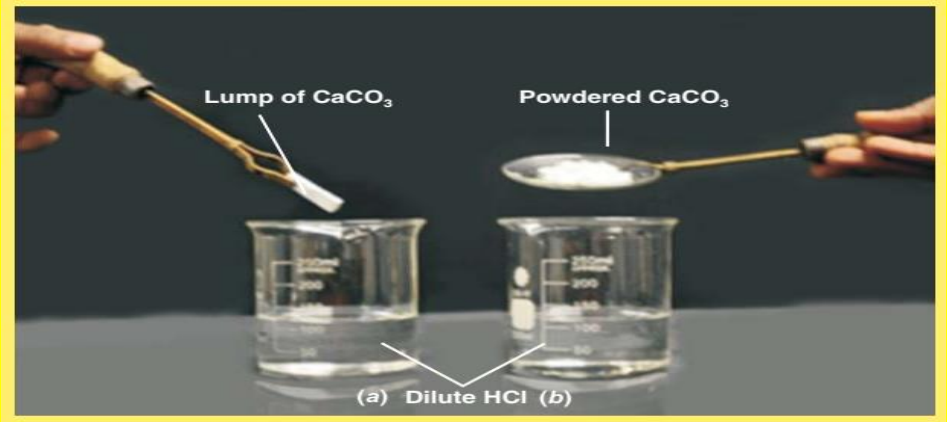


Figure 4.17 Effect of surface area on the rate of a reaction

(v) Catalysts

Catalysis is the backbone of many industrial processes, which use chemical reactions to turn raw materials into useful products. Lower activation energy (Ea) for a reaction corresponds to a higher reaction rate. Fig 4.18 below illustrates how the presence of a catalyst affects activation energy and rate of a reaction. Chemical catalysts can be either positive or negative. A positive catalyst increases the rate of a reaction by providing a path that lowers activation energy, *Ea*, while a negative catalyst (or inhibitor) slows the rate of a reaction by providing a path with higher activation energy.

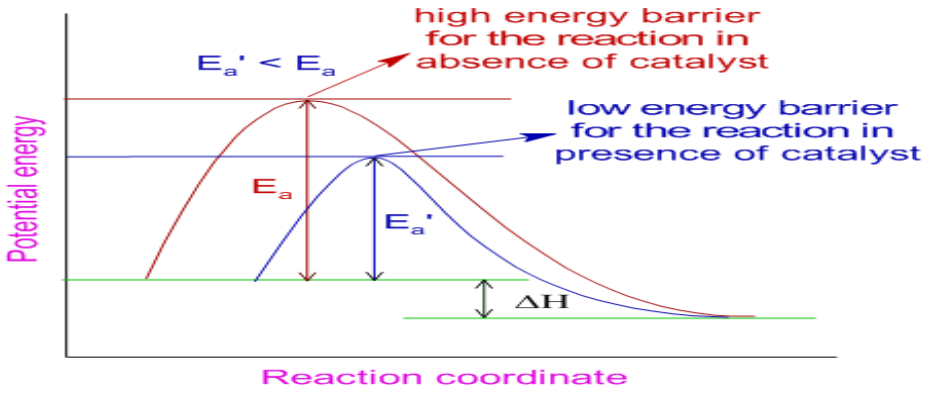


Figure 4. 18 Energy diagram to illustrates effect of a catalyst

Experiment 4.12

Investigating the effect of a catalyst on the rate of a chemical reaction

Objective: To determine the effect of MnO_2 (catalyst) on the rate of decomposition of H_2O_2

Apparatus: Two test tubes, test-tube rack

Chemicals: MnO_2, H_2O_2

Procedure:

1. Pour 5.0 mL of hydrogen peroxide in each of the two test tubes

2. Add a small amount of MnO_2 to one of the test tubes only. Observe if there is any change in each test tube.

3. Introduce a glowing splint to each test tube and check for the evolution of a gas.

Observation and Analysis:

1. In which of the test tubes does the reaction occur at a faster rate? Why?

2. What gas is evolved from the test tube (s)?

3. Make and write your conclusion about the result of the experiment.

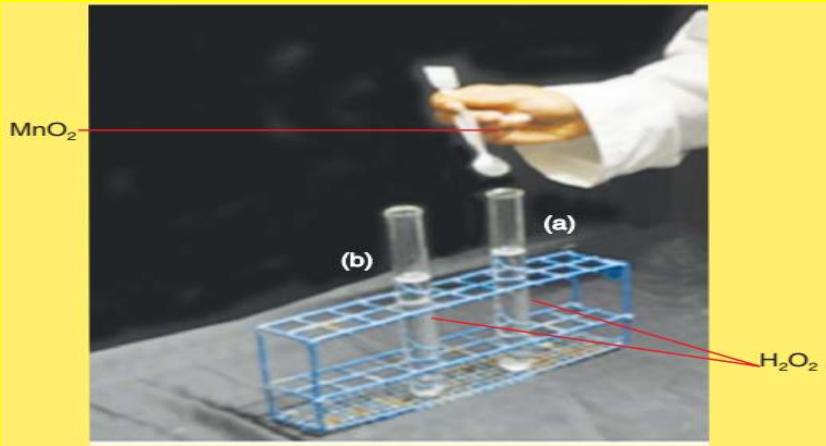


Figure 4.19 Effect of a catalyst on the decomposition of H_2O_2

4.8.2 Chemical Equilibrium

(i) Irreversible and Reversible Reactions

Many chemical reactions convert practically all or at least the limiting reactant (s) to products in a given set of conditions. Under this condition, the reactant(s) *go to completion*. Such types of reactions are known as ***irreversible***. These reactions proceed only in the forward direction and are expressed by a single arrow (→).

In other reactions, as the products are formed, they in turn react or decompose to form the original reactants. In this situation, two opposing reactions occurring at the same time. Even though they are accompanied by the formation of products, the reactants are not completely converted to products. These types of reactions are called ***reversible***. Such reactions take place in both the forward and backward directions under the same condition. A double arrow (⇆) pointing in opposite directions is used for such reaction equations.

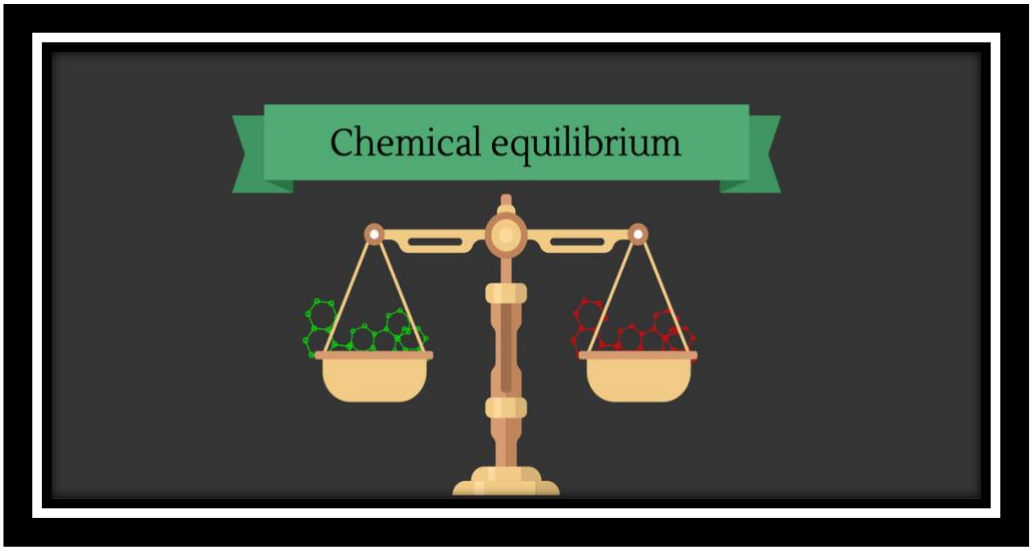
A state in which two exactly opposite reactions occur at the same rate is called ***chemical equilibrium***. For example, nitrogen and hydrogen gases react with each other at 500 ^{0}C and high pressure to form ammonia. Under the same conditions, ammonia decomposes back to hydrogen and nitrogen:

$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$

$$2\ NH_3 \rightarrow 3\ H_2 + N_2$$

To save effort, we often write these two exactly opposite equations as one, with double arrows:

$$3\ H_2 + N_2 \leftrightarrows 2\ NH_3$$



Does a reaction stop when it attains equilibrium?

Chemical equilibrium is the state of a chemical system in which the rates of the forward and reverse reactions are equal. At this state, there is no net change in the concentrations of reactants and products because the system is in dynamic equilibrium. Dynamic equilibrium means the reaction does not stop but both the forward and the backward reactions continue at equal rates.

Characteristics of chemical equilibrium

✓ Equilibrium is achieved only in a closed system. Such a system prevents exchange of matter with the surroundings, so that both reactants and products react and recombine with each other until equilibrium is established.

✓ The rate of the forward reaction is equal to the rate of the backward reaction.

✓ Equilibrium is a dynamic state, meaning the forward and backward reactions still occur.

✓ The concentrations of reactants and products remain constant at equilibrium. They are being produced and decomposed at an equal rate.

✓ At equilibrium there's no change in macroscopic properties.

✓ Equilibrium can be reached from either direction.

At equilibrium, Rate of forward reaction = Rate of reverse reaction

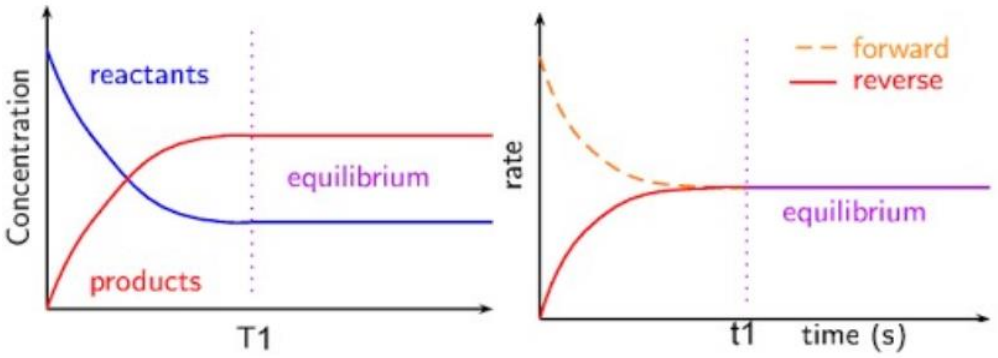


Figure 4.20 Concentration – change and rate of forward and reverse reactions

The law of chemical equilibrium can be expressed mathematically using the concentrations of reactants and products at equilibrium. The concentration of any species is denoted by enclosing the formula in square bracket, [ ]. Thus, for the reversible reaction:

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

Rate of forward reaction = $K_f\ [A]^a\ [B]^b$,

Rate of reverse reaction = $Kr\ [C]^c\ [D]^d$, where K_f and K_r are rate constants for the forward and reverse reactions, respectively.

Since the rates of the forward and reverse reactions become equal at equilibrium, it follows that:

$$K_f\ [A]^a\ [B]^b = Kr\ [C]^c\ [D]^d, \text{ or}$$

$$\frac{K_f}{K_r} = \frac{[C]^c\ [[D]^d}{[A]^a\ [[B]^b}$$

K_f / K_r gives a new constant, termed equilibrium constant, Keq.

$$K\ eq = \frac{K_f}{K_r} = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

Note: *Omit concentration terms for solids and liquids from K eq expressions; include only terms of gases (g) and aqueous solutions (aq).*

Note:

1. *Equilibrium constant expression* is a mathematical equation. Its values are numbers, involving the concentrations of the chemicals and their coefficients.

2. Each concentration is raised to the power given by the coefficient in the chemical equation.

3. The concentrations of the products are written in the numerator of the equilibrium constant expression; the concentrations of the reactants are written in the denominator.

4. The numerator or denominator terms are multiplied together, not added.

5. Each equilibrium constant expression is associated with a particular chemical reaction written in a given direction.

6. Each reaction at equilibrium has its own equilibrium constant at a fixed temperature.

Example 13

1. Write the equilibrium constant expression for each of the following equations.

a. $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$

b. $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$.

c. $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

d. $PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^{--}\,(aq)$

Solution

(a) $K\,eq = \frac{[HI]^2}{[H_2]\ [[I_2]}$

(b) $K\,eq = [CO_2]$

(c) $K\,eq = \frac{[NH_3]^2}{[H_2]^3\ [N_2]}$

(d) $K\,eq = [Pb^{2+}]\,[Cl^-]^2$

2. The following equilibrium has been studied at 230°C.

$$2\,NO\,(g) + O_2\,(g) \leftrightarrows 2\,NO_2\,(g)$$

In one experiment, the concentrations of the substances at equilibrium were found to be: [NO] = 0.50 M, $[O_2]$ = 0.25 M and $[NO_2]$ = 0.15 M. Calculate the equilibrium constant for the reaction at the same temperature.

Solution :

The equilibrium constant is given by: $K = \frac{[NO_2]^2}{[NO]^2\ [O_2]}$

$$K = \frac{(0.15M)^2}{[0.50M]^2\ [0.25M]} = \mathbf{0.36}\ M^{-1}$$

EXERCISE 4.13

1. To speed up the fermentation of alcohol, yeast was added to the reaction mixture. However, additional yeast was required to facilitate the fermentation. What is the rate factor here: catalyst, concentration, nature of reactants or temperature? Explain your answer.

2. Phosphorus burns faster in oxygen than in air. Specify and explain the rate factor.

3. In the reversible reaction equation: A (aq) + B (aq) ⇆ 2 C (aq), the concentrations of A and B at equilibrium were 0.10 M and 0.20 M, respectively. If K eq = 8.0, what is [C]?

4. A 0.70 M N_2O_4 solution decomposed to NO_2 according to the following equation.

$$N_2O_4\,(aq) \leftrightarrows 2\,NO_2\,(aq)$$

If one started with 0.70 M of the reactant and 0.50 M of this reactant remained at equilibrium, what is the concentration of NO_2 at equilibrium and what is the value of K eq?

5. Write the equilibrium constant expression for each of the following reactions.

(a) $CO\,(g) + H_2O\,(g) \leftrightarrows CO_2\,(g) + H_2\,(g)$

(b) $FeO\,(s) + CO\,(g) \leftrightarrows Fe\,(s) + CO_2\,(g)$

(ii) Factors that Affect Chemical Equilibrium

A system remains at a state of chemical equilibrium if there is no change in the external conditions that disturb the equilibrium. But the state of an equilibrium could be affected by external factors like temperature, pressure, concentration and so on. How a system at equilibrium adjusts itself to any of these changes was explained by the French chemist Henri Le Chatelier. It states that "*if a stress is applied to a system at equilibrium, the system will respond in such a way to counteract the stress*." The stress could be change in temperature, concentration or pressure.

(a) Effect of Temperature

Reversible reactions are exothermic in one direction and endothermic in the other. The effect of temperature on equilibrium depends on whether the reaction is exothermic or endothermic. An increase in temperature of a system favors the endothermic path while a decrease in temperature favors the exothermic path.

For example, consider the following equilibrium condition.

$$H_2O\,(g) + CO\,(g) \leftrightarrows H_2\,(g) + CO_2\,(g);\ \Delta H = -41\ kJ$$

Since the reaction is exothermic, an increase in temperature shifts the equilibrium to the reactant side. On the other hand, decrease in temperature shifts the equilibrium to the product side giving more yield. This means, the product of an exothermic reaction at equilibrium can be increased by lowering the working temperature or by cooling the system.

(b) Effect of Pressure or Volume

Pressure affects reactions which involve gaseous reactants and products. The effect of pressure on liquids and solids is negligible. An increase in pressure (or decrease in volume) on a gaseous system shifts the equilibrium in the direction that has ***fewer*** moles of gases. On the contrary, decreasing the pressure at equilibrium shifts the system to the side that has greater number of moles of gases. For example, in the reaction,

$$2\,CO\,(g) \quad + \quad O_2\,(g) \quad \leftrightarrows \quad 2\,CO_2\,(g)$$

3.0 mol 2.0 mol

Increasing the pressure of the above system shifts the equilibrium to the forward direction. This results in a higher yield of CO_2. Decreasing the pressure of the gaseous mixture shifts the equilibrium in the reverse direction. For a gaseous system with equal moles of reactants and products, i.e. $\Delta n = 0$, pressure – change has no effect. For example, the synthesis of hydrogen iodide from its elements is not affected by pressure.

$$H_2\,(g) \quad + \quad I_2\,(g) \quad \leftrightarrows \quad 2HI\,(g)$$

2 mol 2 mol

(c) Effect of Change in Concentration

When a system at equilibrium is disturbed by a change in concentration of the components, the system reacts in the direction that reduces the change. An increase in one of the reactants or a decrease in any of the products shifts the equilibrium to the right side forming more products.

An increase in concentration of a product or decrease in concentration of any reactant shifts the equilibrium to the left side, thus decreasing the amount of product. Therefore, adding more reactant or removing a product as soon as it is formed is one way of increasing yield of a product.

(d) Effect of Catalyst

A catalyst helps a reaction to reach equilibrium faster but it does not change either the value of the equilibrium constant or the equilibrium concentrations. A catalyst increases the rate of the forward and reverse paths by the same factor. This means it does not disturb the equilibrium condition of a system.

Example 14

1. Consider the decomposition of carbon dioxide to carbon monoxide.

$2\ CO_2\ (g) \leftrightarrows 2\ CO\ (g) + O_2\ (g), \quad \Delta H = +566.0\ kJ$

Write all conditions that would increase the concentration of carbon monoxide.

Solution:

(a) Increasing the concentration of CO_2 or removing CO (g) and / or O_2 as soon as they are formed

(b) Since the forward path is endothermic, increasing the temperature favors the product

(c) Reducing the pressure at constant temperature gives more yield because the product side has more number of moles of gases ($\Delta n < 0$)

2. Given: $PCl_3\ (g) + Cl_2\ (g) \leftrightarrows PCl_5\ (g), \quad \Delta H = -21.5\ kJ$

How will each of the following influence the system at equilibrium?

(a) Increasing the temperature (b) Increasing the pressure

(c) Adding Cl_2 gas (d) Adding appropriate catalyst

Solution

(a) An exothermic reaction favors lower working temperature. Therefore, increasing the temperature facilitates the decomposition of PCl_5, thus decreasing the amount of product

(b) Increasing pressure shifts an equilibrium to the side with fewer moles of gases. In the above reaction, $\Delta n < 0$, therefore, increasing the pressure favors the product side

(c) Adding Cl_2 (reactant), shifts the equilibrium to the product side.

(d) A catalyst helps the reaction to reach equilibrium faster without affecting concentration(s)

How can Le-Chatelier's principle help in maximizing yield of industrial production?

Almost all industrial reactions are reversible. The Haber and Contact processes provide good illustration on the effects of temperature, pressure and catalyst at equilibrium.

(i) **Haber process** (the *industrial production of ammonia*)

In the Haber process, ammonia (NH_3) is industrially manufactured using gaseous nitrogen and hydrogen.

$$N_2(g) + 3H_2 \underset{\text{Catalyst}}{\overset{\text{Fe}}{\rightleftharpoons}} 2NH_3(g);\ \Delta H = -92\ kJ/mol$$

Good yield of ammonia is obtained by working at lower to moderate temperature and higher pressure. In addition, the yield per unit time is highly increased by using an iron catalyst.

(ii) **Contact process** (*the industrial production of sulfuric acid*).

In the contact process, sulfuric acid (H_2SO_4) is commercially manufactured by the reaction of SO_2 and O_2 gases. The resulting SO_3 is then converted to H_2SO_4. The conditions for better yield are the same as that of Haber process.

$$SO_2(g) + O_2 \rightleftharpoons[V_2O_5] 2SO_3(g) + \text{heat}$$

EXERCISE 4.14

1. Write the equilibrium constant expression for each of the following reactions.

(i) $N_2\,(g) + 2\,H_2O\,(g) + \text{heat} \leftrightarrows 2\,NO\,(g) + 2\,H_2\,(g)$

(ii) $N_2\,(g) + O_2\,(g) \leftrightarrows 2\,NO\,(g) + \text{heat}$

(iii) $HF\,(aq) \leftrightarrows H^+\,(aq) + F^-\,(aq)$

(iv) $2\,NO_2\,(g) + 7\,H_2\,(g) \leftrightarrows 2\,NH_3\,(g) + 4\,H_2O\,(\ell)$

(v) $Ca\,(HCO_3)_2\,(s) \leftrightarrows CaCO_3\,(s) + H_2O\,(\ell) + CO_2\,(g)$

2. How would each of the following changes affect the equilibrium position of the system?

$$4\,HCl\,(g) + O_2\,(g) \leftrightarrows 2\,H_2O\,(g) + 2\,Cl_2\,(g) + 114\,kJ$$

(a)	adding HCl	b)	Cooling the system
(c)	a catalyst	(d)	removing Cl_2
(e)	decreasing the volume	(f)	removing all the reactants
(g)	decreasing the pressure		

3. Calculate the value of the equilibrium constant for the reaction:

$W + 2\,X \leftrightarrows Y + Z$; if at equilibrium there is 4.0 M W, 2.0 M X, 6.0 M Y and 8.0 M Z.

4. Write all the conditions that re define state of an equilibrium.

Check List

Key terms of the unit

- Activation energy
- Catalysts
- Chemical equilibrium
- Collision theory
- Combination reaction
- Decomposition reaction
- Double displacement reaction
- Dynamic equilibrium
- Endothermic reaction
- Energy diagrams
- Equilibrium constant
- Exothermic reaction
- Heat of reaction
- Irreversible reaction
- Le Chatelier's principle
- Limiting reactant
- Oxidation
- Oxidizing agent
- Percentage yield
- Products
- Reactants
- Reaction rates
- Redox reaction
- Reducing agent
- Reduction
- Reversible reaction
- Single displacement reaction
- Stoichiometry
- Theoretical and actual yield

Unit Summary

- There are three basic laws of chemical reactions, namely the law of conservation of mass, the law of definite composition and the law of multiple proportions.
- Because of the law of conservation of mass, chemical equations must be balanced in terms of number of atoms and mass.
- A chemical reaction is accompanied with change in energy.
- Reactions which release energy to the surroundings are called exothermic and those that absorb energy from the surroundings are called endothermic reactions.
- The amount of energy liberated or absorbed by a reaction is called heat of reaction or enthalpy – change.
- Chemical reactions are mainly classified as combination, decomposition, single displacement, double displacement and combustion.

- The quantitative relationship between reactants and products in a balanced chemical equation is known as stoichiometry.
- Stoichiometric calculations may involve mass – mass, mass – volume or / and volume – volume relationships.
- Reactions that involve change in oxidation number are called oxidation – reduction.
- Oxidation involves loss of electron(s) or increase in oxidation number. Reduction involves gain of electron(s) or decrease in oxidation number.
- The substance that undergoes oxidation is the reducing agent while the substance that is reduced during the reaction is the oxidizing agent.
- Rate of a reaction can be expressed as a decrease in concentration of any one of the reactants or as an increase in concentration of a product with time.
- Reactions which do not go to completion and occur in the forward and reverse paths are called reversible. Reactions that go to completion are called irreversible.
- Chemical equilibrium is a state where the rates of the forward and the reverse paths become equal. At this point, there is no observable change in properties and quantity of reactants and products.
- Le Chatelier's principle states that "when a reaction at equilibrium is subjected to an external stress, the system will shift in direction that reliefs the stress."
- A chemical equilibrium is affected by change in concentration or pressure (for gases) and temperature.
- The extent of the reaction at equilibrium is expressed by its equilibrium constant. An equilibrium constant greater than 1.0 indicates more products than reactants.
- Equilibrium constant is affected only by change in temperature.

REVIEW QUESTIONS ON UNIT 4

PART I: True or False – Type Questions

1. According to the law of conservation of matter, the total number of moles of reactants must be equal to those of products.

2. Heating iron up to its melting point results in a chemical change.

3. The evolution of a gas during mixing solutions indicates the presence of a chemical reaction.

4. Acid – base neutralization is a non – redox reaction.

5. If the percentage yield is high, it indicates a faster rate of reaction.

6. Among all factors of rate of a reaction, temperature has more effect than the others.

7. Synthesis reaction takes place only with elements but not between compounds.

8. Adding a substance to an equilibrium state shifts the equilibrium to the opposite side.

9. If total mole of gaseous reactants is equal to those of products, increase or decrease in pressure has no effect on the equilibrium state.

10. Contact process favors the presence of a catalyst, higher temperature and higher pressure.

PART II. Choose the correct answer from the given alternatives.

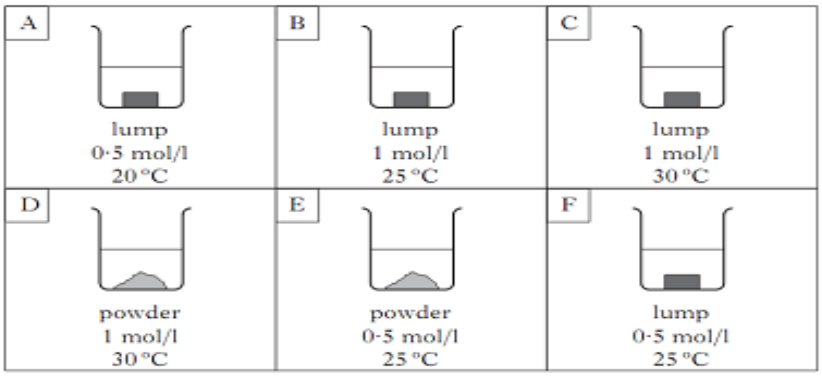
11. Consider the following gaseous reaction.

$$2NO_2\,(g) \leftrightarrows N_2O_4\,(g)$$

1.0 L flask contains 0.030 mol NO_2 and 0.040 mol N_2O_4 at equilibrium. The value of Keq is

A. 0.0225 B. 0.67 C. 1.33 D. 44.4

12. A student investigated the rate of a reaction using chalk ($CaCO_3$) and dilute hydrochloric acid. Identify the two experiments that should be compared to show the effect of concentration on the rate of reaction from the given diagrams below.



I. A & E II. C & D III. B & E IV. B & F

13. Which two reactions above must be compared to see the effect of surface area on rate?

I. B and D II. C and D III. A and E IV. B and E

14. Which of the following statements is correct?

A. The rate of a reaction is the same at any time during the reaction

B. The rate of a reaction is faster at the beginning than at the end

C. The faster the rate of a reaction, the higher is the amount of product.

D. The rate of a reaction increases with increase in amount of catalyst.

15. What is the oxidation number of V in $(V_2O_7)^{4-}$?

A. +5 B. +7 C. +10 D. -5

16. Consider the following reactions:

(I) $CaCl_2\,(aq) + Na_2SO_4\,(aq) \rightarrow CaSO_4\,(s) + 2\,NaCl\,(aq)$

(II) $Mg\,(s) + O_2\,(g) \rightarrow 2\,MgO\,(s)$

(III) $CaCO_3\,(s) + 2\,HCl\,(aq) \rightarrow CaCl_2\,(aq) + H_2O\,(\ell) + CO_2\,(g)$

Surface area will affect the reaction in:

A. II only B. I and III only C. II and III only D. I, II, and III

17. Increasing the temperature increases the rate of reaction. Which one explains this effect?

A. Temperature increases volume of reactants, which in turn increases yield.

B. The concentration of reactants increases with increase in temperature.

C. The average kinetic energy increases, resulting in more collision between reactants.

D. Increase in temperature always favors the forward path of a reaction.

18. Which of the following equations shows a possible displacement reaction?

A. $F_2 + 2\ NaCl \rightarrow 2NaF + Cl_2$

B. $Cl_2 + 2NaF \rightarrow 2\ NaCl + F_2$

C. $Cu + 2NaCl \rightarrow CuCl_2 + 2Na$

D. $Zn + 2NaF \rightarrow ZnF_2 + 2Na$

19. What oxidation number would a neon atom take and what does this suggest?

A. -8 making it inert. B. zero, making it unreactive.

C. +8 making it unreactive. D. zero, making it reactive.

20. A single displacement reaction is represented by $X\ (s) + 2HCl\ (aq) \rightarrow XCl_2\ (aq) + H_2\ (g)$. Which of the following could X represent?

(i) Zn (ii) Ag (iii) Cu (iv) Mg.

A. i and ii B. ii and iii C. iii and iv D. i and iv

21. Which factor explains why potassium reacts faster than sodium?

A. Concentration B. surface area C. nature of reactants D. temperature

22. In an endothermic reaction:

A. Energy is absorbed from the surroundings and temperature of the surroundings increases

B. Energy is released to the surroundings and the temperature increases

C. Energy is absorbed from the surroundings and temperature of the surroundings decreases

D. Energy is absorbed by the surroundings and temperature of the surroundings increases

23. Ammonium nitrate (NH_4NO_3) is used in medical cold packs. When the cold pack is crushed, the ammonium nitrate begins to dissolve in the water inside the cold pack and the temperature of the water drops quickly. Which statement correctly describes the reaction between ammonium nitrate and water?

A. The reaction is endothermic because energy is absorbed.

B. The reaction is endothermic because energy is released.

C. The reaction is exothermic because energy is absorbed.

D. The reaction is exothermic because energy is released.

24. Arrange **t**he following three conventional steps in writing a chemical equation.

(i) balance the equation

(ii) write the symbols and formulas of the reactants and products in an equation form

(iii) write the word equation

A. iii, ii & i B. i, iii & ii C. iii, i & ii D. ii, iii & i

25. For the following equation, what are the balancing coefficients?

w FeS_2 + **x** O_2 → **y** Fe_3O_4 + **z** SO_2.

	w	**x**	**y**	**z**
A.	3	8	1	6
B.	6	1	8	3
C.	1	8	1	6

D. 3 8 6 1

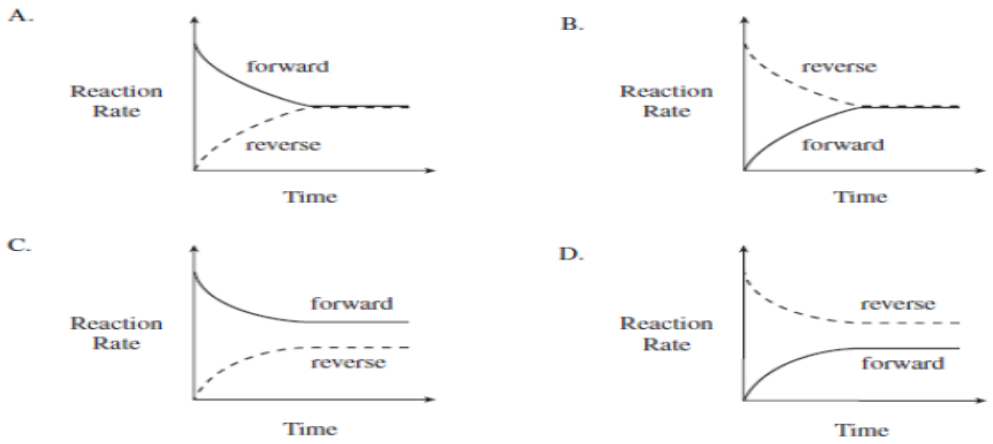
26. Sulfur and oxygen react to produce the environmental pollutant sulfur trioxide. In a particular experiment, the reaction between 1.0 g sulfur and 1.0 g oxygen produced 0.80 g of SO_3. The % yield is _____.

A. 30 B. 48 C. 21 D. 88

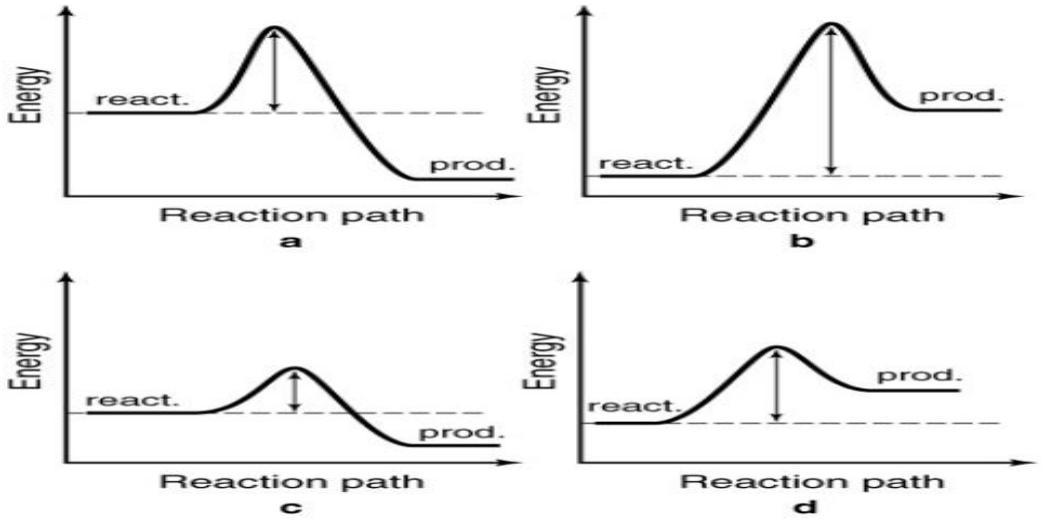
27. How many grams of H_2O will be formed when 32.0 g H_2 is allowed to react with 16.0 g O_2?

A. 9.0 g B. 18.0 g C. 32.0 g D. 36.0 g

28. Sifan is a grade 9 student. She placed some HF (g) into a closed container and waited until the reaction reached equilibrium. $2HF\ (g) \rightleftharpoons F_2(g) + H_2\ (g)$. Which of the following plots describes the forward and reverse reaction rates based on Sifan's experiment?



29. The energy profiles for four different reactions are shown below. Which reaction requires the most energetic collisions to reach transition state (top of the hill)?



30. Which of the following transformations is /are reduction?

(i) OCl^{--} to ClO_3^{--} (ii) MnO_2 to MnO_4^{--} (iii) BiO_3^{--} to Bi^{3+} (iv) N_2O_4 to N_2O

A. ii and iv B. only iii C. i and ii D. iii and iv

PART III Answer the following questions accordingly

31. In the following combustion reaction, 42.50 g of NH_3 were mixed with 4 mol of O_2.

$4\ NH_3\,(g) + 5\ O_2\,(g) \rightarrow 4\ NO\,(g) + 6\ H_2O\,(\ell)$

A. Which substance is the limiting reactant?

B. Calculate the masses of each of NO and H_2O produced by the reaction.

32. For the reaction at equilibrium: $X_2\,(g) + 2\ Y_2\,(g) \leftrightarrows 2\ XY_2\,(g) + 80$ kJ, the equilibrium concentrations at 27 ^{0}C are: $[X_2] = 0.25$ M, $[Y_2] = 0.125$ M and $[XY_2] = 0.50$ M.

A. Find the equilibrium constant with its unit

B. What is the effect on the equilibrium if:

(i) fresh Y_2 (g) is added? (ii) the reaction mixture is cooled to 20 ^{0}C?

(iii) the pressure of the system is increased slightly?

(iv) a new catalyst is added? (v) all the product is removed?

33. For the following equilibrium state, write how each change will affect the indicated quantity. Write "increase", "decrease", or "no change".

$N_2\,(g) + 2\,H_2O\,(g) + \text{Heat} \leftrightarrows 2\,NO\,(g) + 2\,H_2\,(g)$

Change	**$[N_2]$**	**$[H_2O]$**	**$[NO]$**	**$[H_2]$**	**$K_{equilibrium}$**
A. adding N_2					
B. adding NO					
C. removing H_2					
D. increasing the pressure					
E. more heat is added					
F. compressing the reaction vessel					
G. cooling the reaction vessel					

PART IV. Matching

Choose the alphabet from Column B that has matching idea for Column A

Number	**Column A**	**Column B**
34. ___	Ratio of product terms to reactant terms	A. Chemical equation B. Reduction C. Activation energy D. Chemical equilibrium E. Conservation of matter F. Concentration G. Equilibrium constant H. Catalyst I. Rate J. Limiting reactant
35. ___	Principle that forces us to work only with balanced equations	
36. ___	Shows change in oxidation number	
37. ___	Doesn't affect equilibrium state	
38. ___	Expresses the speed at which a reactant is converted to a product	
39. ___	Minimum energy to start a reaction	
40. ___	Field of study that describes how far a reaction proceeds forward	