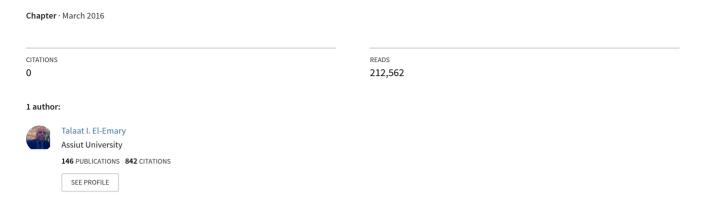
GENERAL CHEMISTRY For first years of Faculties of Science, Medicine and Pharmacy Part 1

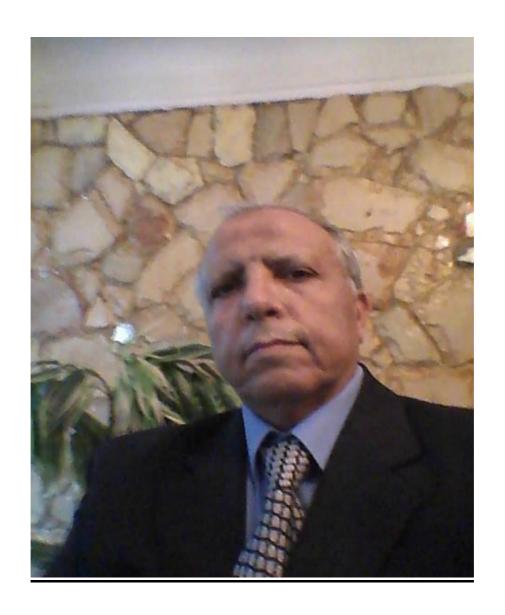


GENERAL CHEMISTRY

For first years of Faculties of Science, Medicine and Pharmacy

Part 1

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CREDIT TEXT BOOKS

- 1. GENERAL CHEMISTRY, Principle& Structure
 Fifth Edition, by JAMES E. BRADY
- 2. GENERAL CHEMISTRY, by Whitten and Gailey
- 3. GENERAL COLLEGE CHEMISTRY,

Further Reading List:

- (1) GENERAL CHEMISTRY, by Ebbing DD
- (2) GENERAL CHEMISTRY, by Hill J. et al

CHAPTER 1

MATTER AND ENERGY

Matter is anything has mass and occupies space. Mass is a measure of the quantity of matter in a sample of any material.

Energy: is most commonly defined to be the capacity to do work. We are all familiar with many forms of energy is every energy life, including mechanical energy, electrical energy, heat energy, and light energy. Energy can be classified into two principal types. Potential energy and kinetic energy.

Potential energy: is the energy that an object or sample of material possesses because of its position or composition.

kinetic energy: is the capacity of doing work directly, and is easily transferred between objects.

Chemical reactions are either exothermic reactions or endothermic ones.

Exothermic reaction: is that type of reaction in which energy is released to the surrounding, usually as heat

Endothermic reaction: is that type of reaction in which energy is absorbed from the surrounding.

The Law of Conservation of Matter: There is no observable change in the quantity of matter during ordinary chemical reaction.

The Law of Conservation of Energy: Energy cannot be created or destroyed, it may only be converted from one form to another.

The Law of Conservation of Matter and Energy

The relationship between matter and energy is given by Albert Einstein's equation:

$$E = mc^2$$

Were, m is the mass of matter, and c is the velocity of light.

States of matter

Matter is conveniently classified into three states, solid state, liquid state and gaseous state.

In the solid state, the substances are rigid and have definite shapes, and the volumes do not vary much with changes in temperature and pressures.

In the liquid state: the substances are not rigid and have no definite shapes, it takes the shape of the container in which it is placed in, and the volumes vary with changes in temperature and slightly compressed with pressures.

In the gaseous state: the substances are not rigid and have no definite shapes and volume, it fills and takes the shape of the container in which it is placed in, and the volumes vary much with changes in temperature and compressed with pressures.

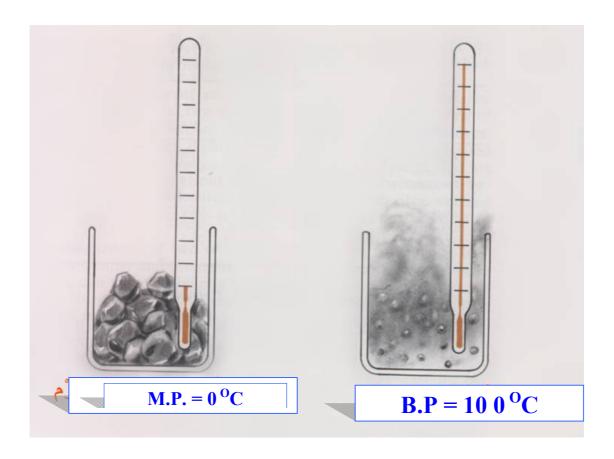
Chemical and physical properties:

Chemical properties: are properties that matter exhibits as it undergoes changes in chemical composition.

Physical properties: are properties that can be observed in the absence of any chemical reaction. Color, density, hardness, melting point, boiling point, and electrical and thermal conductivities are physical properties.

Chemical and physical changes

Both chemical and physical changes are always accompanied by either the absorption or liberation of energy. Energy is required to melt ice, and energy is required to boil water. Conversely, the condensation of steam to form liquid water always liberates energy, as does the freezing of liquid water to form ice.



MEASURMENTS IN CHEMISTRY

The International System of Units (SI) is based on the seven fundamental units listed in table 1-1 & 1-2 & 1-3 and all other units of measurements are derived from these.

Table 1-1
THE SEVEN BASIC UNITS OF MEASURMENT

Physical property	Name of Unit	Abbrevation
Length	Meter	m
Mass	kilogram	Kg
Time	Second	S
Electric current	Ampere	A
Temperature	Kelvin	K
Luminous intensity	Candela	Cd
Quantity of substance	Mole	mol

The distances and masses in metric system illustrate the use of some common prefixes and the relationships among them are listed in table 1-2 &1-3.

Table 1-2. The sixteen SI prefixes

Prefix	Symbol	Factor	Prefix	Symbol	Factor
exa	E	10^{18}	deci	d	10 ⁻¹
peta	P	10^{15}	centi	c	10 ⁻²
tetra	T	10^{12}	milli	m	10 ⁻³
giga	G	10^9	micro	μ	10 ⁻⁶
mega	M	10^6	nano	n	10 ⁻⁹
kilo	k	10^3	pico	р	10^{-12}
hecta	h	10^2	femto	f	10 ⁻¹⁵
deca	da	10 ¹	atto	a	10 ⁻¹⁸

Table 1-3

COMMON PREFIXES USED IN THE METRIC
SYSTEM

Prefix	Abbreviation	Measuring	Example
mega	M	10^6	1 megameter(Mm) = 1 x 10 ⁶ m
kilo	k	10 ³	1 kilometer (km) = 1 $\times 10^3$ m
dec-	d	10 ⁻¹	1 decimeter (dm)= 0.1 m
centi-	c	10 ⁻²	1 centimeter (cm) = 0.01 m
micro-	μ	10 ⁻⁶	1 microgram (μg)= 1 x 10 ⁻⁶ g
nano-	n	10 ⁻⁹	1 nanogram (ng) = 1 x 10 ⁻⁹ g
pico-	p	10 ⁻¹²	1 picogram (pg) = 1 $\times 10^{-12}$ g

Mass and Weight

The basic unit of mass in the SI system is kilogram is shown in table 1-4. one kilogram weight 2.205 pounds, and a one-pound object has a mass of 0.4536 kilogram.

Table 1-4

SI UNITS OF MASS

Kilogram	Base unit
Gram, g	1000 g = 1 kg
Milligram, mg	1000 mg = 1 g
Microgram, μg	1 million $\mu g = 1 g$

Table 1-5 illustrate conversion factors relating length, volume and mass units

Table 1-5
CONVERSION FACTORS RELATING LENGTH, VOLUME
AND MASS UNITS

Metric	English	Metric-English Equivlents	
Length 1 km = 10 ³ m 1 cm = 10 ⁻² m 1 mm = 10 ⁻³ m 1 nm = 10 ⁻⁹ m 1 A ⁰ = 10 ⁻⁸ cm	1 ft = 12 in 1 yd = 3 ft 1 mile = 5280 ft	1 in = 2.54 cm 1 m = 39.37 in 1 mile = 1.609 km	
Volume 1 mL = 1 cm ⁻³ = 10 ⁻³ liter 1 m ³ = 10 ⁶ cm = 10 ³ liter		1 liter = 1.057 qt 1 ft ³ = 28.32 liter	
Mass 1 kg	1b = 16 oz 1 short = 2000 1b ton	1b = 453.6 g 1 g = 0.03527 oz 1 = 1.102 short metric ton	

ft: foot, 1 yd, pt: pint, qt: quart

Dimensional analysis

Unit factor method

Unit factor may be constructed from any two terms that describe the same amount of whatever we my consider. For example, 1 foot is equal to exactly 12 inches, by definition, and we may write an equation to describe this equality:

$$1 \text{ ft} = 12 \text{ in}$$

Dividing of both sides of the equation by 1 ft gives

$$\frac{1 \text{ ft}}{1 \text{ ft}} = \frac{12 \text{ in}}{1 \text{ ft}} \qquad \text{or} \qquad 1 = \frac{12}{1 \text{ ft}}$$

We can write numerous unit factors, such as

$$\frac{1 \text{ yd}}{3 \text{ ft}}$$
, $\frac{1 \text{ yd}}{36 \text{ in}}$, $\frac{1 \text{ mile}}{5280 \text{ ft}}$, $\frac{4 \text{ qt}}{1 \text{ gal}}$, $\frac{2000 \text{ 1b}}{1 \text{ ton}}$

Conversion from decimal to exponential

In scientific (exponential) notation, we place one nonzero digit to the left of the decimal as in the following examples

$$4,300,000. = 4.3 \times 10^6$$

6 is places to the left, therefore, exponent of 10 is 6

$$0.000348 = 3.48 \times 10^{-4}$$

4 is places to the right, therefore, exponent of 10 is -4

CONVERSIONS AMONG' SI' UNITS

Example 1.1: A desk is found be 1437 mm wide. What is this width expressed in meters?

Solution:

$$1437 \text{ mm} = 1437 \text{ x } 10^{-3} \text{ m}$$

$$1437 \text{ mm} = 1437 \text{ x } 10^{-3} \text{ m}$$

Example 1.2: A certain person is 172 cm tall. Express this height in decimeter.

Solution: As a beginning let's relate the problem in the form of an equation.

$$172 \text{ cm} = ? \text{ dm}$$

We can write the following relationships

$$1 \text{ cm} = 10^{-2} \text{ m}$$

 $1 \text{dm} = 10^{-1} \text{ m}$

We can construct the following two conversion factors:

$$\frac{1 \text{ cm}}{10^{-2} \text{ m}}$$
 and $\frac{10^{-2} \text{ m}}{1 \text{ cm}}$

If we multiply our given 172 cm by the second factor, the units cm will cancel and we will have converted centimeters to meters.

$$172 \text{ cm/x} \left(\frac{10^{-2} \text{ m}}{1 \text{ cm}} \right) = 1.72 \text{ m}$$

Similarly, we use the second equation to convert meters to decimeters.

$$1.72 \text{ m/x} \left(\frac{1 \text{ dm}}{10^{-1} \text{ m}} \right) = 17.2 \text{ dm}$$

We can also " string together" conversion factors and obtain the same net result.

$$172 \text{ cm} \times \left(\frac{10^{-2} \text{ m}}{1 \text{ cm}}\right) \times \left(\frac{1 \text{ dm}}{10^{-1} \text{ m}}\right) = 17.2 \text{ dm}$$
to decimeter

Example 1.3: Calculate the number of cubic centimeter in 0.225 dm³.

Solution:

$$0.225 \text{ dm}^3 = ? \text{ cm}^3$$

$$1 \text{ dm} = 10^{-1} \text{ m}$$

$$1 \text{ cm} = 10^{-2} \text{ m}$$

$$(1 \text{ dm})^3 = (10^{-1} \text{ m})^3$$

$$1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$(1 \text{ cm})^3 = (10^{-2} \text{ m})^3$$

$$1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

$$0.225 \text{ dm}^3 \text{ x} \left(\frac{10^{-3} \text{ m}^3}{1 \text{ dm}^3}\right) \text{ x} \left(\frac{1 \text{ cm}^3}{10^{-6} \text{ m}^3}\right) = 255 \text{ cm}^3$$

Example 1.4: How many millimeter are in 1.39 x 10⁴ meters?

Solution:

? mm = 1.39 x
$$10^4$$
 m/x $\frac{1000 \text{ mm}}{1 \text{ m}}$ = 1.39 x 10^7 mm

Example 1.5: A sample of gold weigh 0.234 mg. what is its weight in g? in cg?

Solution:

?
$$g = 0.234 \text{ mg/x} \frac{1 \text{ g}}{1000 \text{ mg}} = 2.34 \text{ x} 10^{-4} \text{ g}$$

? $cg = 0.234 \text{ mg/x} \frac{1 \text{ cg}}{10 \text{ mg}} = 0.0234 \text{ cg}$ or $2.34 \text{ x} 10^{-2} \text{ cg}$

Example 1.6: How many square decimeters are there in 215 square centimeters?

Solution:

?
$$dm^2 = 215 \text{ cm}^2 \text{ x} (\frac{1 \text{ dm}}{10 \text{ cm}})^2 = 2.15 \text{ dm}^2$$

Example 1.7: How many cubic centimeters are there in 8.34×10^5 cubic decimeters?

Solution:

$$?1 \text{ cm}^2 = 8.34 \times 105 \text{ dm}^2 \times (\frac{10 \text{ cm}}{1 \text{ dm}})^2 = 8.34 \times 10^8 \text{ cm}^2$$

Example 1.8: A common unit of energy is the erg. Convert 3.74 x 10^{-2} erg to the SI units of energy, joules and kilojoules. One erg is exactly 1 x 10^{-7} joule.

Solution:

$$3.74 \times 10^{-2} \text{ erg x } \frac{1 \times 10^{-7} \text{ J}}{1 \text{ erg}} = 3.74 \times 10^{-9} \text{ J}$$

$$3.74 \times 10^{-9} \text{ J} \times \frac{1 \times 10^{-3} \text{ kj}}{\text{J}} \neq 3.74 \times 10^{-12} \text{ kj}$$

Example 1.9: Express 1.0 mL in gallons.

Solution: 1 quart (qt) = 0.9463 liter, 1 liter = 1.056 quarts (qt)

١٢

? gal = 1.0 mL x
$$\frac{1 \text{ L}}{1000 \text{ mL}}$$
 x $\frac{1.06 \text{ qt}}{1 \text{ L}}$ x $\frac{1 \text{ gal}}{4 \text{ qt}}$ = 2.7 x 10⁻⁴ gal

Density and specific gravity

The density of a substance is defined as the mass per unit volume.

density =
$$\frac{\text{mass}}{\text{volume}}$$
 or $D = \frac{M}{V}$

Densities may be used to distinguish between two substances or to assist in identifying a particular substance. They are usually expressed as g/cm^3 or g/mL for liquids and solids, and as g/L for gases. These units can also be expressed as g/cm^3 , g/mL^{-1} , respectively.

Density is constant for a given substance at a given temperature. It is also an intensive property, that is, a property that does not depend on the amount of material examined. Both mass and volume are extensive properties, in that they depend on the amount of material in the sample. Obviously, the volume occupied by two kilogram of lead is twice that of one kilogram of lead, but both samples have the same density. Table 1- 5 illustrate the densities of some common substances.

Substance	Density, g/mL
Hydrogen (gas)	0.000089
Carbon dioxide (gas)	0.0019
Cork	0.21
Oak wood	0.71
Ethyl alcohol	0.79
Water	1.00
Magnesium	1.74
Table salt	2.16
Sand	2.32
Aluminum	2.70
Iron	7.86
Copper	8.92
Lead	11.34
Mercury	13.59
Gold	19.3

Example 1-7: A 47.3 mL sample of liquid weighs 53.74 g. What is its density?

Solution:

$$D = \frac{M}{V} = \frac{53.74 \text{ g}}{47.3 \text{ mL}} = 1.14 \text{ g/mL}$$

Example 1-8: If 100 g of the liquid described in example 1-7 is needed for a chemical reaction, what volume of liquid would you use?

Solution:

$$D = \frac{M}{V}$$
, so $V = \frac{M}{D} = \frac{100 \text{ g}}{1.14 \text{ g/mL}} = 87.7 \text{ mL}$

The specific gravity of a substance is the ratio of its density to the density of water.

$$Sp. Gr. = \frac{D_{Substance}}{D_{Water}}$$

The density of water is 1.000 g/ml at 3.98°C, the temperature at which the density of water is greatest. However, variation in the density of water with changes in temperature are small enough that we may use 1.00 g/mL up to 25°C without introducing significant errors into our calculations.

Specific gravities are dimensionless numbers, as the following example demonstrates.

Example 1-9: The density of table salt is 2.16 g/mL at 20°C. What is its specific gravity?

Sp. Gr. =
$$\frac{D_{Salt}}{D_{Water}} = \frac{2.16 \text{ g/ mL}}{1.00 \text{ g/ mL}} = 2.16$$

Example 1-10: Battery acid is 40.0% sulfuric acid H_2SO_4 , and 60% water by weight. Its specific gravity is 1.31. Calculate the weight of pure sulfuric acid, H_2SO_4 , in 100 ml of battery acid.

Solution:

We may write

Density = 1.31 g/mL

The solution is $40.0\%~H_2SO_4$ and $60\%~H_2O$ by weight. From this information we may construct the desired unit factor.

$$\frac{40.0\,\mathrm{g\,H_2SO_4}}{100\,\mathrm{g\,soln.}}$$

We can now solve the problem:

$$? H_2SO_4 = 100 \text{ mL soln } X \frac{1.31 \text{ g soln}}{1 \text{ mL soln}} X \frac{40.0 \text{ g H}_2SO_4}{100 \text{ g soln}} = 52.4 \text{ g H}_2SO_4$$

We first used the density as a unit factor to convert the given volume of solution to mass of solution, and then used the percentage by weight to convert the mass of solution to mass of acid.

Heat and temperature

Heat is one form of energy. Temperature measures the intensity of heat, the "hotness" or "coldness" of a body. Heat always flows from a hotter to a colder body-never in the reverse direction.

Temperatures are commonly measured with mercury-in-glass thermometers. As mercury expands in the reservoir, its movement up into the thin column is clearly visible.

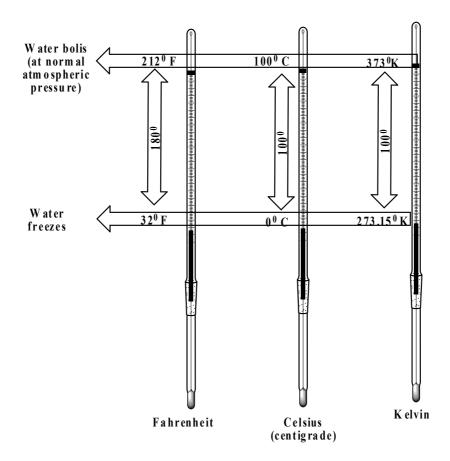
<u>Anders Celsius</u>, a Swedish astronomer, developed the <u>Celsius</u> <u>temperature</u> scale formally called the centigrade temperature scale.

Temperature are frequently measured in the united state on the temperature scale devised by **Gabriel Fahrenheit**, a German instrument maker. On this scale the freezing and boiling points of water are defined as 32 0 F and 212 0 F, respectively.

In scientific work, temperature are expressed on the **Kelvin (absolute)** temperature scale.

Relationships among the three scales illustrated in the following figure. Every Kelvin temperature is 273.150 above the corresponding Celsius temperature. Thus the relationship between the two scales is simply

K =
$$(x^{0} C + 273.15^{0} C) \frac{1.0 K}{1.0^{0} C} OR ^{0} C = (xK - 273.15 K) \frac{1.0^{0} C}{1.0 K}$$



We can construct the unit factors

$$\frac{1.8^{0} \text{ F}}{1.0^{0} \text{ C}}$$
 and $\frac{1.0^{0} \text{ C}}{1.8^{0} \text{ F}}$

?
$${}^{0}F = (x^{0}C \times \frac{1.8^{0} F}{1.0^{0} C}) + 32^{0}F$$

?
$${}^{0}C = \frac{1.0^{0} \text{ C}}{1.8^{0} \text{ F}} (x^{0} \text{F} - 32^{0} \text{ F})$$

Example : When the temperature reaches " $100\ ^0F$) in the shade," it's hot. What is this temperature on the Celsius scale?

?
$${}^{0}C = \frac{1.0^{0} \text{ C}}{1.8^{0} \text{ F}} (100^{0} \text{ F} - 32^{0} \text{ F})$$

?
$${}^{0}C = \frac{1.0^{0} \text{ C}}{1.8^{0} \text{ F}} (100^{0} \text{ F} - 32^{0} \text{ F}) = 38^{0} \text{ C}$$

Example: When the absolute temperature is "400 K). What is Fahrenheit?

?
$${}^{0}C = (400 \text{ K} - 273 \text{ K}) \frac{1.0^{0} \text{ C}}{1.0 \text{ K}} = 127^{0} \text{ C}$$

? ${}^{0}C = \left(127^{0} \text{ C X} \frac{1.8^{0} \text{ F}}{1.0^{0} \text{ C}}\right) + 32^{0} \text{ F} = 261^{0} \text{ F}$

Another expressions for the relationships among the three scales of temperature.

$$t_{({}^{0}C)} = \frac{5}{9} [t_{({}^{0}F)} - 32]$$
$$t_{(k)} = t_{({}^{0}C)} + 273.15$$
$${}^{0}F = 32 + ({}^{0}C) (1.8)$$

SIGNIFICANT FIGURES, EXACT, PRECISE AND ACCURATE

<u>Significant figures</u> are digits believed to be correct by the person who makes a measurements. We assume that the person is competent to use the measuring device. Suppose one measures a distance with a meter stick and reports the distance as 343.5 mm. what does this number mean? In this person's judgment, the distance is greater than 343.3 mm but less than 343.7 mm, and the best estimate is 343.5 mm. The 343.5 mm contains four significant figures-the last digit, 5, represents a best estimate and therefore doubtful, but it is considered to be a significant figure. In reporting numbers obtained from measurements, we report one estimated digit, and no more. Since the person making the measurement is not certain that the 5 is correct, clearly it would be silly, meaningless, and wrong to report the distance as 343.53 mm.

Strictly speaking, the distance should be reported as 343.5 ± 0.2 mm because it is difficult to estimate distances less than 0.2 mm on an ordinary meter stick

<u>The term exact</u> is used for quantities that have an infinite number of significant figures. For example, by definition there are exactly 1,000 cubic centimeters in 1 liter. We could write that there are 1,000.0000000... cubic centimeters in 1.00000000... liter, with no limit to the number of zeros. For example, the inch is defined as exactly 254×10^{-2} meter, or 254 centimeters. Exact quantities either are defined arbitrarily or result from counting objects one by one; no measured quantities, other than by simple counting, are exact.

مضبوط، دقيق = Exact

<u>The term precise</u> refers to how reproducible measurements of the same quantity are. Suppose that two calibrated 250 cm³ beakers are each tested three times to determine their volumes. Beaker A is found to have volumes of 248, 249, and 247 cm³. The set of values for beaker A is more precise, varying only ± 1 from the average value of 248 cm³.

صحيح، مدقق

The term accurate (صحیح) refers to how closely a measured value is a true or accepted value. In the case of the two beakers, beaker B, with an average volume of 249 cm³, is closer to the calibrated value of 250 cm³. For most experimental measurements a true value is not known, so the accuracy cannot be determent. The accuracy is commonly expressed in terms of the error or the percent error. Error is defined as the difference between a measured value and true (or most probable)value. In the case of beaker A, the error between the average of the three measurements and the calibrated value is

$$250 \text{ cm}^3 - 248 \text{ cm}^3 = 2 \text{ cm}^3$$

The error is a positive quantity whether the measured value is higher or lower than the true (or most probable) value. The percent error is

% error =
$$\frac{\text{error}}{\text{true (or most probable) value}} \times 100$$

% error =
$$\frac{2 \text{ cm}^3}{250 \text{ cm}^3} \times 100 = 0.8 \%$$

Scientific notation and significant figures

For instance, a measured length of 23.6 cm obviously contains three significant figures, and a measured length of 1.203 cm has four. But how about the numbers 0.00215 m and 12.30 m?. Do the zeros in these measured value count as significant figures?

The general rule is that a zero does not count as significant figures if its function is merely to locate the position of the decimal point. For example, consider the measured value 0.00215 m. Without the zero to the left of the 2, we wouldn't know where the decimal point belongs and we wouldn't know how large

the measurement is. Now, notice what happens to these zeros when we rewrite the number in scientific notation.

$$0.00215 \text{ m} = 2.15 \text{ x } 10^{-3} \text{ m}$$

We see that the zeros disappear; their function was just to locate the decimal point and they are really not measured digits. A rule that we can apply, therefore, is that zeros that lie to the left of the first nonzero digit are not counted as significant figures.

How about the zero in the measured value 12.30 m? This zero is counted as a significant figures because it would not have been written unless the digit had been estimated to be a zero. Also note that this zero does not disappear when the number is written in scientific notation.

$$12.30 \text{ m} = 1.230 \text{ x } 10^{1} \text{ m}$$

This leads to another general statement: in a measured quantity, a zero that lies to the right of the decimal point and also to the right of the first nonzero digit always counts as a significant figures. If we put all this together, in the measurement below only the nonzero digit plus the zeros above the line is count as significant figures

0.0054070 m

And the measurement therefore contain five significant figures. Below we see three different ways of expressing a length of 1200 m, each expressing a different number of significant figures.

1.200 x 10³ m (four significant figures)

1.20 x 10³ m (three significant figures)

1.2 x 10³ m (two significant figures)

Significant figures and calculations

In almost all cases, the numbers that we obtain from measurement are used to calculate other quantities, and we must exercise care to report the calculated result in a way that neither overstates nor understates the amount of confidence we have in it. This mean that we must be careful to report the computed value with the proper number of significant figures.

To see problems can arise, suppose we wished to calculate the area of a rectangular carpet whose sides have been measured using two different rulers, to be 6.2 m and 7.00 m long. We know the area is the product of this two numbers.

area =
$$6.2 \text{ m} \times 7.00 \text{ m} = 43.7 \text{ m}^2$$

The question is "How many significant figures are justified in the answer?

The length 6.2 m has two significant figures, which implies an uncertainty of about $\pm~0.1$ m. suppose an error of 0.1 m had, in fact, been made and that the scale of the ruler should have read 6.3 m. How much of an error would this have caused in the area? Let's see by recalculating the area using 6.3 m instead of 6.2 m.

area =
$$6.3 \text{ m} \times 7.00 \text{ m} = 44.1 \text{ m}^2$$

notice that this error in the measured length would cause a change in the second digit of the answer (it changes from a 3 to a 4). An uncertainty in the second digit of the length causes an uncertainty in the second digit in the answer.

The length of the other dimension, 7.00 m, has an implied uncertainty of about ± 0.01 m. if the 7.00 m were in error by this amount, instead of the other measurement, how much would this influence the answer? As before, let's recalculate the area, this time using 7.01 m.

area =
$$6.2 \text{ m} \times 7.01 \text{ m} = 43.5 \text{ m}^2$$

An error in the third digit of 7.00 m causes a change in the third digit of the answer, so if only the 7.00 m were in error, the answer would have its uncertainty in the third digit.

For multiplication or division, the product or quotient should not have more significant figures than are present in the least precise factor in the calculation.

As an illustration, consider the calculation below, in which we will assume that all the numbers are measured values. A calculator gives the answer shown.

$$\frac{21.95}{3.62 \times 4.5} = 1.347452425$$

The least precise factor (i.e., the one with the fewest number of significant figures) is the value 4.5, which contain two significant figures. The answer, therefore, should contain no more than two significant figures and should be rounded* to 1.3.

For addition and subtraction, the procedure used to determine the number of significant figures in an answer is different. Here, the number we write as the result of a calculation is determined by the figures with the largest amount of uncertainty. For example, consider the following sum:

The first quantity, 4.371 m, has an uncertainty of ± 0.001 m; the second an uncertainty of ± 0.1 m. When we add these quantity, we expect the answer to be uncertainty by at least ± 0.1 m, so we must round the answer in this case to the nearest tenth; it should be reported as 306.9 m. The rule for addition and subtraction, therefore, can be stated as follows.

The amount of uncertainty in a sum or difference will be at least as large as the largest uncertainty in any of the terms involved in the calculation.

• when wish to round off a number at a certain point, we simply drop the digit that follows if the first of them is less than 5. Thus, 6.2317 rounds to 6.23, if we wish only two decimal places. If the first digit after the point of round off is larger than 5, or if it is a 5 followed by other nonzero digits, then we add 1 to the preceding digit. Thus, 6.236 and 6.2351 both round to 6.24. Finally, when the digit after the point of round off is a 5 and no other digits follow the 5, then we drop the 5 if the preceding digit is even and we add 1 if it is odd. Thus, 8.165 rounds to 8.16, but 8.175 rounds to 8.18.

A little practice will enable you to determine with confidence the number of significant figures in different quantities. The following examples illustrate some typical cases:

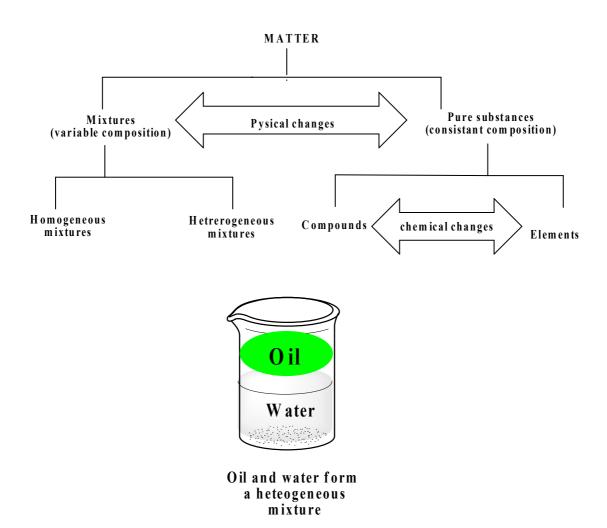
Quantity	No. of figures
1.062	4
751	3
0.006110 centimeters	4
1.2 x 10 ⁸ stars	2
\$ 683,462.02	8
7,685,000	4
7.6850 x 10 ⁶ people	5

SUBSTANCES, MIXTURES, ELEMENTS, AND COMPOUNDS

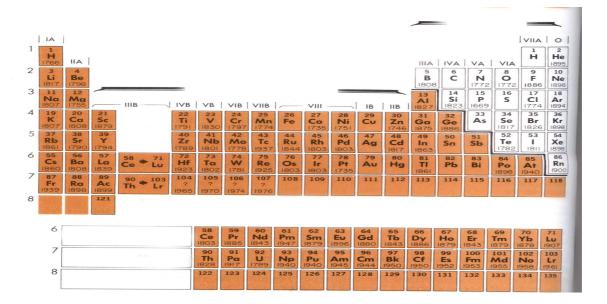
A pure substance is defined as any kind of matter for which all samples have identical composition and identical properties.

Mixtures are combinations of two or more substances in which each substances retains its own identity and properties. Mixtures can be separated by

physical means. For example, the mixture of salt and water can be separated by evaporating the water and leaving the solid salt behind. A mixture of sand and salt can be separated by dissolving the salt in water, filtering out the sand, and then evaporating the water to obtain the solid salt. Very fine iron powder can be mixed with powdered sulfur to give a mixture. The iron may be removed by magnet, or the sulfur may be dissolved in carbon disulfide, which does not dissolve iron.



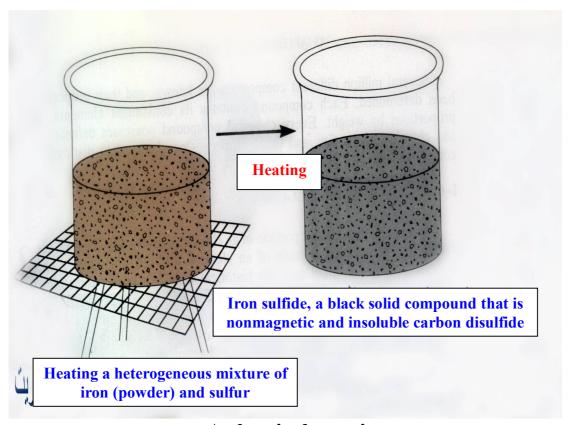
Elements are pure substances that cannot be decomposed into simpler substances by chemical changes. Oxygen, nitrogen, silver, aluminum, copper, gold, and sulfur are all elemental substances. A list of the currently known elements is included inside the periodic table.



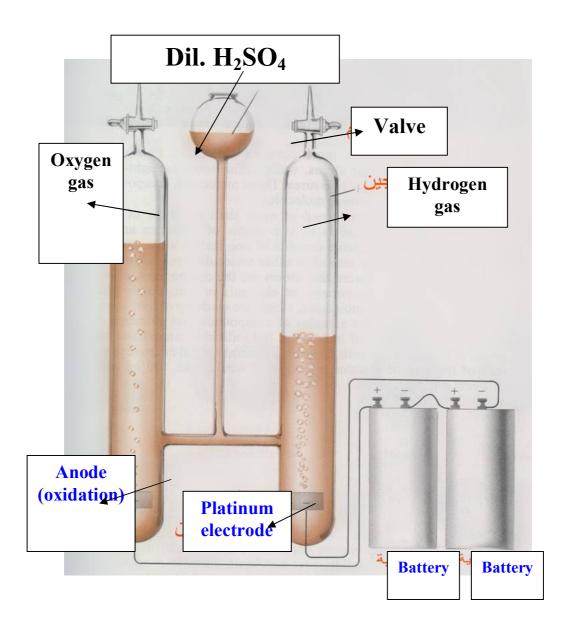
The periodic table of the elements

Compounds are pure substances consisting of two or more different elements in a fixed ratio. All compounds can be decomposed or resolved into their constituent element by chemical changes. The physical and chemical properties of a compound are different from the properties of its constituent elemental. A chemical reaction between iron and sulfur gives iron sulfide.

Water can be decomposed into hydrogen and oxygen by electrical energy



A chemical reaction



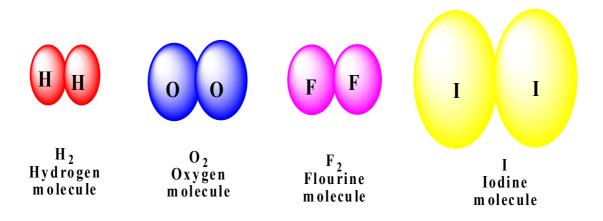
Electrolysis of water

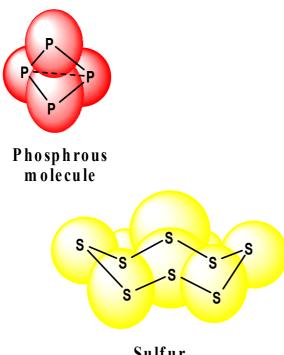
CHAPTER 2

ATOMS, MOLECULES AND MOLES

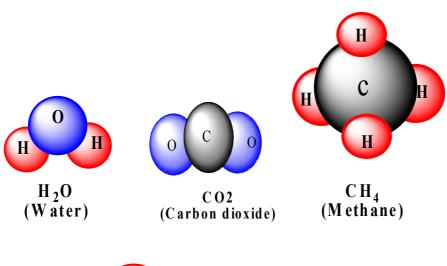
An atom is the smallest particle of an element or compound that can have a stable independent existence. A molecule that consist of one atom is called a monatomic molecule, like helium, neon, and argon. A molecule that consist of two atoms is called a diatomic molecule, like oxygen, nitrogen, fluorine, chlorine, bromine and iodine. Other elements exist as more complex molecules. Phosphrous exist as molecule consisting of four atoms, while sulfur exist as eightatom molecule.

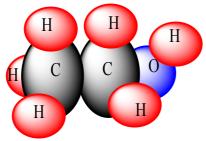
Most molecules are composed of more than one type of atom. A water molecule, for example, consists of two atoms of hydrogen and one atom of oxygen. A molecule of methane consists of one carbon atom and four hydrogen atoms.





Sulfur molecule





C₂H₆OH (Ethylalcohol)

SYMBOLS, FORMULA, AND EQUATIONS

Each of the elements has been assigned a **chemical symbol** that we can think of as a shorthand way of representing the element. The symbol consist of one or two letters that usually bear a resemblance to the **English name** of the element. For instance, carbon = C, Chromium = Cr, Chlorine = Cl, Calcium = Ca, and Zinc = Zinc. Notice that the first letter is capitalized, but if there is a second letter, it is not. Some of the elements have symbols have **Latin names**. Some examples are Potassium (L *Kaluim*) = K, Sodium (*Natrium*) = Na, Silver (*Argentium*) = Ag, mercury (*hydrargyrum*) = Hg, and copper (*cuprum*) = Cu.(cf. the periodic table of elements).

A chemical compound is represented symbolically by its **chemical formula**. For example, water is represented by H_2O , carbon dioxide by CO_2 , methane (natural gas) by CH_4 , and aspirin by $C_9H_8O_4$. The formula H_2O , for instance, describes a substance containing two hydrogen atoms for every oxygen atom. Similarly, the compound CH_4 contain one atom of carbon for every four atoms of hydrogen.

Often, two or more atoms are able to join tightly together so that they behave as a single particle called a **molecule**. If the atoms are of different elements, as in water (H2O) or methane (CH₄), it is a molecule of a compound. If the atoms of the same element, it is a molecule of an element. Some common and important elements that occur in nature as molecules composed of two atoms are, hydrogen, H₂; oxygen, O₂, nitrogen, N₂; fluorine, F₂; chlorine, Cl₂; bromine, Br₂; and iodine, I₂.

A chemical equation is written to show the chemical changes that occur during a chemical reaction. In a sense, it's a "before and after" description of the reaction. For example, the equation

$$\underbrace{Zn + S}_{reactants} \longrightarrow \underbrace{ZnS}_{product}$$

describes the reaction between Zinc (Zn) and Sulfur (S) to produce zinc sulfide (ZnS), a substance used on the inner surface of TV screens. The substances on the left of the arrow are called **reactants** and are the chemical present before the reaction takes place. Those on the right of the arrow are called the **products** and are the substance present after the reaction is over. (In the reaction above, there is only one product). The arrow is read as "react to yield" or simply "yield". Thus, the equation above can be read as "zinc plus sulfur react to yield zinc sulfide" or "zinc plus sulfur yield zinc sulfide", or "zinc recta with sulfur to yield zinc sulfide."

Sometimes it is necessary to indicate whether the reactants and the products are solids, liquids, gases, or dissolved in solvent such as water. This is done by placing the letters s = solid, l = liquid, g = gas, or aq = aqueous (water) solution in parentheses following the formula of substances in the equation. For instance, the equation

$$C a C O_3 (s) + H_2 O (l) + C O_2 (g) \longrightarrow C a (H C O_3)_2 (aq)$$

Many of the equations that we write contain numbers, called **coefficients**, preceding the chemical formulas. An example is the reaction of hydrogen (H_2) with oxygen (O_2) to form water.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Such equation is said to be **balanced** because it contains the same number of atoms of each element on both sides of the arrow. A coefficient of 1 is assumed if none is written.

LAWS OF CHEMICAL COMBINATION

DALTON'S ATOMIC THEORY AND ATOMIC MASSES

POSTULATIONS OF DALTON'S ATOMIC THEORY AND ATOMIC MASSES

- 1- Matter is composed of tiny indivisible particles called atoms.
- 2- All atoms of a given elements are identical, but differ from elements to other elements.
- 3- A chemical compound is composed of the atoms of its elements in a definite fixed numerical ratio.
- 4- A chemical reaction merely consists of a reshuffling (rearrangements) of atoms from one set of combinations to another. The individual atoms themselves however, remain intact and do not change.

Atomic masses

The law of definite proportions is easy to explain. Let's imagine that two elements, say A and B, form a compound in which each molecule of the substance is composed of one atom of A and one atom of B. Let's also suppose that an atom of A is twice as heavy as atom of B, so if an atom of B were arbitrary assigned a mass of 1 unit, then the mass of an atom A would be 2 units. Below we see how the masses of A and B vary for various numbers of molecules.

Number of Molecules	Number of Atoms of	Mass of A	Number of Atoms B	Mass of B	Mass Ratio, (mass A/ (mass B)
1	1	2 units	1	1 unit	2/1
2	2	4 units	2	2 units	4/2 = 2/1
10	10	20 units	10	10 units	20/10 = 2/1
500	500	1000 units	500	500 units	1000/500 =
					2/1

Now, notice that no matter how may molecules we have, each with the same 1- to 1- ratio by atoms, *the ratio by mass is the same*. This is exactly what the law of

definite proportions says: In any sample of compound, regardless of sise, the elements are always present in the same proportion (ratio) by mass.

Atomic masses

Because atoms are too small to be seen and too small to have their masses measured individually on laboratory balance in a unit of grams, an atomic mass scale was devised in which mass is measured in **atomic mass units** (the SI symbol is \mathbf{u}).

The atomic mass unit is defined as 1/12th of the mass of atom of carbon-12 isotope. The atomic masses of elements are given along with the symbols of the elements in the periodic table. The numbers in these table are relative average atomic masses, expressed in atomic mass units.

The law of multiple proportions

The law of multiple proportions can be expressed as follows: "Suppose we have samples of two compounds formed by the same two elements. If the masses of one elements are the same in the two samples, then the masses of the other elements are in a ratio of small whole numbers. This can be understand by the following example. We know that carbon forms two different compounds with oxygen called carbon monoxide and carbon dioxide. In 2.33 g of carbon monoxide, we find 1.33 g of oxygen combined with 1.00 g of carbon. Notice that the masses of oxygen that are combined with the same mass of carbon (1.00 g) are in a ratio of 2 to 1 (a ratio of small whole numbers).

$$\frac{2.66\,\mathrm{g}}{1.33\,\mathrm{g}} = \frac{2}{1}$$

The result is consistent with the atomic theory if a molecule of carbon monoxide (CO) contain 1 atom of C and 1 atom of O, and a molecule of carbon dioxide (CO₂) contain 1 atom of C and 2 atoms of O, so the ratio of the oxygen masses has to be 2 to 1.

The mole concept

As we've learned, atoms react to form molecules in simple-whole-number ratio. Carbon and oxygen atoms, for instance, combine in 2 to 1 ratio to form carbon monoxide (CO)

We really can't work with individual atoms because they are so tiny., so we must increase the sizes of the samples to the point where we can see them and manipulate them, but we do this in a way that maintains the proper ratio of atoms.

One way we could enlarge amounts in a chemical reaction would be to work with dozens of atoms instead of individual atoms.

A dozen atoms or molecules is still much too small to work with, so we must find a larger unit. The "chemist's dozen" is called the <u>mole</u> or (<u>mol</u>, for abbreviation) is a larger unit to be used instead of using a dozen atoms or molecules.

1 dozen = 12 objects
1 mol =
$$6.022 \times 10^{23}$$
 objects

The atomic weight of carbon to four significant figures is 12.01 atomic mass unit **(amu) or (u)**. How many atoms are in 12.01 g of carbon? Modern experimental methods show that this number of atoms is 6.022×10^{23} . This huge number is called **Avogadro's number**, named in honor of Amadeo Avogadro, the brilliant contemporary of Dalton. The weight of 6.022×10^{23} atoms of oxygen is 16.00 g; the weight of 6.022×10^{23} molecule of carbon monoxide (CO), is 28.01 g; and the weight of 6.022×10^{23} molecule of carbon dioxide (CO₂), is 44.01 g. a **mole** or (**mol**, for abbreviation) of a substance is the amount that contains 6.022×10^{23} units of substance.

Example: what is the mass of one atom of calcium?

Solution: we can restate the problem as

1 atom
$$Ca = (?) Ca$$

We have the relationships

$$6.02 \times 10^{23}$$
 atoms Ca = 1 mol Ca(to 3 significant figures)
1 mol Ca = 40.1 g Ca

The solution to the problem can be set up as

$$6.02 \times 10^{23}$$
 atom Ca

1 atom Ca x
$$\left(\frac{1 \text{ mol Ca}}{6.02 \text{ x } 10^{23} \text{ atom s Ca}}\right) \text{ x } \left(\frac{40.1 \text{ g Ca}}{1 \text{ mol Ca}}\right) = 6.66 \text{ x } 10^{-23} \text{ g Ca}$$

Example: How many moles of calcium (Ca) are required to react with 2.5 mole of chlorine (Cl) to produce the compound CaCl₂ (calcium chloride)?

Solution: we can restate the problem:

$$2.5 \text{ mol C1} \iff (?) \text{ mol Ca}$$

We know from the formula that 1 atom of Ca combines with 2 atoms of Cl. Thus,

Because moles combine in the same ratio as atoms

We can obtain the answer as follows:

2.5 mol
$$el X$$
 $\left(\begin{array}{c} 1 \text{ mol } Ca \\ \hline 2 \text{ mol } el \end{array}\right) \longleftrightarrow 1.25 \text{ mol } Ca$

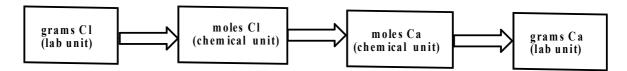
Example: How many grams of Ca must react with 41.5 g of Cl to produce CaCl₂?

Solution:

$$1 \text{ mol Ca} \iff 2 \text{ mol Cl}$$

$$1 \text{ mol Ca} = 41.1 \text{ g Ca}$$

Now we have all the information needed to solve the problem, but before we actually go to the solution, let's diagram how it will work.



we follow the outline above, being careful to set up the conversion factors so that units cancel correctly.

$$41.5 \text{ gCl X} \left(\frac{1 \text{ mol Cl}}{35.5 \text{ gCl}} \right) = 1.17 \text{ mol Cl}$$

1.17 mol Cl X
$$\left(\begin{array}{c} 1 \text{ mol Ca} \\ 2 \text{ mol Cl} \end{array}\right)$$
 0.585 mol Ca

$$0.585 \text{ mol Ca } X \left(\begin{array}{c} 40.1 \text{ g Ca} \\ \hline 1 \text{ mol Ca} \end{array} \right) = 23.5 \text{ g Ca}$$

Usually, we put all the three steps together as follows.

41.5 g e I X
$$\left(\begin{array}{c} 1 \text{ mol cl} \\ \hline 35.5 \text{ g e I} \end{array}\right)$$
 X $\left(\begin{array}{c} 1 \text{ mol ca} \\ \hline 2 \text{ mol cl} \end{array}\right)$ X $\left(\begin{array}{c} 40.1 \text{ g Ca} \\ \hline 1 \text{ mol ca} \end{array}\right)$ \rightarrow 23.5 g Ca to moles of Cl to moles of Ca

Example: How many moles of silicon, Si, are in 30.5 g of Si?

Solution: we know from the table of atomic masses that

$$1 \text{ mol Si} = 28.1 \text{ g Si}$$

To convert from Si to moles, we must multiply 30.5 g Si by a factor that contains the units "g Si" in the denominator, that is,

$$\frac{1 \, \text{mol Si}}{28.1 \, \text{g Si}}$$

Thus,

$$30.5 \text{ g Si X} \left(\frac{1 \text{ mol Si}}{28.1 \text{ g Si}} \right) = 1.09 \text{ mol Si}$$

Therefore, 30.5 g Si = 1.09 mol Si

Example: How many moles of carbon atoms are needed to combine with 4.87 mol Cl to form the substance C_2H_6 ?

Solution: Let's restate the problem as follows:

We have conversion factors to choose from

Of course, we would also simplify these ratio to give

To get rid of the units "mol Cl" we must use the one on the left.

$$4.87 \text{ mol Cl X} \left(\begin{array}{c} 2 \text{ mol C} \\ \hline 6 \text{ mol Cl} \end{array} \right) \Longleftrightarrow 1.62 \text{ mol C}$$

We need 1.62 mol C.

Example: How many moles of are in 2.65 mol C₂Cl₆?

Solution: our problem can be stated as

$$2.65 \text{ mol } C_2Cl_6 \iff ? \text{ mol } C$$

And then use it to construct the necessary conversion factor.

$$2.65 \text{ mol } C_2\text{Cl}_6 \text{ X} \qquad \left(\begin{array}{c} 2 \text{ mol } C \\ \hline 1 \text{ mol } C_2\text{Cl}_6 \end{array} \right) \iff 5.30 \text{ mol } C$$

Thus, 2.65 mol C₂Cl₆ contain 5.30 mol C.

Measuring moles of compounds: Molecular mass and formula mass

The simplest way of obtaining the weight of one mol of a substance is merely to add up the atomic masses of all the elements present in the compound. If the substance is composed of molecules (for example, CO, H₂O, or NH₃), the sum of the atomic masses is called the **molecular mass** (or **molecular weight**-the terms are used interchangeably). Thus, the molecular mass of CO2 is obtained as

Similarly , the molecular mass of $H_2O=18~u$ and that of $NH_3=17.0~u$. The weight of one mol of a substance is obtained simply by writing its molecular mass followed by the units, grams. Thus,

One mole samples of several different compounds, contains the same number of the **formula units**, although the number of atoms is different form sample to sample. They differ because the number of atoms per formula unit is different for each compound. *Atoms or groups of atoms that have acquired an electrical charge are called ions*. Since solid NaCl is composed of Na⁺ and Cl⁺ ions, it is said to be an **ionic compound.**

For ionic compounds, the sum of the atomic masses of the elements present in one formula unit is known as the **formula mass or formula weight.** For NaCl, this is 22.99 + 23.45 = 58.44.

Na	22.99 u
Cl	35.45 u
NaCl	58.44 u

One mole of NaCl (6.022×10^{23} formula units of NaCl) would contain 58.44 g NaCl. Use of terms formula mass, of course, is not restricted to ionic compounds. It can be applied to molecular substances, in which case the terms formula mass and molecular mass mean the same thing.

Example: sodium carbonate, has molecular formula Na₂CO₃

- (a) How many grams does 0.250 mol Na₂CO₃?
- (b) How many moles of Na₂CO₃ are in 132 g Na₂CO₃?

Solution: we calculate the formula mass of Na₂CO₃ from the atomic masses of its elements

2 Na		$2 \times 23.0 = 46.0u$
1 C		1 X 12.0 = 12.0 u
3 O		$3 \times 16.0 = 48.0 \text{ u}$
	Total	106.0 u

The formula mass is 106.0 u; therefore,

$$1 \text{ mol Na}_2\text{CO}_3 = 106.0 \text{ g Na}_2\text{CO}_3$$

This can be used to make conversion factors relating grams and moles of Na₂CO₃, which we need to answer the questions

(a) to covert 0.250 mol Na₂CO₃ to grams, we set up the units to cancel.

$$0.250 \text{ mot Na}_{2}CO_{3} X \left(\frac{106.0 \text{ g Na}_{2}CO_{3}}{1 \text{ mol Na}_{2}CO_{3}} \right) = 26.5 \text{ g Na}_{2}CO_{3}$$

(b) Again, we set the units to cancel.

$$132 \text{ g.Na}_{2}CO_{3} \times \left(\frac{1 \text{ mol Na}_{2}CO_{3}}{106.0 \text{ g.Na}_{2}CO_{3}}\right) = 1.25 \text{ mol Na}_{2}CO_{3}$$

Percentage composition: Percentage composition of a compound is that, the percentage of the total mass (also called the percent by weight) contributed by each element. The procedure to determine the percentage composition is illustrated in the following example.

Example: What is the percentage composition of chloroform, CHCl₃, a substance once used as an anesthetic?

Solution: the total mass of 1 mol of CHCl₃ is obtained from the molecular mass

$$12,01 u + 1.008 u + 3 X 35.45 u = 119.37 u$$

Or for 1 mol of CHCl₃,

$$12,01 \text{ g} + 1.008 \text{ g} + 3 \text{ X} 35.45 \text{ g} = 119.37 \text{ g}$$

In general,

% by weight =
$$\frac{\text{weight of part}}{\text{weight of whole}} \times 100$$

Then,

$$\% C = \frac{\text{weight carbon}}{\text{weight CHCl}_3} \times 100$$

% C =
$$\frac{12.01 \text{ g C}}{119.37 \text{ g CHCl}_3}$$
 X 100 = 10.06 % C

% H =
$$\frac{1.008 \text{ g H}}{119.37 \text{ g CHCl}_3}$$
 X 100 = 0.844 % H

% Cl=
$$\frac{106.35 \text{ g Cl}}{119.37 \text{ g CHCl}_3}$$
 X 100=89.09 % Cl

Total
$$\% = 100.00$$

Example on calculating the percentage composition of the compound (percent mass)

Problem: Calculate the percentage composition of sodium sulfate whose formula is Na_2SO_4 (Atomic mass Na = 23, S = 32, O = 16), or: find the mass percent of each element of sodium sulfate (Na_2SO_4).

Solution:

Percent mass =
$$\frac{\text{weight of element (or atom)}}{\text{molecular mass (wt.) or of compound}} \times 100$$

Wt. of 2 Na = 2 X 23 = 46

Wt. of S = 32

Wt. of 4 O = 4 X 16 = 64

Molecular mass of $Na_2SO_4 = 46 + 32 + 64 = 142$

Percentage of Sodium (Na) =
$$\frac{46}{142}$$
 X 100 = 32.39%

Percentage of Sulfur (S) =
$$\frac{32}{142}$$
 X 100 = 22.54%

Percentage of Oxygen (O) =
$$\frac{64}{142}$$
 X 100 = 45.08%

$$Total = 32.39 + 22.54 + 45.08 = 100.0$$

Calculation of the mass of an element in a sample of compound

Example: calculate the mass of iron in a 10.0 g sample of iron oxide, Fe_2O_3 , commonly refereed to as rust

Solution: In one mole of this compound, there are 2 mol Fe and 3 mol O. Therefore,

2 Fe: 2 X 55.85 g = 111.7 g Fe
3 O:
$$3 \times 16.00 \text{ g} = 48.0 \text{ g} \text{ O}$$
this mass of Fe this mass of Fe QO₃ = 159.7 g Fe₂O₃ this mass of Fe₂O₃

We can write

111.7 g Fe
$$\iff$$
 159.7 g Fe₂O₃

$$10.0 \text{ g} \xrightarrow{\text{Fe}_2\text{O}_3 \text{ X}} \left(\begin{array}{c} 111.7 \text{ g} \text{ Fe} \\ \hline 159.7 \text{ g} \xrightarrow{\text{Fe}_2\text{O}_3} \end{array} \right) \Longleftrightarrow 6.99 \text{ g Fe}$$

Thus, in 10.0 g Fe₂O₃ there is 6.99 g Fe.

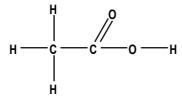
Chemical formulas

There are different kinds of chemical formulas, and each conveys certain kinds of information. This include the elemental composition, the relative numbers of each kind of atom present, the actual members of atoms of each kind in a molecule of the substance, or structure of a molecule of the substance.

A formula that uses the smallest set of whole-number-subscripts to specify the relative number of atoms of each element present in a formula unit is called **simplest formula**. It is also called an **empirical formula** because it is normally derived from the results of some experimental analysis. The formulas NaCl, H₂O, and CH₂ are empirical formulas.

A formula that states the actual number of each kind of atom found in a molecule is called a **molecular formula**. H_2O is a molecular formula (as well as an empirical formula) since a molecule of water contains 2 atoms of H and 1 atom of O. The formula C_2H_4 is a molecular formula for a substance (ethylene) containing 2 atoms of carbon and 4 atoms of hydrogen. The simplest formula CH2 is not unique to C2H4, however. A substance whose empirical formula is CH_2 could have as a molecular formula CH_2 , C_2H_4 , C_3H_8 , and so on.

A third type of formula is a **structural formula**, for example,



Acetic acid (present in vinegar)

In a structure formula the dashes between different atomic symbols represent the "chemical bonds" that bind the atoms to each other in the molecule. A structural formula gives us information about the way in which the atoms in a molecule are linked together and allow us to write the molecular and empirical formulas. Thus, for acetic shown above, we can write its molecular formula $(C_2H_4O_2)$ and its empirical formula (CH_2O) .

To calculate an empirical formula, we need to know the mass of each of the elements in a given mass of the compound.

Problems on calculating an empirical formula

Problem: A sample of a brown-colored gas that is a major air pollutant is found to contain 2.34 g of N and 5.34 g of O. What is the simplest formula of the compound?

Solution: We know that

Therefore,

$$2.34 \text{ g N } X \left(\frac{1 \text{ m ol N}}{14.0 \text{ g N}} \right) = 0.167 \text{ m ol N}$$

$$5.34 \text{ g O } X \left(\frac{1 \text{ m ol } 0}{16.0 \text{ g O}} \right) = 0.334 \text{ m ol } 0$$

We might write our formula $N_{0.167}O_{0.334}$. However, since the formula should have meaning on a molecular level where whole numbers of atoms are combined, the subscripts must be integers. If we divide each subscript by the smallest one we obtain

$$5.34 \text{ g O } X \left(\frac{1 \text{ mol } O}{16.0 \text{ g O}} \right) = 0.334 \text{ mol } O$$

$$N_{\frac{0.167}{0.167}}O_{\frac{0.334}{0.167}} = NO_2$$

Example on calculating an empirical formula from percentage composition

Problem: what is the empirical formula of a compound composed of 43.7% P and 56.3% O by weight?

Solution: We imagine having a 100-g sample of the compound. From the analysis, this sample would contain 43.7 g P and 56.3 g O (notice that the percents become grams of compound). We know that

We convert the masses to moles

43.7 g P X
$$\left(\frac{1 \text{ mol P}}{31.0 \text{ g P}}\right) = 1.41 \text{ mol P}$$

56.3 g O X $\left(\frac{1 \text{ mol O}}{16.0 \text{ g O}}\right) = 3.52 \text{ mol O}$

The formula is

$$P_{1.41}O_{3.52} = P_{\underbrace{1.41}_{1.41}}O_{\underbrace{3.52}_{1.41}} = PO_{2.50}$$

Whole numbers can be obtained by doubling each of the subscripts. Thus, the empirical formula is P_2O_5 .

Problem on determining the empirical formula from a chemical analysis

Problem: 1.025-g sample of a compound that contains carbon and hydrogen was burned in oxygen to give carbon dioxide and water vapor as products. These products were trapped separately and weighed. It was found that 3.007 g of CO₂ and 1.845 g H₂O were formed in this reaction. What is the empirical formula of the compound?

Solution: in 1 mol CO_2 (44.01 g), there is 1 mol (12.01 g) of C. In the 3.007 g of CO_2 , therefore, the mass of carbon is

$$3.007 \text{ g CO}_2 \text{ X} \left(\frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} \right) \Leftrightarrow 0.8206 \text{ g C}$$

Similarly, in 1 mol of H_2O (18.02 g), there are 2 mol (2.016 g) of H, so the mass of H in the 1.845 g of H_2O is

1.845 g H₂O X
$$\left(\frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}}\right) \Leftrightarrow 0.2064 \text{ g H}$$

Now we have the masses of C and H in the sample, so we can calculate the number of moles of each,

and

$$0.8206 \text{ g C X} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 0.06833 \text{ mol C}$$

$$0.2064 \text{ g H X} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 0.2048 \text{ mol H}$$

Now we determine the subscripts:

$$C_{0.06833}H_{0.2048}$$

Dividing by the smallest value (0.06833)

$$C_{\frac{0.06833}{0.06833}}H_{\frac{0.2048}{0.06833}}$$

gives C₁H_{2.977}. The empirical formula, therefore, is CH₃.

Problem on determining the empirical formula from a chemical analysis

Problem: A 0.1000-g sample of ethyl alcohol, known to contain only carbon, hydrogen, and oxygen, was burned completely in oxygen to form the products CO_2 and H_2O . These products were trapped separately and weighed; 0.1910 g CO_2 and 0.1172 g H_2O were found. What is the empirical formula of this compound?

Solution: First we calculate the mass of carbon and hydrogen in the CO_2 and H_2O .

$$0.1910 \text{ g CO}_2 \text{ X} \left(\frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} \right) \Leftrightarrow 0.05212 \text{ g C}$$

$$0.1172 \text{ g H}_2\text{O } \text{ X} \left(\frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}} \right) \Leftrightarrow 0.0131 \text{ g H}$$

When we add the masses of C and H, we get a total of 0.06523 g, so the mass of oxygen in the sample must have been

Mass of O = (mass of sample)- (total mass of C and H)
=
$$0.1000 \text{ g} - 0.06523 \text{ g} = 0.0348 \text{ g O}$$

Now we convert the masses of C, H, and O to moles of each of the element. Thus, for carbon we have

$$0.05212 \text{ g.C/X} \left(\frac{1 \text{ mol C}}{12.01 \text{ g.C}} \right) = 0.04340 \text{ mol C}$$

Similar calculation for other two elements give 0.0130 mol H and 0.00218 mol O. This empirical formula is therefore

$$C_{0.00434}H_{0.0130}O_{0.00218}=C_{\underbrace{0.0434}_{0.00218}}H_{\underbrace{0.0130}_{0.00218}}O_{\underbrace{0.00218}_{0.00218}}$$

Dividing we get $C_{1.99}H_{5.96}O_1$, which rounds to C_2H_6O .

Molecular formulas

It is possible for more than one compound to have the same empirical formula. For example, the molecules C_2H_4 , C_3H_6 , and C_5H_{10} all have a 1-to-2 ratio of carbon to hydrogen atoms and the empirical formula CH_2

Molecular formula = (Empirical formula) X n

$$n = \frac{Molecular mass (Formula mass (FM.))}{Empirical mass}$$

<u>Table: molecular masses as multiple</u> <u>of the empirical formula mass</u>

Formula	Molecular mass
CH ₂	$14.0 = 1 \times 14.0$
C_2H_4	28.0 = 2 X 14.0
C_3H_8	$42.0 = 3 \times 14.0$

C_4H_8	$56.0 = 4 \times 14.0$
C_nH_{2n}	n X 14.0

Ionic compounds don't have molecular formulas because they don't contain molecules.

Example on determining the molecular formula of a compound

Problem: A colorless liquid used in rocket engines, whose empirical formula is NO₂, has a molecular mass of 92.0. What is its molecular formula?

Solution:

$$n = \frac{\text{Molecular mass (Formula mass (FM.))}}{\text{Empirical mass}}$$

The empirical mass of NO_2 is 46.0. the number of times the empirical formula, NO_2 , occurs in the compound is

$$\frac{92.0}{46.0} = 2$$

The molecular formula is the $(NO_2)_2 = N_2O_4$ (dinitrogen tetroxide). N_2O_4 is the preferred answer because $(NO_2)_2$ implies a knowledge of the structure of the molecule (i.e., that two NO_2 units are somehow joined together).

CHAPTER 3

CHEMICAL REACTIONS AND THE MOLE CONCEPT

3.1 Chemical Reactions and Chemical Equations

We recall that a chemical equation is written to show the chemical changes that occur during a chemical reaction. In a sense, it's a "before and after" description of the reaction. For example, the equation

$$Zn + S$$
reactants
 ZnS
product

describes the reaction between Zinc (Zn) and Sulfur (S) to produce zinc sulfide (ZnS), a substance used on the inner surface of TV screens. The substances on the left of the arrow are called **reactants** and are the chemical present before the reaction takes place. Those on the right of the arrow are called the **products** and are the substance present after the reaction is over.

In order to write an equation, we must be able to write the formulas of the reactants.

If an experiment has just been carried out, the equation might be meant to describe what has just occurred in a chemical reaction. In this case, the reactants are known because the chemist knows what chemicals were placed in the vessel. The products, however, must be collected and identified (by a chemical analysis, for example) before a valid equation can be written.

Often we write chemical equations to help us plan experiments. One way that chemical equations are particularly useful in planning experiments is that they allow us to determine the quantitative relationships that exist among the amounts of reactants and products. To be helpful in this way, however, chemical equations must be **balanced**, which means that they must obey the law of conservation of mass by having the same number of atoms of each kind on both sides of the arrow.

Balancing chemical equations

In order to minimize errors, writing a balanced equation should always be viewed as two-step process.

- Step 1. First write an unbalanced equation, being careful to write the correct formula for each substance involved.
- Step 2. Balance the equation by adjusting the coefficients that precede the formula of the reactants and products so that there are the same number of atoms of each kind on both sides of the arrow.

It is very important to remember that in carrying out step 2, you must not alter the formulas of the reactants or products

For example, consider the reaction between hydrochloric acid (HCl) and sodium carbonate (Na₂CO₃). The product of the reaction are sodium chloride (NaCl), gaseous carbon dioxide (CO₂) and water.

To obtain the balanced equation for the reaction, we proceed as follows.

Step 1. Write the unbalanced equation, being sure to give the correct formulas for the reactants and products.

$$Na_2CO_3 + HCI \rightarrow NaCI + H_2O + CO_2$$

Step 2. Place coefficients in front of chemical formulas to balance the equation. Although there are no set rules to tell you where to start, it is often best to seek out the most complex formula in the equation and begin there by given it coefficient 1. in this case, we start with the Na₂CO₃. there are two atoms of Na in this formula, so to balance the Na we need to place a coefficient 2 in the front of NaCl on the right. This gives

$$Na_2CO_3 + HCl \rightarrow 2 NaCl + H_2O + CO_2$$

Although this balances the Na, it cause the Cl to become out of balance, but we can correct this by placing a 2 in the front of HCl on the left.

$$Na_2CO_3 + 2HCl \rightarrow 2 NaCl + H_2O + CO_2$$

Notice that this also brings hydrogen into balance, and a quick counts for each elements reveals that the equation is now balanced.

Example on balancing an equation by inspection

Problem: Balance the following equation for the combustion of octane, C_8H_{18} , which is a compound of gasoline:

$$C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$$

Solution: First, we assign C_8H_{18} (the most complex formula) a coefficient of 1. Next, we see that we need to have $8CO_2$ on the right to balance the carbon and 9 H_2O on the right to balance the hydrogen (9 H_2O contain 18 H atoms because each H_2O contains 2 H atoms). This gives

$$C_8H_{18} + O_2 \rightarrow 8CO_2 + 9H_2O$$

Now we can work on the oxygen. On the right there are 25 O atoms (2 X 8 + 9 = 25). On the left the oxygen (O) atoms come in pairs. This means that we must have $12\frac{1}{2}$ pairs (O₂ molecules)to have 25 O atoms on the left. This gives us

$$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$$

Finally, we can eliminate the fractional coefficient by doubling each coefficient.

$$2 C_8 H_{18} + 25 O_7 \rightarrow 16 CO_7 + 18 H_2 O_7$$

3.2 Calculations based on chemical equations

A chemical equation can be interpreted in several ways. Consider, for example, the balanced equation for the combustion of ethanol, C2H5OH, the alcohol that's blensed with gasoline in the fuel known as gasohol.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

On a molecular, submicroscopic level, we can view this as a reaction between individual molecules. But we can just as easily scale this up to lab-sized amounts by applying the same mole ratio.

The coefficient in a chemical equation provide the ratios by which moles of one substance react with or form moles of another.

For example, the equation for combustion of C_2H_5OH gives six chemical equivalents that we can use to form conversion factors for calculations.

$$1 \bmod C_2H_5OH \Leftrightarrow 3 \bmod O_2$$

$$1 \bmod C_2H_5OH \Leftrightarrow 2 \bmod CO_2$$

$$1 \bmod C_2H_5OH \Leftrightarrow 3 \bmod H_2O$$

$$3 \bmod O_2 \Leftrightarrow 2 \bmod CO_2$$

$$3 \bmod O_2 \Leftrightarrow 3 \bmod H_2O$$

$$2 \text{ mol CO}_2 \Leftrightarrow 3 \text{ mol H}_2\text{O}$$

Let's look at some examples that illustrate how we use this information in a chemical calculation.

Example 3.2. using a chemical equation in a calculation involving moles

<u>Problem</u>: How many moles of oxygen are needed to burn 1.80 mol C₂H₅OH according to the balanced equation

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Solution: the coefficient of the equation gives us the relationship

$$1 \text{ mol } C_2H_5OH \Leftrightarrow 3 \text{ mol } O_2$$

Which we can use for a conversion factor. We set up arithmetic so the units mol C_2H_5OH cancel

$$1.8 \text{ mol } C_2H_5OH \times \left(\frac{3 \text{ mol } O_2}{1 \text{ mol } C_2H_5OH}\right) \Leftrightarrow 5.40 \text{ mol } O_2$$

We need 5.40 mol O₂.

Example 3.3. Using a chemical equation in a calculation involving moles

Problem: How many moles of CO₂ will be formed when 0.274 mol C₂H₅OH burns?

Solution: Now we look at the coefficient for C₂H₅OH and CO₂, which give us

1 mol
$$C_2H_5OH \Leftrightarrow 2 \mod CO_2$$

Then we set up the arithmetic to get the proper units in the answer.

$$0.274 \text{ mol-} C_2H_5OH \times \left(\frac{2 \text{ mol CO}_2}{1 \text{ mol-} C_2H_5OH}\right) \Leftrightarrow 5.48 \text{ mol CO}_2$$

Example 3.4. Using a chemical equation in a calculation involving moles

Problem: How many moles of water will form when 3.66 mol CO_2 are produced during the combustion of C_2H_5OH ?

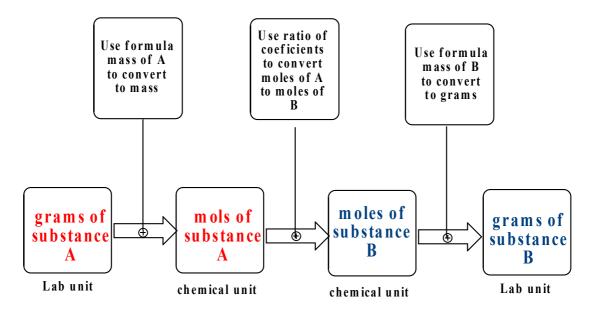
Solution: the coefficients in the equation tell us that

$$2 \text{ mol CO}_2 \Leftrightarrow 3 \text{ mol H}_2\text{O}$$

Therefore,

$$3.66 \text{ mol-} CO_2 \times \left(\frac{3 \text{ mol } H_2O}{2 \text{ mol } CO_2}\right) \Leftrightarrow 5.49 \text{ mol } H_2O$$

General way to tackle stoichiometry problems that involve a chemical reaction.



A diagram showing in a general way to tackle stoichiometry problems that involve a chemical reaction.

Example 3.5. Using a chemical equation in a calculation involving grams

Problem: Aluminum react with oxygen to aluminum oxide Al₂O₃, as shown below

$$4 \text{ Al} + 3 \text{ O}_2 \rightarrow 2 \text{ Al}_2 \text{O}_3$$

How many grams of O_2 are required to react with 0.300 mol Al?

Solution: we restate the problem as

$$0.300 \, \text{mol Al} \Leftrightarrow ? \, \text{g O}_2$$

The balanced equation provide a path between moles of Al and moles of O₂.

$$4 \text{ mol Al} \Leftrightarrow 3 \text{ mol O}_{2}$$

We know that

$$1 \text{ mol O} \Leftrightarrow 32.0 \text{ g O}_2$$

$$0.300 \text{ mol Al } X \left(\frac{3 \text{ mol } O_2}{4 \text{ mol Al}} \right) X \left(\frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} \right) \Leftrightarrow 7.20 \text{ g } O_2$$

We need 7.20 g O2 to react with 0.300 mol Al.

Example 3.6. Using a chemical equation in a calculation involving grams

Problem: Aluminum react with oxygen to aluminum oxide Al₂O₃, as shown below

$$4 \text{ Al} + 3 \text{ O}_2 \rightarrow 2 \text{ Al}_2 \text{ O}_3$$

Calculate the number of grams of Al_2O_3 that could be formed if 12.5 g O_2 react completely with aluminum.

Solution: we can restate the problem in equation form

$$12.5 \text{ g O2} \Leftrightarrow ? \text{ g Al}_2\text{O}_3$$

The central route we have to follow

$$3 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } Al_2O_3$$

The three relationships needed to solve the problem are

$$1 \operatorname{mol} O_2 \Leftrightarrow 32.0 \operatorname{g} O_2$$

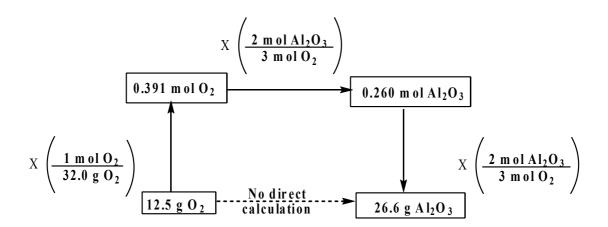
$$3 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } Al_2O_3$$

$$1 \operatorname{mol} \operatorname{Al}_2 O_3 \Leftrightarrow 102 \operatorname{g} \operatorname{Al}_2 O_3$$

We use them to construct conversion factors and arrange them so that the units cancel correctly.

$$12.5 \text{ g O}_2 \text{ X} \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) \text{X} \left(\frac{2 \text{ mol Al}_2 \text{O}_3}{3 \text{ mol O}_2} \right) \text{X} \left(\frac{102 \text{ g Al}_2 \text{O}_3}{1 \text{ mol Al}_2 \text{O}_3} \right) \Leftrightarrow 26.6 \text{ g Al}_2 \text{O}_3$$

The following diagram summarizes the steps involved.



3.3 Theoretical yield and percentage yield

<u>The theoretical yield</u> of a given product is the maximum yield that could be obtained if the reactants gave only that product with no side reactions.

The actual vield: is the amount of product actually obtained in a given experiment

The percentage yield is a measure of the efficiency of the reaction and is defined as

percentage yield =
$$\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Example: 3.48 g of CO_2 was obtained when 1.93 g a mixture of ethylene (C_2H_4) and 5.92 g O_2 is ignited according to the following equation. Calculate the percentage yield of CO_2

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Solution:

percentage yield of
$$CO_2 = \frac{3.48 \text{ g CO}_2}{5.43 \text{ g CO}_2} \text{ X } 100\%$$

= 64.1%

3.4 Reaction in solution

In many chemical reactions, one or more of the reactants are present in **solution-that is are dissolved in some fluid such as water**. In bodies, for instance, nutrients are dissolved in blood and are carried to our cells where they undergo the complex chain of reaction called metabolism.

Terminology applied to solutions

Molar concentration: Molarity(*M***)** this is defined as the number of moles of solute in the solution divided by the volume of the solution expressed in liters.

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

 $M = \text{mol}/L$ or $= \text{mmol}/L$

Example: Calculate the molarity of 2.0 L solution that contains 10 moles of NaOH.

Solution:

molarity
$$(M) = \frac{10}{2} = 5 M$$

Example: What is the molarity of a solution that has 18.23 g HCl in 2.0 L?

Solution:

- a) Mol.wt. of HCl = 1.0 + 35.5 = 36.5 g/mol
- b) Number of moles of HCl = 18.23 g HCl / 36.5 = 0.5 mol
- c) Molarity of HCl = 0.5 mol / 2.0 L = 0.25 M

Example: A 2.00-g sample NaOH, was dissolved in water to give a solution with a volume of exactly 200 mL. What is the molarity of NaOH in solution?

Solution:

The formula mass of NaOH is 40.0 g/ mol, so

$$2.00 \text{ g NaOH X} \left(\frac{1 \text{ mol NaOH}}{40 \text{ g NaOH}} \right) = 0.0500 \text{ mol NaOH}$$

When expressed in liters, 200 mL becomes 0.200 L. The molarity is therefore

molarity =
$$\frac{0.0500 \text{ mol NaOH}}{0.200 \text{ L sol}}$$
$$= 0.25 \text{ mol NaOH / L}$$
$$= 0.250 M \text{ NaOH}$$

Example: How many milliliters of 0.250 *M* NaOH solution are needed to provide 0.0200 mol of NaOH?

Solution: We can restate the problem as

By choosing a conversion factor with "mol NaOH" IN denominator we get the answer

$$0.0200 \text{ mol NaOH X} \left(\frac{1000 \text{ mL soln}}{0.250 \text{ mol NaOH}} \right) \Leftrightarrow 80.0 \text{ mL soln}$$

Thus, if we measure out 80.0~mL of this solution, it will contain the desired 0.0200~mol of NaOH

Example: How many grams of NaOH are in 50.0 mL of 0.400 M NaOH solution?

Solution: We can restate the problem as

$$50.0 \, \text{mL soln} \Leftrightarrow ? \, \text{g NaOH}$$

First, we have to translate 0.400 M to the corresponding ratio of moles to volume.

$$0.400 M \text{ means} \frac{0.400 \text{ mol}}{1000 \text{ mL soln}}$$

Now we apply the ratio as a conversion factor to cancel "mL soln"

$$50.0 \text{ mL soln } X \left(\frac{0.400 \text{ mol NaOH}}{1000 \text{ mL soln}} \right) \Leftrightarrow 0.0200 \text{ mol NaOH}$$

The formula mass of NaOH is 40.0 g/mol. Therefore,

$$0.0200 \text{ mol NaOH X} \left(\frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) = 0.800 \text{ g NaOH}$$

Thus, 50.0 ml of 0.400 M NaOH contains 0.800 g NaOH.

Molal concentration: (Molality) (m) this is defined as the number of moles of solute in the solution divided by the volume of the solvent expressed in kilograms.

Example: What is the molality of solution that contains 330 g of CaCl2 per kilogram of solvent?

Solution:

m = number of moles of solute/ Kg of solvent = 3/1 = 3 molal solutiom CaCl₂

Example: How many grams of NaOH are needed to make 2 molal solution?

Solution:

So,

$$2 = \frac{\text{wt/40}}{1}$$

$$\therefore \text{ wt} = 80 \text{ g}$$

Equivalent weight and normality (N)

The normality (N) of a given solution is the number of equivalents of solute per one liter of solution.

N = number of equivalents of solute/ liter of solution N = equivalents / L

$$Normality = \frac{\begin{array}{c} \text{number of grams of solute} \\ \hline \\ 1 \, \text{Liter (L) of solution} \end{array}}$$

Normality =
$$\frac{\text{number of grams of solute}}{1 \text{ Liter (L) of solution}}$$

Equivalents: are the amounts of replaceable H⁺ or OH⁻ or valence

equivalent weight (eq. wt) =
$$\frac{\text{mol.wt}}{\text{valnce}(n)}$$

In case of acids: e.g
$$H_2SO_4$$
 eq.wt = $98/2 = 49$
In case of bases: e.g. $Ba(OH)_2$ eq. wt = $171/2 = 85.5$
In case of salts: e.g. $NaCl$ eq.wt = $58.5/1 = 58.5$
 $NaCO_3$ eq.wt = $106/2 = 53$

Examples: (1) Calculate the normality of solution containing 98.0 g of H_2SO_4 in 0.5 L solution?

Solution:

Normality (N) =
$$\frac{98/49}{0.5}$$
 = 4.0 eq / L

(2) How many grams of NaOH are required to prepare 2.00 L of 0.5 N solution?

Normality (N) =
$$\frac{\text{number of grams of solute}}{\text{1 Liter (L) of solution}}$$

$$0.5 = \frac{? g / 40}{2 L}$$

$$? g = 40 g$$

Thus, the number of grams of NaOH that required to prepare 2.00 L of 0.5 N solution is 40 g.

Interconversion between molarity and normality

$$N = n \times M$$

N = normality

N = valance

M = Molarity

Example: What is the normality of 2.3 molar HCl solution?

Solution: The valance of HCl = 1, because, the number of replaceable H^+ is 1 So,

$$N = 1 \times 2.3 = 2.3$$

Mole fractions

Is the ratio of number of moles of one component to the total number of moles of all components in the solution

$$X_{A} = \frac{n_A}{n_A + n_B + \dots + n_n}$$

 X_A = mole fraction of A

 n_A = number of moles of component A

 $n_A + n_B + \dots + n_n = total$ number of moles

Example: What is the mole fraction of ethyl alcohol (C_2H_5OH) and H_2O if 0.5 mol of ethyl alcohol and 1.5 mol of H_2O is mixed?

Solution:

$$X_{H_2O} = \frac{1.5}{0.5 + 1.5} = 0.75$$

$$X_{C_2H_5OH} = \frac{0.5}{0.5 + 1.5} = 0.25$$

Dilution of solutions

The process involves mixing a concentrated solution with additional solvent to give larger final volume is known as dilution. Throughout this process, the number of moles of the solute remains constant, and only the volume increases.

If we multiply a solution's molarity M by its volume V, we obtain the number of moles of the solute

$$M X V = \frac{\text{mol}}{\text{L}} X \text{L} = \text{mol}$$

Since the number of moles of solute stays the same during a dilution, the product of the final molarity and volume (M_IXV_I) must be equal to the product of the final molarity and volume (M_2XV_2) . This give the useful equation

$$M_1 \times V_1 = M_2 \times V_2$$

Example: What is the concentration of solution produced by diluting 100 mL of 1.5 M NaOH to 2 L?

Solution:

$$M_1 \times V_1 = M_2 \times V_2$$

(1 = Initial, 2 = Final)

$$M_1 = 1.5 M$$

 $M_2 = ?$
 $V_1 = 100 \text{ mL}$
 $V_2 = 2000 \text{ mL}$

$$1.5 \times 100 = M_2 \times 2000$$

 $M_2 = 0.075 M$

Example: How many milliliters of concentrated H_2SO_4 (18.0 M) are required to prepare 750 ml of 3.00 M H_2SO_4 solution?

Solution:

$$M_1 X V_1 = M_2 X V_2$$

$$M_1 = 18.0 M$$
 $M_2 = 3.00 M$ $V_1 = ?$ $V_2 = 750 \text{ ml}$

Solving for V_1 gives

$$V_1 = \frac{M_2 \times V_1}{M_1}$$

$$V_1 = \frac{(3.00 \,M)(750 \,\mathrm{mL})}{18.0 \,M}$$

$$V_1 = 125 \,\mathrm{mL}$$

To prepare the solution, we dilute 125 mL of the concentrated $H_2\mathrm{SO}_4$ to a total final volume of 750 mL.

Example: How much water must be added to 25.0 mL of 0.500 M KOH solution to produce a solution whose concentration is 0.350 M?

Solution:

$$M_1 \ X \ V_1 = M_2 \ X$$
 V_2
 $M_1 = 0.500 \ M$
 $V_1 = 25.0 \ \text{mL}$
 $M_2 = 0.350 \ M$
 $V_2 = ? \ \text{ml}$

$$M_1 = 0.500 M$$
 $M_2 = 0.350 M$
 $V_1 = 25.0 \text{ mL}$ $V_2 = ? \text{ ml}$

Solving for V_1 and substituting, we get

$$V_2 = \frac{(0.500 \,M)(25.0 \,\mathrm{mL})}{0.350 \,M}$$

$$V_2 = 37.5 \,\mathrm{mL}$$

Since the initial volume was 35 mL, we must add 10.7 mL water to get final volume 37.5 mL of 0.350 M concentration.

CHAPTER 4

THE PERIODIC TABLE AND SOME PROPERTIES OF THE ELEMENTS

4.1 Some properties of the elements

One of the simplest methods of classification of elements is to divide the elements into three categories: **metals**, **nonmetals** and **metalloids**. The elements in each of these categories have distinctive characteristics.

Metals

More than 70% of the elements are metals, some examples are iron (Fe), aluminum (Al), copper (Cu). Chrome (Cr) gold (Au), lead (Pb), sodium (Na)---etc. They have distinctive appearance, shiny with a luster. They have abilities to deform without breaking when hit with hammer and to stretch when pulled. The ability to deform when hammered is called **malleability**. The ability of metal to stretch when pulled from the opposite directions is called **ductility**.

Metals are good conductors of electricity. They are also good conductors of heat. Some metals are very reactive like sodium, while other like gold are very unreactive. Some metal are very hard, and other are very soft. Chromium (Cr) and iron (Fe) are example of hard metals; gold and lead are example of soft ones. Sodium is also a soft metal. The extremes of melting point are even more impressive. Tungsten has the highest melting point of any element, 3400 OC. Mercury has the lowest point of any metal, -38 OC. Mercury is fluid at room temperature, commonly used in thermometers.

Nonmetals

Just as the properties of metals cover a broad range, so do the properties of nonmetals. As we've seen some, are gases, like oxygen (O), nitrogen (N), hydrogen (H), fluorine(F), chlorine(Cl), helium (He), neon (Ne), argon (Ar). One is liquid (bromine) (Br). Some are solid, like carbon C, and iodine (I).nonmetals differ from each other in their chemical properties. Fluorine, for example, is extremely reactive, while helium is inert (totally unreactive)

Metalloids

Metalloids (also called semimetals) are elements that have properties between those of metals and those of nonmetals. The best-known example is the element silicon. Two others are arsenic (As) and antimony (Sb).

Metalloids are typically semiconductors-they conduct electricity, but not nearly as well as metals.

4.2 The first periodic table

In 1869 a Russian chemist Dimitri Mendeleev and Lothar Meyer, a German independently published arrangements of known elements that closely resemble the periodic table of elements in use today. Mendeleev's classification was based primarily on chemical properties of elements, while Meyer's classification was based largely on physical properties. The tabulations were surprisingly similar and both emphasized the periodicity, or regular periodic repetition, of properties with increasing with atomic weight. Mendeleev discovered that if he arranged the elements in order of increasing atomic mass, elements with similar properties occurred at periodic intervals.

When Mendeleev constructed his table, not all the elements had yet been discovered. He realized this because in order to always have similar elements in the same column, or group, he was forced to leave occasional blanks in his table.

4.3 The modern view of the atom

Dalton's vision of atoms as indivisible particles in known now to be incorrect. Experiments begun in the late of 19th century and continued to the present day have shown that atoms are themselves composed of still simpler *subatomic* particles. Many such particles have been discovered. The principal ones-those most important to us- are called **protons**, **neutrons**, and **electrons**.

Some properties of these subatomic particles are shown in the following table

	Mass		Cha	ırge
	Grams	Atomic Mass	Coulombs	Electronic
		units (u)		charge
Proton	1.67 X 10 ⁻²⁴	1.007276	+ 1.602 X 10	1+
Neutron	1.67 X 10 ⁻²⁴	1.008665	0	0
Electron	9.11 X 10 ⁻²⁸	0.0005486	-1.602 X 10 ⁻¹⁹	1-

<u>Table 4.1. Some properties of subatomic particles</u>.

The concept of an **atomic nucleus** should be familiar to anyone. The nucleus is the name given to the extremely small and very dense particle that experiments have shown is located at the center of every atom.

Protons and neutrons are found in the nucleus at the center of an atoms. Electrons fill the space around the nucleus.

The number of protons in the nucleus, which is referred to as an atom's **atomic number**, determines the number of electrons that the atom must have in order to be electrically neutral. The **mass number of an atom** is determined primarily by the number of protons and neutrons in its nucleus, each of which contributes approximately one atomic mass unit.

mass number = number of protons + number of neutrons = atomic number + neutron number Mass number are always integral numbers.

<u>Isotopes</u>

As mentioned before, not all atoms of the same element have identical masses as first suggested by Dalton. It is referred to these different kinds of atoms as **isotopes**. The existence of isotope is a common phenomenon, and most of the elements occur naturally as mixtures of isotopes.

A particular isotope of an element is identified by specifying its atomic number given the symbol Z, and its mass number A.

We represent an isotope symbolically by writing its mass number as a superscript and its atomic number as subscript, both preceding the atomic symbol.

$${}_{Z}^{A}X$$

For example, a carbon atom (Z = 6) that has 6 neutrons would be given the symbol ${}^{12}_{6}$ C. This is the carbon-12 isotope that is serves as the basis of the atomic-mass scale.

The mass number (Z) of normal hydrogen is 1, for deuterium 2, and for tritium 3, and the atomic number for each is 1, so, we can write their symbols as follows

Atomic numbers and the modern periodic table

When the elements are arranged in the periodic table in order of their atomic numbers, all the inconsistencies that had occurred in Medeleev's table disappear.

The periodic table that is used today is shown in the next separate sheet. The numbers printed above the chemical symbols are atomic numbers, and those below are atomic amass. Like Medeleev's table, it consists of a number of rows called **periods**, which are identified by Arabic numerals. The vertical columns are called **groups**, each containing a *family of elements*. The groups are identified by Roman numeral and letter, either A or B.

The groups labeled with the letter A (Groups IA through VIIA) and Group 0 are referred to collectively as the **representative elements**. Those labeled with the letter B (Groups IB through VIIB) plus Group VIII are called **transition element**

Finally, there are two long rows of elements placed just below the main part of the table. These elements, known as **inner transition elements**, actually belong in the body of the table.

4.4 Reactions of metals with nonmetals; the formation of ionic compounds

The reaction between sodium (Na) and chlorine (Cl) atoms to form sodium chloride (NaCl) is a clear example for the reactions of metals with nonmetals to form ionic compounds.

$$2 \text{ Na}_{(s)} + \text{Cl}_{2(g)} \rightarrow 2 \text{ NaCl}_{(s)}$$

When the reaction occurs, each atom of sodium loses one electron, which is transferred to chlorine atom. The loss of an electron leaves the particle with one more positive charge than negative charge. As a result, the sodium ion carries charge of 1+ and is written as Na+. When the chlorine atom gains an electron, it acquires an additional negative charge, so the chloride ion carries a charge of 1- and is written Cl. Because NaCl contains these ions, it is called an ionic compound.

Metal tend to react with nonmetals to form ionic compounds.

In these reactions, the metal atoms each lose one or more electrons and become positive ions, or **cations**, and the nonmetal atoms each gain one or more electrons and become negative ions, or **anions**.

The strong electrostatic forces of attraction among ions in ionic compounds account for their relatively high melting points. According to Coulombs's Law, the force of attraction, F, between two oppositely charged particles of charge magnitude q is directly proportional to the product of the charges and inversely proportional to the square of the distance separating them, r.

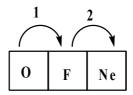
$$F \propto \frac{q^+ q^-}{r^2}$$

Table 4.2 lists the ions formed by most of representative elements. Notice first that the atoms in any particular group form ions with the same charge.

Table 4.2. Ions formed by the representative elements

Group number						
IA	IIA	IIIA	IVA	VA	VIA	VIIA
Li ⁺	Be ²⁺		C ⁴⁻	N ³⁻	O ²⁻	F1 ⁻
Na ⁺	Mg^{2+}	Al^{3+}	Si ⁴⁻	P ³⁻	S ²⁻	Cl
K ⁺	Ca ²⁺				Se ²⁻	Br ⁻
Rb ⁺	Sr ²⁺				Te ²⁻	I-
Cs ⁺	Ba ²⁺					

We can use the periodic table to help us remember the ions formed by the nonmetals. The number of negative charges is just the number of step to the right that you have to go in the table to get the noble gas column. Consider oxygen, for example. It is in Group VIA, and to get the noble gas column requires moving two steps to the right.



Oxygen forms an ion with a negative *two* charge, O^{2-} . Similarly, to move from fluorine to the noble gas column is just one step, and fluorine forms the ion F^{-} .

The ions formed by the transition metals is different from that formed by representative elements, because the transition elements to form more than one ion. Some of these ions are listed in Table 4.3.

Table 4.3. cations formed by some transition elements

Chromium	Cr ²⁺	Gold	\mathbf{Au}^{+}
	Cr ³⁺		Au ³⁺
Manganese	Mn ²⁺	Zinc	\mathbf{Zn}^{2+}
	Mn ³⁺ Fe ²⁺	Cadmium	Cd ²⁺
Iron		Mercury	Hg ⁺ Hg ²⁺ Sn ²⁺
	Fe ³⁺		Hg^{2+}
Cobalt	Co ²⁺	Tin	Sn ²⁺
	Co ³⁺		Sn ⁴⁺
Nickel	Ni ²⁺	Lead	Pb ²⁺
Copper	Cu ⁺		Pb ⁴⁺
	Cu ²⁺	Bismuth	Bi ³⁺
Silver	\mathbf{Ag}^{+}		

Rules for writing formula for ionic compounds

- 1. The positive ion is always written first in the formula.
- 2. The ratio of positive ions to negative ions must be such that the total number of positive charge equals the total number of negative charges; the formula unit must be electrically neutral.
- 3. The smallest set of subscripts that give electrical neutrality is always chosen. We always write empirical formulas for ionic compounds.

The reason for the third rule is that there are no molecules in an ionic compound. Each positive ion is surrounded by and attracted equally to some number of negative ions, and vice versa, so we can't say that any particular positive ions belongs to any particular negative ion. All we can do is specify the ratio in which the ions occur in the compound.

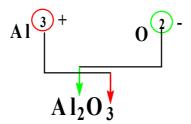
Let's look now at a few simple examples of how the rules are applied.

- 1. The compound formed from calcium and oxygen. Looking at the periodic table we see that calcium is in Group IIA, soothe calcium ion is Ca²⁺. Oxygen is a nonmetal in group VIA, so its ion is O²⁻.To make an electrically neutral compound, we take the ions in a 1-to-1 ratio, and the formula is CaO.
- 2. The compound formed from zinc and chlorine. Zinc is a transition metal and it forms the ion Zn²⁺. Chlorine is Group VIIA, so its ion is Cl⁻. To give an

electrically neutral compound, we must have two Cl^- for each Zn^{2^+} , so the formula is $ZnCl_2$.

3. The compound formed from of aluminum with oxygen. Aluminum forms Al^{3+} and oxygen forms O^{2-} . In the compound, we need a ratio of ions that makes the total positive and negative charges the same. This requires that we take two Al^{3+} ions for every three O^{2-} ions, because

There is a very simple shortcut that can use to obtain the formula of an ionic compound. It involves exchanging superscripts for subscripts.



Ions that contain more than one atom

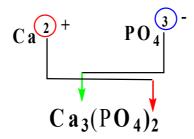
Some of most common polyatomic ions are given in table 4.4.

Table 4.4. Some common polyatomic ions

Cations			
NH ₄ ⁺			
H_3O^+			
	names in parentheses	s)	
CO_3^{2-}	Carbonate	ClO ₂	Chlorite
HCO ₃	Hydrogen	ClO (or OCl)	hypochlorite
	carbonate		
	(bicarbonate)		
C ₂ H ₄ ²⁻ CN ⁻	Oxalate	PO ₄ ³⁻ HPO ₄ ²⁻	Phosphate
CN-	Cyanide	$\mathrm{HPO_4}^{2-}$	Hydrogen
			phosphate
NO_3	Nitrate	H_2PO_4	Dihydrogen
			phosphate
NO_2	Nitrite	CrO ₄ ²⁻	Chromate
OH-	Hydroxide	$\operatorname{Cr_2O_7}^{2-}$	Dichromate
SO_4^{2-}	Sulfate	MnO ₄	Permanganate
HSO ₄	Hydrogen sulfate	$C_2H_3O^2$	Acetate
	(bisulfate)		
SO_3^{2-}	Sulfite		
HSO ₃	Hydrogen sulfite		
	(bisulfite)		
ClO ₄	Perchlorate		

61 6		
ClO_2^{-1}		
()()2		
CIO_3		

Writing the formula for a compound that contains a polyatomic ions follows the same rules that we've applied in the previous discussion. The only difference is that when two or more of the polyatomic ions occur in the formula, the formula for the ion is enclosed in parentheses. Thus, the compound composed of Ca^{2+} and PO_4^{3-} has the formula $Ca_3(PO_4)_2$:



4.5. Reactions of nonmetals with each other; the formation of molecular compounds

The nonmetals react not only with metals but also with each other. However, when two nonmetals combine to form a compound, electrically neutral molecules are formed instead of ions. An example of such a reaction occurs between oxygen and hydrogen to form water.

$$2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2 O_{(l)}$$

The number of compounds formed among the nonmetals is enormous. There are millions of organic compounds, for example, whose molecules are composed chiefly of carbon and hydrogen, but that often contain other nonmetals as well (principally oxygen, nitrogen, sulfur, and the halogens).

Table 4.5. Simple hydrogen compounds of the nonmetals

Group IVA	Group VA	Group VIA	Group VIIA
CH ₄	NH ₃	H ₂ O	HF
SiH ₄	PH ₃	H_2S	HC1
GeH ₄	AsH ₃	H ₂ Se	HBr
	SbH ₃	H ₂ Te	HI

Simple compounds of the nonmetals with oxygen

Finding correlations between the formulas of nonmetal oxides and the positions of the nonmetals in the periodic table isn't easy as with hydrogen compounds because so many of these elements form more than one oxide. Nitrogen, for example, forms N2O, NO, NO2, N2O3, N2O4, and N2O5. Nevertheless, there are some similarities within groups of elements that are listed by oxides listed in Table 4.6.

Table 4.6. Empirical formulas of some oxides of nonmetals

Group IIIA	Group IVA	Group VA	Group VIA
B_2O_3	CO_2	N_2O_3	-
		N_2O_5	
	SiO ₂	P_2O_3	SO_2
		P_2O_5	SO ₃
	GeO ₂	As ₂ O ₃	SeO ₂
		As_2O_5	SeO ₃
		Sb ₂ O ₃	TeO ₂
		Sb ₂ O ₅	TeO ₃

Some of the properties associated with many simple ionic and covalent compounds in the extreme cases are summarized Table 4.7 shown below.

Table 4.7 Some of the properties associated with many simple ionic and covalent compounds

Ionic compounds	Covalent compounds
1.High melting solids	1. Gases, liquids or low melting solids
2.Most are soluble in polar solvents	2. most are insoluble in polar solvents
such as water	
3. Most are insoluble in nonpolar	3. most are soluble in nonpolar solvents
solvents such as benzene or hexane	
4. Molten compounds conduct	4. liquid molten compounds do not
electricity well because they contain	conduct electricity
charged particles (ions)	
5. Aqueous solutions conduct electricity	5. aqueous solutions are usully poor
well because they contain charged	conductors of electricity because they
particles	do not contain charged particles

4.5 Oxidation-reduction reactions

Oxygen reacts with most of elements to form compounds we call oxides, and from the time that oxygen was discovered, the term *oxidation* has been associated with that kind of reaction. For example iron is oxidized slowly in air and form rust, which is composed of Fe₂O₃. it has also been known since the iron age that the substance we now call iron oxide can be broken down, or reduced, to give the free metal. Recovery of metal from its oxide therefore became known as *reduction*.

In modern terms, oxidation and reduction have been given broader meanings, which we can see if we analyze what happens when metal such iron is oxidized and its oxide is reduced. Iron oxide, Fe_2O_3 , is an ionic compound composed of the ions Fe^{3+} and O^{2-} . When iron reacts with oxygen,

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$$

Iron begins as electrically neutral atoms that lose electrons to become Fe³⁺ ions. When the oxide is reduced to give metallic iron, the reverse process must happen, so Fe³⁺ ions must gain electrons to give Fe atoms. It is this loss and gain of electrons, which occurs in many similar reactions, that is now associated with the terms oxidation and reduction.

Oxidation is the loss of electrons by a substance.

Reduction is the gain of electrons by a substance.

Reactions that involve oxidation and reduction are called oxidation-reduction reactions or redox reactions, for short.

Now, let's examine a reaction to see how we apply terms. Consider the oxidation of magnesium .

$$2 Mg_{(s)} + O_{2(g)} \rightarrow 2 MgO_{(s)}$$

The product MgO is ionic and contains the ions Mg^{2+} and O^{2-} , which are formed by transfer of electrons from magnesium to oxygen.

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$
 (oxidation)

$$O_2 + 4e^- \rightarrow 2O^{2-}$$
 (reduction)

Two terms that we often use in discussing redox reactions are **oxidizing agent** and **reducing agent**.

The **oxidizing agent** is the substance that takes electrons from the substance that is oxidized, thereby causing oxidation to take place. That's what O_2 does in the reaction between Mg and O_2 , it takes electrons from Mg and causes Mg to be oxidized, so O_2 is oxidizing agent. Notice that the oxidizing agent (O_2) becomes reduced in the reaction.

The **reducing agent** is the substance that gives electrons from the substance that is reduced, thereby causing reduction to take place. That's what Mg does when it reacts with O_2 ; it gives electrons to O_2 and causes O_2 to be reduced. Notice that the reducing agent (Mg) is oxidized.

Oxidation numbers

Oxidation numbers are numbers (either positive or negative) that we assign to atoms in a compound so we can follow the changes that take place in redox reactions. For the purposes of assigning oxidation numbers, we do this whether or

not the compound is ionic or molecular, which means that for molecular substances the oxidation numbers are really fictitious charges.

Rules for assigning oxidation numbers

- 1. The oxidation number of any element in its elemental form is zero, regardless of the complexity of the molecule in which it occurs. Thus, the atoms in Ne, F_2 , P_3 , and S_8 all have oxidation number of zero.
- 2. The oxidation number of any monatomic ion (an ion composed of only one atom) is equal to the charge on the ion. The ions Na⁺, Al³⁺, and S²⁻ have oxidation numbers equal to +1, +3, and -2, respectively.
- 3. The sum of all oxidation numbers of all the atoms in a compound is zero. For polyatomic ions, the sum of oxidation numbers must equal the charge of the ion.

In addition to these basic rules, we obey the following when assigning oxidation numbers to specific atoms in a compound:

- 4. Fluorine has an oxidation number of -1.
- 5. Hydrogen has an oxidation number of +1.
- 6. Oxygen an oxidation number of -2.

When assigning oxidation numbers, you will sometimes encounter situations in which these rules conflict with one another. When this happens, the rule higher up takes precedence. Let's look at a few examples.

Example 4.1. Assigning oxidation numbers of atoms

<u>Problem:</u> Assign oxidation numbers of each of the atoms in the following: (a) FeCl₃, (b) KNO₃, (c) H₂O₂, (d) Fe₂(SO₄)₃, (e) Cr₂O₇²⁻, (f) ClO₃⁻, and (g)NaS₄O₈.

Solution: the oxidation number of the Fe can then be obtained by the summation rule (rule 3).

(a) FeCl₃

Cl
$$3 \times (-1) = -3$$

Fe $1 \times (x) = x$
Sum = 0

For the sum to be zero, the oxidation number of the iron must be +3

(b) KNO₃

potassium (Group IA) forms ions with a charge of 1+(K+), so the oxidation number of K must be +1 (rule 2). Oxygen is assigned an oxidation number of -2 (rule 6). We get the oxidation number of N by applying rule 3.

K 1 X (+1) = +1 (rule 2)
O 3 X (-2) = -6 (rule 6)
N 1 X
$$(x)$$
 = x
Sum = 0 (rule 3)

(c) H₂O₂ is hydrogen peroxide compound formed between nonmetals, so we expect it to be molecular. Since there is no ions, we can't use rule 2. Rules 5 and 6 refer to H and O, so we can use these, but there is a conflict. If we take H to be +1 according to rule 5, then O must be assigned an oxidation number of -1 in order for the sum of oxidation numbers to be zero. On the other hand, if we take O to be -2 according to rule 6, then H must be +2 for the sum to be zero. As mentioned earlier, however, when two rules conflict, we apply the one higher up on the list. Therefore, we take H to be +1 and the oxidation number of O in the compound is -1.

(d) $Fe_2(SO_4)_3$

Fe
$$2 X (+3) = +6 \text{ (rule 2)}$$

S $3 X (x) = 3x$
O $12 X (-2) = 24 \text{ (rule 6)}$
Sum = 0
 $3x + (+6) + (-24) = 0$
 $3x = +18$
 $x = +6$

The oxidation number of S must be +6 in this compound.

(e)For the $Cr_2O_7^{2-}$ ion, the sum of oxidation numbers must equal the charge on the ion. Therefore,

Cr 2 X (x) = 2x
O 7 X (-2) = -14 (rule 6)
Sum = -2 (rule 3)

$$2x + (-14) = -2$$

 $x = +6$

In this ion, the oxidation number of Cr is +6. However, you should keep in mind that the atoms in a polyatomic ion are held together by the same kinds of attractions that hold together atoms in molecules. There are really no Cr^{6+} ions within the $Cr_2O_7^{2-}$ ion. As in molecular substances, the oxidation numbers of Cr and O here are not their actual charges.

(f) ClO₃⁻ ion is composed of two nonmetals, which means that the ion is held together by the same kind of attractions that exist within molecules. This means that we can't just assume that the Cl exist as Cl ion within the ClO₃⁻ ion, so we can't apply rule 2 in this case. However, rule 6 tells us that oxygen has an oxidation number of -2, so we can calculate what Cl must be in order for the sum of oxidation numbers to be equal to the charge on the ion.

It's not hard to see that chlorine must have an oxidation number of +5.

 $(g)NaS_4O_8$

sodium is an alkali metal and must be Na+, so its oxidation number is +1. oxygen is -2 according to rule 6. therefore,

Na 2 X (+1) = +2 (rule 2)
S 4 X (x) = 4x
O 6 X (-2) = -12 (rule 6)
Sum = 0
(+2) + (4x) + (-12) = 0

$$4x = 0$$

 $x = +5/2$

The oxidation number of sulfur is +5/2. notice that oxidation numbers don't have to be whole numbers (although they usually are).

Using oxidation numbers

In redox reaction, there is a change in the oxidation number or oxidation state (we use the terms interchangeably) of two or more elements. Consider, for example the reaction between magnesium and oxygen

$$2Mg + O_2 \rightarrow 2MgO$$

$$0 + 2 - 2$$

The oxidation number of Mg changes from 0 to +2 and that of O changes from 0 to -2. thus, the oxidation of Mg is accompanied by an increase in oxidation number (become more positive). The reduction of O_2 , is accompanied by a decrease in the oxidation number 9become less positive or more negative)

Oxidation is increase in oxidation number.

Reduction is decrease in oxidation number.

To be in consistent with the earlier definitions, the **oxidizing agent** is the substance that is reduced and the **reducing agent** is that substance oxidized.

By using these definitions, we can now see that the reaction between sulfur and oxygen is also a redox reaction. Let's rewrite the equation with the oxidation number below the symbols.

$$S + O_2 \rightarrow SO_2$$
 $0 \quad 0 \quad +4 \quad -2$

The oxidation number of sulfur (S) increase from 0 to +4, so the sulfur is oxidized. The oxidation number of O decreases from 0 to -2, so O2 is reduced. This means that O2 is oxidizing agent and S is reducing agent.

Example 4.2. identifying oxidation and reduction in reaction

Problem: In the following reaction, which substance is oxidized and which is reduced? Which substance is the oxidizing agent and which is the reducing agent?

$$14HCl + K_2Cr_2O_7 \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Solution: Let's begin by writing the oxidation numbers under each of the chemical symbols.

$$14HCl + K_2Cr_2O_7 \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O_{+1 -1} + 1 + 6 - 2 + 1 - 1 + 3 - 1 + 0 + 1 - 2$$

Now we look for changes in oxidation numbers. We see that the oxidation number of Cl changes from -1 to 0. this is an increase in oxidation number, so the substance oxidized is HCl. We also see that Cr changes from +6 to +3. this is a decrease in oxidation number, so the $K_2Cr_2O_7$ is reduced.

The oxidation agent is the substance that's reduced; it is $K_2Cr_2O_7$. The reducing agent is the substance that's oxidized is HCl.

CHAPTER 5 CHEMICAL REACTIONS IN AQUEOUS SOLUTION

When the **reactants** are dissolved in a **solvent**, we said that we have a **solution.** One of the most important solvents for chemical reactions is water. It is a common substance, and it is also a good solvent for many different kinds of chemicals, both ionic and molecular.

5.1 Solution Terminology

Many terms that used in discussing solutions were introduced in previous chapters. These include the terms *solvent* and *solute*. The solvent is generally taken to be the substance present in solution in largest proportion, and all other substances are considered to be solutes. In solutions that contain water, however, water is almost always thought of as the solvent even if it is present in relatively small amounts. For example, a mixture composed of 96% H₂SO₄ and 4% H₂O by mass is called "concentrated sulfuric acid," which implies that a large amount of sulfuric acid is dissolved in a small amount of water-water is taken to be the solvent and H₂SO₄ the solute.

Another set of terms is concentrated and diluted. A concentrated solution has a relatively large proportion of solute to solvent, and a dilute solution has a relatively smaller proportion of solute to solvent.

A solution that contains as much dissolved solute as it can hold while in contact with excess solute is said to be a **saturated** solution, and the amount of solute needed to give a saturated solution with a given amount of solvent is called the **solubility** of that particular solute. Thus, the solubility of sodium chloride in water at 0 $^{\circ}$ C is 35.7 g of NaCl per 100 mL of water. Usually a solute's solubility change with temperature. For example, at 100 $^{\circ}$ C the solubility of NaCl is 39.1 g/ 100 mL of H₂O. this means that we should always specify the temperature when stating the solubility.

If a particular solution contains less solute than is needed for saturation, it is said to be an **unsaturated solution**. An example would be a solution of 20 g of NaCl in 100 mL of $\rm H_2O$ at 0 $^{\rm 0}C$. An unsaturated solution is capable of dissolving more solute-in this case, an additional 15.7 g of NaCl could be dissolved in each 100 mL.

Finally, there are some substances that frequently form supersaturated solutions, solutions that contain more solute than ordinary required for saturation. Sodium acetate, $NaC_2H_3O_2$, is an example. At 0 0 C, this compound is soluble in water to the extent of 119 g/ 100 mL, but its solubility increase greatly with increasing temperature. If a hot unsaturated solution that contains more than 119 g of $NaC_2H_3O_2$ per 100 mL is cooled to 0 0 C, the excess solute should separate from the solution and settle to the bottom, but usually it does not. The excess solute remains in the solution, and the solution is supersaturated.

5.2 Electrolytes

Water is generally a good solvent for ionic compounds, and water solutions (aqueous solutions) that contain these substances have some unusual properties, one of which is that they conduct electricity. A compound such as NaCl that gives an electrically conducting solution is said to be an **electrolyte**.

When an ionic compound dissociate in water, its ions are not really entirely free. Instead, they become surrounded by water molecules and said to be **hydrated**. We indicate this by writing (aq) after formulas of ions. For example, the dissociation of sodium chloride (NaCl) that occurs when the solid is dissolved in water can be represented by the equation

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

The production of ions in solutions is not limited to ionic compounds. There are many molecular substances that react with water to produce ions and therefore qualify as electrolytes. Hydrogen chloride is a typical example. When HCl gas is dissolved in water, the following reaction takes place:

$$HCl(g) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$$

This reaction is properly called an **ionization** reaction because it produces ions where there was none before.(However, it is often referred to as dissociation). The reaction occurs by the transfer of proton, or hydrogen ion (H^+) , from the HCl molecule to water molecule to produce **hydronium ion**, H_3O^+ , and a chloride ion $C\Gamma$. We often speak of the H3O+ ion as the hydrogen ion. By leaving out the H_2O of H_3O^+ ion, we can write the dissociation of HCl

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Strong and weak electrolytes-chemical equilibrium

The two examples of electrolytes discussed above, NaCl and HCl, are essentially completely dissociated in aqueous solution. The electrolytes that are completely dissociated in solution are called **strong electrolytes**.

There are also many molecular substances that have no tendency at all to undergo ionization when dissolved in water. Sugar and ethyl alcohol, for example, do not produce ions in solution, the solution doesn't conduct electricity and these solutes are therefore called **nonelectrolytes**.

Between the extremes of strong electrolytes and nonelectrolytes exists a large collection of compounds called **weak electrolytes**. These compounds produce aqueous solution that conduct electricity, but only very weakly. An example is acetic acid $HC_2H_3O_2$.

In a solution of acetic acid, only a small fraction of all the acetic acid molecules are present as ions, produced by the reaction

$$HC_2H_3O_2(aq) + H_2O \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

For example, in a 1.0 M solution of $HC_2H_3O_2$, only about 0.42% of the solute has undergone this reaction. The rest of acetic acid exists as uncharged molecules. In this solution there are two reactions occurring simultaneously,

$$HC_2H_3O_2 + H_2O \rightarrow H_3O^+ + C_2H_3O_2^-$$
 (1)

$$H_3O^+ + C_2H_3O_2^- \rightarrow H_3O^+ + HC_2H_3O_2 + H_2O$$
 (2)

Such a state is called **equilibrium**. It said to be dynamic equilibrium because things are continually happing in the solution-two reaction are taking place: ions reacting to yield molecules and molecules reacting to produce ions.

To indicate chemical equilibrium in a reacting system, we use a set of double arrows, in the chemical equation. Thus, the equilibrium that we have been discussing is expressed as

$$HC_2H_3O_2(aq) + H_2O \longrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Some additional examples of weak electrolytes are found in Table 5.1. notice that water itself is included in this table because it is actually a very weak electrolyte by virtue of the reaction.

$$H_2O + H_2O \longrightarrow H_3O^+(aq) + OH^-(aq)$$

Table 5.1 Some weak electrolytes

Substance	Dissociation Reaction	Present
		Dissociation
		of the solute
		in 1.00 <i>M</i>
		Solution
Water	$H_2O + H_2O \rightarrow H_3O^+ + OH^-$	1.8 X $10^{-7}(55.5)$
		moles of H ₂ O per
		liter)
Acetic acid	$HC_2H_3O_2 + H_2O \rightarrow H_3O^+ + C_2H_3O_2^-$	0.42
Ammonia	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	0.42
Hydrogen cyanide	$HCN + H_2O \rightarrow H_3O^+ + CN^-$	2.0 X 10 ⁻³

5.3 Reactions between ions

Many of chemical reactions that carry out in the laboratory involve electrolytes dissolved in water. Usually, these reactions take place between the ions present in the solution and can therefore be called **ionic reactions**. A typical reaction is the reaction occurs when solutions of sodium chloride and silver nitrate are mixed, a white solid, silver chloride, is formed. The chemical equation for this reaction is

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

This kind of reaction, in which cations and anions have changed partners, is called metathesis or double replacement (Cl has replaced NO₃ and NO₃ has replaced Cl).

The equation above is called a molecular equation, because all the reactants and products are written as if they were molecules. (of course, we know that ionic substances don't exist as molecules either in the solid state or in solution. We just call this molecular equation because we haven't indicated the presence of ions).

A more accurate representation of the reaction as actually occurs is obtained if we take into account what happens to the solutes when they dissolved in water. In water the NaCl exist as Na⁺ and Cl⁻ ions. Similarly, in its solution, the AgNO₃ exists as Ag⁺ and NO₃ ions. When the two solutions are mixed, solid AgNO₃ is formed by combination of the Ag⁺ and Cl⁻ ions. We call such a solid, formed in the solution as the result of a chemical reaction, a **precipitate**. The solution that exist after the formation of AgCl contains just Na+ and NO3- ions, and is therefore a solution of sodium nitrate. To show those substance that are completely dissociated in the reaction, we rewrite the equation as

$$Ag^{+}(aq) + NO_{3}^{-}(aq) + Na^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + Na^{+}(aq) + NO_{3}^{-}(aq)$$

This is called the **ionic equation** and is obtained by writing the formulas of any soluble strong electrolytes in "dissociated form" and the formulas of any insoluble substances in molecular form."

The net ionic equation is obtained by removing the spectator ions Na⁺ and NO₃⁻ as follows,

$$\operatorname{Ag^{+}}(aq) + \operatorname{No'_{3}}(aq) + \operatorname{Na'^{+}}(aq) + \operatorname{Cl^{-}}(aq) \to \operatorname{AgCl}(s) + \operatorname{Na'^{+}}(aq) + \operatorname{NO'_{3}}(aq)$$

$$\operatorname{Ag^{+}}(aq) + \operatorname{Cl^{-}}(aq) \to \operatorname{AgCl}(s)$$

5.4 Acid-Base Reactions

Among the kinds of substances are compounds that we call **acids** and **bases**. **Arrhenius** also recognized these substance as electrolytes, and they include for example, vinegar and lemon, acetic acid and citric acid, ascorbic acid

(vitamin C), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃).

Among important bases are ammonia (NH₃), sodium hydroxide (NaOH), potassium hydroxide (KOH).

Acids and bases have certain properties that help us identify them, for example, a solution of an acid has a sour taste. On the other hand, bases have a bitter taste. (Caution: you should never test for acids and bases by tasting a chemical in the laboratory. It might not be healthy). Another property of acids and bases is their effect on **indicators** (chemicals whose colors depend on the acidity or basicity of their solutions). A typical example is the dye called litmus. Litmus is a chemical that has a blue color in a basic solution and a pink color in an acidic solution.

Stated in modern terms, the Arrhenius definitions of acids and bases are as follows: An **acid** is a substance that increases the concentration of hydronium ion, H_3O^+ , in an aqueous solution, and a **base** is a substance that increases the concentration of hydroxide ion, OH.

Acids

In general, acids are molecular substances that produce hydronium ion by reaction with water. For example, hydrogen chloride (HCl) is an acid, because when it is dissolved in water, it reacts with the solvent to produce H₃O.

$$HCl(aq) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$$

If we use H⁺ as an abbreviation for the hydronium ion and leave out the molecule of water that carries the H⁺, we can also express this reaction as

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

As it is known HCl is strong electrolyte, meaning that it is essentially 100% dissociated in solution. Therefore, HCl is **strong acid.**

There are also many acids that are week electrolytes. Acetic acid, $HC_2H_3O_2$, is an example. Recall that this acid reacts with water according to the equation

$$HC_2H_3O_2(aq) + H_2O \longrightarrow HO_3^+(aq) + C_2H_3O_2^-(aq)$$

Or more simply

$$HC_2H_3O_2(aq) \implies H^+(aq) + C_2H_3O_2^-(aq)$$

This is an equilibrium, and in a solution of $HC_2H_3O_2$ only a small fraction of the solute is dissociated into ions. This means that the concentration of H_3O^+ in the solution is low. As a result, acetic acid and other acids that are weak electrolytes are called **weak acids**.

Both HCl and $HC_2H_3O_2$ are able to furnish only one hydrogen ion (one proton) per molecule of the acid. Such acids are said to be **monoprotic acids**. There are also many acids that are able to furnish more than one proton per molecule of the acid. As a class, they are referred to as **polyprotic acids**. Two examples are sulfuric acid, H_2SO_4 , and phosphoric H_3PO_4 .

Sulfuric acid is also called a diprotic acid because each molecule of it is able to give up two protons. This happens in two distinct steps

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4(aq)$$

$$HSO_4^{-}(aq) \longrightarrow H^{+}(aq) + SO_4^{2-}(aq)$$

Similarly, phosphoric acid, which is an example of a triprotic acid, dissociates in three separate steps.

$$H_3PO_4(aq) \longrightarrow H^+(aq) + H_2PO_4^-(aq)$$
 $H_2PO_4^-(aq) \longrightarrow H^+(aq) + HPO_4^{2-}(aq)$
 $HPO_4^{2-}(aq) \longrightarrow H^+(aq) + PO_4^{3-}(aq)$

Notice that the second step in dissociation of H₂SO₄ is an equilibrium (only about 10% of HSO₄⁻ is actually dissociated). Despite this, sulfuric acid is considered a strong acid because the first dissociation step is complete. Phosphoric acid, is a weak acid because all three of its dissociation steps are equilibria that do not proceed very far toward completion.

There are substances that do not contain hydrogen, yet still produce acidic solutions when dissolved in water. A common example is carbon dioxide (CO₂). When dissolved in water, it reacts as follows:

$$CO(g) + H_2O \longrightarrow H_2CO_3(aq)$$

The compound H₂CO₃ is called carbonic acid; it is a weak diprotic acid that is dissociated in two steps, the first of which is

$$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$$

Bases

There are two principal kinds of bases: ionic hydroxides and molecular substances that react with water to produce OH. Sodium hydroxide (NaOH),

and calcium hydroxide (Ca(OH)₂) are typical ionic hydroxides. In the solid state they consist of a metal ion and hydroxide ion, and when they dissolve in water, they dissociate.

$$NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

$$\operatorname{Ca}(\operatorname{OH})_2(s) \to \operatorname{Ca}^{2+}(aq) + 2\operatorname{OH}^{-}(aq)$$

As is typical ionic compounds when they dissolve in water, this dissociation is complete, so ionic metal hydroxide are **strong bases**.

The most common molecular substance that is base is ammonia, NH₃. It reacts with water in an equilibrium.

$$NH_{3}(aq) + H_{2}O \longrightarrow NH4^{+}(aq) + OH^{-}(aq)$$

In this case, a proton is transferred from a water molecule to an ammonia molecule. After the H_2O loses an H^+ , the particle left behind is a hydroxide ion OH^- .

The reaction of NH_3 with water is an equilibrium, and only a small fraction of the NH_3 placed into the solution is present as NH_4^+ and OH^- ions. Ammonia is a weak electrolyte, and because its solution have relatively few OH^- ions, it is also said to be a **weak base**. In general, molecular bases are weak bases.

Table 5.2 Some acids and bases

Acids (Those followed by an asterisk(*) are strong electrolytes and are completely				
ionized in aqueous solutio	n.)			
Monoprotic acids	HF	Hydrofluoric	$HClO_3$	Chloric acid*
$HX \rightarrow H^+ + X^-$		acid		
	HCl	Hydrochloric acid*	HClO ₄	Perchloric acid*
	HBr	Hydrobromic acid*	HIO_4	Periodic acid*
	HI	Hydroiodic acid*	HNO_3	Nitric acid*
	HOC1	Hydrochlorous acid	HNO_2	Nitrous acid
	$HClO_2$	Chlorous acid	$HC_2H_3O_2$	Acetic acid
Diprotic acids	H_2SO_4	Sulfuric acid*	H_2S	Hydrosulfuric acid
$H_2X \rightarrow H^+ + HX^-$				aciu
$HX^- \to H^+ + X_2^-$				
	H_2SO_3	Sulfurous acid	H ₃ PO ₃	Phosphorous acid (only two

		hydrogen can be removed as
		protons)
	H ₂ CO ₃	Carbonic acid
T · · · · 1	$H_2C_2O_4$	Oxalic acid
Triprotic acids	H_3PO_4	Phosphoric acid (orthophosphoric
$H_3X \to H^+ + H_2X^-$		acid)
$H_2X^- \to H^+ + HX^{2-}$		
$HX^{2-} \rightarrow H^+ + X_3^-$		
Typical acidic oxides (nonmetal oxides)	SO_2	$SO_2 + H_2O \rightarrow H_2SO_3$
	SO_3	$SO_3 + H_2O \rightarrow H_2SO_4$
	N_2O_3	$N_2O_3 + H_2O \rightarrow 2HNO_2$
	N_2O_5	$N_2O_5 + H_2O \rightarrow 2HNO_3$
	P_4O_6	$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
	P_4O_{10}	$P_4O_{10} + 6H_2O \rightarrow 4H_3SO_4$
Bases		
Molecular bases	NH_3	Ammonia
(weak bases)		$(NH_3 + H_2O \longrightarrow NH_4^+ + OH^-)$
	N_2H_4	Hydrazine
		$(N_2H_4 + H_2O \implies N_2H_5^+ + OH^-)$
	NH ₂ OH	Hydroxyl amine
		$(NH_2 + H_2O \longrightarrow NH_2OH^+ + OH^-)$
Ionic bases	Metal	$M(OH)_n \rightarrow M^{n+} + nOH^{-}$
(strong bases)	hydroxides NaOH	n = n + 1
	Ca(OH) ₂	
Typical basic oxides	M- O)	
(metal oxides)	$- > M_{\circ}$	$O + H_2O \rightarrow 2MOH$
	$\mathbf{K}_{2}\mathbf{O}$	
	CaO	
	SrO $MO +$	$-\mathrm{H_2O} \rightarrow M(\mathrm{OH})_2$
	BaO	

Neutralization

The most important reaction that acids and bases undergo is their reaction with each other, a reaction called neutralization. In aqueous solutions the

neutralization reaction between a strong acid and strong base takes the form of the net ionic equation

$$H_3O^+$$
 $(aq) + OH^ (aq) \rightarrow 2H_2O$

Or if we use H⁺ as an abbreviation for the hydronium ion,

$$H^+$$
 $(aq) + OH^ (aq) \rightarrow H_2O$

If we examine the molecular equation for a typical acid-base reaction, the reaction between sodium hydroxide and hydrochloric acid,

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O$$

we can arrive at another generalization. The products of a neutralization reaction in aqueous solution are a salt and water.

THE BRØNSTED-LOWRY ACID AND BASES THEORY

In 1923 BrØnsted and Lawry independently presented logical extensions of Arrhenius theory.

An **acid** is defined in this theory as a proton donor, H⁺, and a **base** is defined as a proton acceptor.

When an acid gives up a proton, the remaining species is a base and is referred to as the conjugate base of the acid.

The relationship between an acid and its **conjugate base** can be represented in general terms as:

Water itself is both BrØnsted acid and base.(Has amphoteric behavior, act as acid and base). Careful measurements have shown that pure water ionizes ever so slightly to produce equal numbers of hydrated hydrogen ions and hydroxide ions:

$$H_{2}O + H_{2}O = H_{3}O^{+} + HO^{-}$$

Or in simplified notation,

$$H_2O \longrightarrow H^+(aq) + HO^-(aq)$$

The **autoionization** of water is an acid-base reaction according to Brønsted-lowry acid and bases theory. One H_2O molecule (the acid) donates a proton to another H_2O molecule (the base). The H_2O molecule that donates a proton becomes an OH^- ion, which s called the conjugate base of water. The H_2O molecule that accepts a proton becomes an H_3O^+ . Examination of the reverse

reaction (right-to-left) shows that H_3O^+ (an acid) donates a proton to OH^- (a base) to form two H_2O molecules. in the notation under the equation:

$$H_2O + H_2O \longrightarrow H_3O^+ + HO^-$$

acid₁ base₂ acid₂ base₁

The subscripts refer to conjugate acid-base pairs. Note that each acid differs from its conjugate base by a proton.

The following equations provide specific examples of this relationship.

Acid ₁		Base ₂		Acid ₂		Base ₂	
HC1	+	H_2O		H_3O^+		Cl	(1)
$HC_2H_3O_2$	+	H_2O		$\mathrm{H_3O}^+$	+	$C_2H_3O_2$	(2)
$\mathrm{NH_4}^+$	+	H_2O		$\mathrm{H_3O}^+$	+	NH_3	(3)

Relative strengths of conjugate acids and bases pairs

The stronger the acid the weaker the conjugate base and the stronger the base the weaker the conjugate acid. Acid and bases are ranked in order of their comparative strengths as shown in Table 5.3.

Table 5.3 Relative strengths of conjugate acids and bases pairs

Acid		Conjugate base	weak
HClO ₄	strong	ClO ₄	bases
HC1	acids	Cl ⁻	
H ₂ SO ₄		HSO ₄	
HNO ₃		NO ₃	
$\mathrm{H_3O}^+$		H ₂ O]
H ₂ SO ₃		HSO ₃	
HSO ₄		SO ₄ ²⁻	
H3PO ₄		HPO ₄	inaraggina
HF	decreasing	F ⁻	increasing strength
HC ₂ H ₃ O ₂	strength	$C_2H_3O_2^-$	Strongth
H ₂ CO ₃		HCO ₃]
H ₂ S		HS ⁻	
HSO ₃		SO ₃ ² -	
HCN		CN⁻]
NH ₄ ⁺		NH ₃	
HCO ₃		CO ₃ ²⁻	
HS ⁻		S^{2-}	strong
H ₂ O	w eak	OH-	bases
NH ₃	acids	NH ₂ -]
OH-	*	O^{2-}	

LEWIS ACIDS AND BASES; COMPLEX ION OF METALS

The American chemist Gilbert N. Lewis provide a further extension for the acid-base concept. Thus, in the Lewis definition of acid and base: A base is defined as a substance that can donate a pair of electrons to the formation of covalent bond. An acid is a substance that can accept a pair of electrons to form the bond.

A simple example of a Lewis acid-base reaction is the reaction of a hydrogen ion with a hydroxide ion

The hydroxide ion is the Lewis base because it furnishes the pair of electrons that become shared with the hydrogen. The hydrogen ion, on the other hand, is the Lewis acid because it accept a share of pair of electrons when the O-H bond is created.

Another example is the reaction between BF₃ and ammonia,

In this case, the NH₃ functions as the base and BF₃ serves as the acid. Compounds elements with incomplete valence shells, such as BF₃ or AlCl₃, tend to be Lewis acids, while compounds or ions that have lone pairs of electrons can behave as Lewis bases. When the Lewis acid-base reaction occurs, a coordinate covalent bond is formed.

Some common Lewis bases are amines and alcohols.

The Ionization of Water

As we've known in earlier chapter that water itself is a very weak electrolyte because of the reaction

$$H_2O + H_2O \implies H_3O^+(aq) + HO^-(aq)$$

This kind of reaction, in which two molecules of the solvent react with each other to form ions, is called autoionization. Since autoionization is an equilibrium, we can write an equilibrium expression for it as follows

$$K_c = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{H_2O}\right]\left[\mathrm{H_2O}\right]}$$

The molar concentration of water, which appears in the denominator of this expression, is very nearly constant (=55.6 M) in both pure and dilute aqueous solutions. Therefore, $[H_2O]^2$ can be included with the equilibrium constant, K_c , on the left side of the equation. This gives

$$K_c X[H_2O]^2 = [H_3O^+][OH^-]$$

The left side of this expression is the product of two constants which, must also a constant. This combined constant is written as

$$K_w = K_c [H_2 O]^2$$

The equilibrium law therefore becomes

$$K_w = K_c[H_3O^+][OH^-]$$

Because $[H_3O^+][OH^-]$ is the ion concentration, K_w is called **ion product constant for water**, or simply the **ionization constant** or **dissociation constant** of water. At 25°C, K_w = 1.0 X 10⁻¹⁴, and is one equilibrium constant that you should be memorize.

The density of H_2O is 1.00 g/ml, so 1.00 L has a mass of 1.00X 10^3 g. therefore,

$$[H_2O] = \frac{1.00X10^3 \text{ g H}_2O}{1.00 \text{ L}} X$$
$$\frac{1 \text{mol H}_2O}{18.0 \text{ g H}_2O} = 55.6 \text{ mol H}_2O/L$$

 K_w varies with temperature. At 37^{0} C(body temperature) $K_w = 2.42 \times 10^{-14}$

The equation for autoionization of water is often simplified by omitting the water molecule that picks up the H^+ and abbreviating the hydronium ion as H^+ . The chemical equation becomes

$$H_2O \implies H^+ + HO^-$$

When we use this simplified equation, the expression for the ionization constant for water is

$$K_{w} = [H^{+}][OH^{-}]$$

This equation can be used to calculate the molar concentration of both H⁺ and OH ions in pure water. From the stoichiometry of dissociation, we see that for each 1 mol of H⁺ formed 1 mol of OH⁻ is also produced. This means that at equilibrium, $[H^{+}] = [OH^{-}]$. If we let x equal the hydrogen ion concentration, then

$$x = [H^+] = [OH^-]$$

Therefore,

$$K_{w} = x.x = x^{2}$$

 $K_w = x.x = x^2$ Or, because $K_w = 1.0 \times 10^{-14}$,

$$x^2 = 1.0 \times 10^{-14}$$

Taking the square root yields

$$x = 1.0 \times 10^{-7}$$

Which means that the concentration of hydrogen ion and hydroxide ion in pure water are

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} M$$
 (at $25^{\circ}C$)

The pH concept

Hydrogen ion and hydroxide ion enter into many equilibria in addition to the dissociation of water, so it is frequently necessary to specify their concentrations in aqueous solutions. The concentrations may range from relatively high values to very small ones (for example, 10 M to 10-14), and a logarithmic notation has been devised to simplify the expression of these quantities. In general, for some quantity X, the pX is defined as

$$pX = log \frac{1}{X} = -log X$$

For example, if we wish to specify the hydrogen ion concentration in a solution, we speak of pH. This is defined as

$$pH = log \frac{1}{[H^+]} = -log[H^+]$$

In a solution where the hydrogen ion concentration is 10⁻³ M, we therefore have

$$pH = log \frac{1}{[10^{-3}]} = -log[10^{-3}] = -(-3)$$
 Notice that logs to the base 10 (common logs) are used here, not natural logs.

Similarly, if the hydrogen ion concentration is 10^{-8} M, the pH of the solution is 8 Following the same approach for the hydroxide ion concentration, we can define the pOH of a solution as

$$pOH = log \frac{1}{[OH^-]} = -log[OH^-]$$

Just as the H+ and OH- ion concentration in as solution are related to each other, so also are the pH and pOH. From the equilibrium expression for the dissociation of water, we obtain the following by taking the logarithm of both sides.

$$\log K_{w} = \log[\mathrm{H}^{+}] + \log[\mathrm{OH}^{-}]$$

Multiplying through by -1 gives

$$(-\log K_w) = (-\log[H^+]) + (-\log[OH])$$

By definition, $-\log K_w = pK_w$, therefore,

$$pK_w = pH + pOH$$

Since $K_w = 1.0 \times 10^{-14}$, $pk_w = 14.00$. this gives the useful relationship

$$pH + pOH = 14.00$$

$$pK_{w} = -\log K_{w}$$

$$= -\log(1.0X10^{-14})$$

$$= 14.00$$

In a neutral solution, $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$, and pH = pOH = 7.00. In an acidic solution the hydrogen ion concentration is greater than 1.0 $\times 10^{-7} M$ (for example, $10^{-3} M$) and the pH is less than 7.00. By the same, in basic solution the $[H^+]$ is less than 1.0 $\times 10^{-7} M$ (for example, $10^{-10} M$) and the pH is greater than 7.00. this is summarized as follows:

	$[H^{+}]$	[OH ⁻]	рН	рОН
Acidic	$>(1.0 \times 10^{-7})$	<(1.0 X10 ⁻⁷)	< 7.00	>7.00
solution				
Neutral	1.0 X 10 ⁻⁷	1.0 X 10 ⁻⁷	7.00	7.00
solution				
Basic solution	<(1.0 X 10 ⁻⁷)	$>(1.0 \times 10^{-7})$	>7.00	< 7.00

Measuring pH; acid-base indicators and pH meters

One of the earliest ways of judging the acidity or basicity of solution was the use of substances called **acid-base indicators**. These are organic compounds whose color depends on the pH of the solution in which they're dissolved. A typical example is litmus, which is pink in an acidic solution and blue in a basic solution.

It is quite common today to find instruments called **pH meters** in labs of all kinds. These are electronic devices that enable the pH of a solution to be measured with a high degree of precision and accuracy.

Example: calculating the pH of a solution of strong acid

Problem: What is the ph of a 0.0020 M solution of HCl?

Solution:

$$pH = -log[H^+]$$

 $pH = -log(2.0 \times 10^{-3})$
 $pH = 2.70$

Example: calculating the pH of a solution of strong base

Problem: What is the ph of a 5.0 X 10-4 M solution of NaOH at 25^oC?

Solution: We know that

$$K_{w} = [H^{+}][OH^{-}]$$

Therefore,

$$[H^{+}] = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-4}}$$
$$= 2.0 \times 10^{-11} M$$

From this we calculate the pH

$$pH = -\log(2.0 \times 10^{-11})$$

 $pH = 10.70$

Another solution: By definition

$$pOH = -log[OH^{-}]$$

 $[OH^{-}] = 5.0 \times 10^{-4} M$

$$pOH = -log(5.0 \times 10 - 4)$$

= 3.30

Therefore,

$$pH = 14 - 3.30$$

= 10.70

Example: Calculating [H⁺] and [OH⁻] from pH

Problem: A sample of orange juice was found to have a pH of 3.80. what were the H⁺ and OH⁻ concentrations in the juice?

Solution:

$$pH = -log[H^+]$$

The antilogarithm of this gives the following relationship:

$$[H^+] = 10^{-pH}$$

For the sample of orange juice, therefore,

$$[H^+] = 10^{-3.80}$$

= 1.6X10⁻⁴

Once we have obtained $[H^+]$, we can calculate $[OH^-]$ from K_w .

$$[OH^{-}] = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-4}}$$
$$= 6.3 \times 10^{-11} M$$

Alternatively, we could first calculate pOH from pH and the take the antilogarithm.

$$pOH = 14 - pH$$

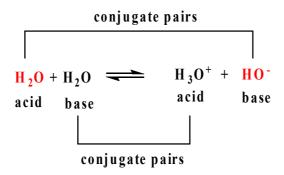
= 14.00 - 3.8 = 10.20

$$[OH^{-}] = 10^{-pH}$$

= $10^{-10.20}$
= $6.3 \times 10^{-11} M$

Conjugate acid-base systems in aqueous solutions

The most important equilibrium in aqueous solutions is the ionization of water. If we look at this equilibrium in BrØnsted-Lowry terms and consider one water molecule the acid and the other the base, we have



Equilibrium constant expressions for acids in water

For strong acid, such as HCl, we never bother to write an equilibrium law because the dissociation is taken to be complete. Acetic acid, however, is a weak acid and its reaction with water is in equilibrium., thus

$$\begin{aligned} HCl + H_2O &\rightarrow H_3O^+ + Cl^- \\ HC_2H_3O_2 + H_2O &\rightleftharpoons H_3O^+ + C_2H_3O_2^- \end{aligned} \begin{tabular}{ll} Cl^- is the conjugate base of HCl. \\ C_2H_3O_2^- is the conjugate base of HCl. \\ HC_2H_3O_3 \\ \end{tabular}$$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[H_2O][HC_2H_3O_2]}$$

The concentration of water in diluted aqueous solution is constant, and it can incorporated into the equilibrium constant to give a new constant that we call K_a . This constant is called **ionization constant** or **dissociation constant** for the acid.

$$K_c X [H_2 O] = K_a = \frac{[H_3 O^+][C_2 H_3 O_2^-]}{[HC_2 H_3 O_2]}$$

We can also simplify this somewhat by using H+ in place of H₃O⁺ and writing the simplified equation as

$$HC_2H_3O_2 \implies H^+ + C_2H_3O_2^-$$

From which we obtain the simplified expression

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm C}_2{\rm H}_3{\rm O}_2^-]}{[{\rm HC}_2{\rm H}_3{\rm O}_2]}$$

Some anions, such as the bisulfate ion, HSO₄, are also acids. This anion is formed in the first step in the ionization of H₂SO₄, reacts with water as follows.

$$HSO_4^- + H_2O \implies H_3O^+ + SO_4^{2-}$$

Acids can even be cations, such as the ammonium ion, NH4+, which undergo reaction.

$$NH_4^+ + H_2O \implies H_3O^+ + NH_3$$

We can write similar equilibrium laws for acids such as HSO₄ and NH₄

$$K_{\rm a} = \frac{[{\rm H}_3{\rm O}^+][{\rm SO_4}^{2^-}]}{[{\rm HSO_4}^-]}$$

The simplified equation for the reaction is

$$HSO_4^- \longrightarrow H^+ + SO_4^{2-}$$

For which we write the equilibrium expression

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm SO_4}^2]}{[{\rm HSO_4}^2]}$$

Similarly, for ammonium ion, we have

$$K_{\rm a} = \frac{[{\rm H_3O^+}][{\rm NH_3}]}{[{\rm NH_4}^+]}$$

The simplified equation for the equilibrium and the corresponding equilibrium law are

$$NH_4^+ \longrightarrow H^+ + NH_3$$

$$K_{a} = \frac{[H^{+}][NH_{3}]}{[NH_{4}^{+}]}$$

Usually, it is easier to write everything in the abbreviate simpler form

$$HA \longrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Where K_a is called ionization constant or dissociation constant for the acid, A- is the conjugate base

Equilibrium constant expressions for bases in water

As with acids, bases also undergo the same kinds of reactions with water. An example is ammonia (the conjugate base of NH_4^+).

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

The equilibrium law for this reaction is

$$K_c = \frac{[NH_4^+][OH^-]}{[H_2O][NH_3]}$$

Once again, the concentration of water appearing in the denominator is essentially a constant that we incorporate into the equilibrium constant k_c to give a new constant that we will call k_b .

$$K_c X[H_2O] = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Many anions are bases and produce hydroxide ion in water just as ammonia does. For example, acetate ion, C2H3O2-, which is conjugate base of acetic acid, reacts with water as follows.

$$C_2H_3O_2^- + H_2O \implies HC_2H_2O_2 + OH^-$$

We write the equilibrium expression as

$$K_b = \frac{[HC_2H_3O_2][OH^2]}{[C_2H_3O_2]}$$

There is general equation that we can write for the reaction of base with water. If we use the symbol B to stand for a base, then

$$B^- + H_2O \longrightarrow HB + OH^-$$

And the equilibrium law is written as

$$K_b = \frac{[\mathrm{HB}^+][\mathrm{OH}^-]}{[\mathrm{B}]}$$

You can apply this equation to solve equilibrium problems that involve weak bases in water.

The relationship between ka and kb for an acid-base conjugate pair

$$K_a \times K_b = K_w$$

Example: using the pH of a solution of an acid to calculate k_a

Problem: A student prepared a 0.1 *M* acetic acid solution and measured its pH to be 2.88. calculate Ka for acetic acid.

Solution: the chemical equilibrium and equilibrium constant are

$$HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$$

$$K_a = \frac{[H^+][C_2H_3O_2]}{[HC_2H_3O_2]}$$

To evaluate K_a , we need to have all the equilibrium concentrations to substitute into the mass action expression. They are obtained from the information given in the problem as follows:

$$pH = 2.88$$

[H⁺] = 10-pH = 1.3 x 10⁻³ M

At equilibrium, the concentrations of ions must be equal, thus

$$[H^+] = [C_2H_3O_2^-] = 1.3 \times 10^{-3} M$$

Equilibrium concentration				
H^{+} 1.3 X 10^{-3} M				
$C_2H_3O_2^-$	$1.3 \times 10^{-3} M$			
$HC_2H_3O_2$	$10^{-1} - 0.013 \text{ X } 10^{-1} = 1.0 \text{ X } 10^{-1} \text{ M}$			

Note that when we compute the acetic acid concentration rounded to the proper number of significant figures, the amount that has dissociated is negligible compared tom the amount initially present. Thus,

$$0.10 M - 0.0013 M = (0.0987 M) = 0.1 M$$
 (rounded)

Substituting the equilibrium concentrations into the expression for k_a , we have

$$K_a = \frac{[1.3 \times 10^{-3}][1.3 \times 10^{-3}]}{[1.0 \times 10^{-1}]}$$
$$= 1.7 \times 10^{-5}$$

Percent dissociation or percent ionization

The percent dissociation or percent ionization is given by the following relation

percent dissociation =
$$\frac{\text{(mol/L of acid or base dissociated)}}{\text{(mol/L of acid or base available)}} X100$$

For the acetic acid in the preceding example, the mol/L dissociate equals the mol/L of H+ formed, which is 1.3 x 10-3 M. the mol/L available is the original concentration, 0.01 M. Therefore,

percent dissociation =
$$\frac{1.3 \times 10^{-3} M}{0.10 M} \times 100 = 1.3\%$$

Example: Using the percent dissociation to calculate an equilibrium constant

Problem: A 0.010 M NH₃ solution was prepared and it was determined that the NH₃ had undergone 4.2% ionization. Calculate the k_a for NH₃.

Solution: Ammonia ionizes in water according to the reaction

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

For which we write

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At equilibrium

$$[NH_4^+] = [OH^-]$$

Since the 0.010 M solution undergoes 4.2 % ionization, the number of moles per liter of these ions at equilibrium is

$$[NH_4^+] = [OH^-] = 0.042 \times 0.010 M = 4.2 \times 10^4 M$$

The number of moles per liter of NH₃ at equilibrium would be $[NH_3] = 1.0 \times 10^{-2} - 0.042 \times 10^{-2} = 0.958 \times 10^{-2} M = 1.0 \times 10^{-2} M$ (rounded)

The amount ionized per liter is 4.2% of 0.010 mol/L

Equilibrium concentration				
NH_4^+ 4.2 X $10^{-4} M$				
OH.	$4.2 \times 10^{-4} M$			
NH ₃	$1.0 \times 10^{-2} M$			

By substitution for k_b , we have

$$K_b = \frac{[4.2 \times 10^{-4}][4.2 \times 10^{-4}]}{[1.0 \times 10^{-2}]}$$
$$= 1.8 \times 10^{-5}$$

Example: Using k_a to calculate the concentration of the species in a solution of a weak acid

Problem: What are the concentrations of all the species present in a 0.50 M solution of acetic acid. For HC₂H₃O₂, $k_a = 1.8 \times 10^{-5}$.

Solution: The chemical equation and the equilibrium law are

$$HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$$

$$K_a = \frac{[H^+][C_2H_3O_2]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

We assign the initial $[C_2H_3O_2^-]$ a value of zero. We also expect the initial concentration of H^+ to be zero.

In reaching equilibrium, some of $HC_2H_3O_2$ will dissociate, so its concentration will decrease. We don't know how much, so let's say that the change in $HC_2H_3O_2$ concentration is x. Since all the coefficient in the equation are equal to 1, the concentrations of H^+ and $C_2H_3O_2^-$ will increases by x. this gives us the quantities in the center column of the table. The quantities corresponding to the equilibrium concentrations are obtained by adding the "change" to the initial concentration algebraically

	Initial Molar	Change	Equilibrium Molar
	Concentration		concentration
H^{+}	0.0	$+\chi$	X

$C_2H_3O_2^-$	0.0	+x	x
HC ₂ H ₃ O ₂	0.50	- <i>x</i>	0.50 - x

.

Substituting these values into the equilibrium expression gives us

$$\frac{(x)(x)}{(0.50-x)} = 1.8 \times 10^{-5}$$

Let us assume that x will be negligible compared to 0.50; that is

$$0.50 - x = 0.50$$

Our equation the becomes

$$\frac{(x)^2}{0.50} = 1.8 \times 10^{-5}$$

$$x = 3.0 \times 10^{-3}$$

If we look back on our assumption, we see that x is in fact small compared to 0.50 and that, when rounded to the proper number of significant figures,

$$0.50 - 0.0030 = 0.50$$
 (rounded)

Equilibrium concentration (M)			
H ⁺ 3.0 X 10 ⁻³			
$C_2H_3O_2^{-1}$ 3.0 X 10^{-3}			
$HC_2H_3O_2$ 0.50			

Therefore, the equilibrium concentrations of the species involved in the dissociation of the acid are those given in the previous table. Since the question asks for all concentrations, we must also calculate the concentration of OH, which comes from the dissociation of water. Here we use k_w .

$$[OH^{-}] = \frac{K_{w}}{[H^{+}]}$$

$$= \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-3}}$$

$$= 3.3 \times 10^{-12} M$$

Example: Calculating the pH of a solution that contains a weak acid and strong acid

Problem: What is the pH of a solution that contains 0.10 M HCl and 0.10 M HC₂H₃O₂? For acetic acid $k_a = 1.8 \times 10^{-5}$.

Solution: The 0.10 M solution of HCl contains 0.10 mol/L of H^+ , because HCl is a strong acid. This is the concentration of H^+ before the HC₂H₃O₂ is added. Then we place 0.10 M HC₂H₃O₂ into it, but we imagine that none of it dissociates. This gives us the initial concentrations of H^+ and HC₂H₃O₂.

$$[H^{+}]_{initial} = 0.10 M$$

 $[HC_{2}H_{3}O_{2}]_{initial} = 0.10 M$

Now, we have to consider the ionization of acetic acid. The chemical equilibrium and equilibrium law are the same as in preceding problem.

$$HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$$

$$K_a = \frac{[H^+][C_2H_3O_2]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

Since there is no $C_2H_3O_2^-$ present initially, some of it must form by the dissociation of the $HC_2H_3O_2$. Therefore, we let the concentration of $HC_2H_3O_2$ decrease by x and the concentrations of H^+ and $C_2H_3O_2^-$ increases by x and then add the initial concentrations and the changes to get the equilibrium quantities.

	Initial Molar	Change	Equilibrium Molar
	Concentration		Concentration
H^{+}	0.10	+ <i>x</i>	$0.10 + x \approx 0.10$
$C_2H_3O_2^-$	0	+ <i>x</i>	x
HC ₂ H ₃ O ₂	0.10	- x	$0.10 - x \approx 0.10$

We expect x to be small, so we've assumed $0.10 \pm x \approx 0.10$. substituting into the k_a expression, we get

$$1.8 \times 10^{-5} = K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{(0.10)(x)}{(0.10)}$$

$$1.8 \times 10^{-5} = \frac{(0.10)(x)}{(0.10)}$$

$$x = 1.8 \times 10^{-5}$$

We see that x is indeed small compared to 0.10, so the solution [H+] = 0.10 M. This gives a pH of 1.00.

Example: Calculating the pH of a solution of a weak base

Problem: What is the pH of a 0.010 M solution of the weak base diethylamine $(C_2H_5)_2NH$, for which $k_b = 9.6 \times 10^{-4}$?

Solution: Since the solute is a base, the equilibrium is

$$(C_2H_5)_2NH + H_2O$$
 \longrightarrow $(C_2H_5)_2NH_2^+ + OH^-$
Therefore,

$$K_b = \frac{[(C_2H_5)NH_2^+][OH^-]}{[(C_2H_5)_2NH]} = 9.6 \times 10^{-4}$$

We take the $(C_2H_5)_2NH$ concentration specified in the problem as its initial concentration and the concentration of $(C_2H_5)_2NH_2^+$ to be zero. As usual, we assume the solvent makes no contribution to $[OH^-]$. Therefore, we take the initial OH- concentration to be zero, too. This gives us the entries for the initial concentration column in the concentration table. Next, we realize that some of the diethylamine must react, so we let its concentration decrease by x, and we increase the concentrations of $(C_2H_5)_2NH_2^+$ and OH^- by x. adding the "changes" to the initial concentrations gives the equilibrium quantities.

	Initial Molar	Change	Equilibrium Molar
	Concentration	_	Concentration
$(C_2H_5)_2NH_2^+$	0.0	x	X
OH-	0	x	x
$(C_2H_5)_2NH$	0.010	- x	0.010-x

Substituting these into the mass action expression gives

$$\frac{(x)(x)}{(0.010-x)} = 9.6 \times 10^{-4}$$

Now let's see what happens if we assume that x is negligibly small compared to 0.010 M. This gives the equation

$$\frac{(x)(x)}{0.010} = 9.6 \times 10^{-4}$$

$$x^2 = 9.6 \times 10^{-6}$$

 $x = 3.1 \times 10^{-3}$

If we aren't careful, we might accept this as the answer. However, if we check our assumption, we find that x is not negligible compared to 0.010. In decimal form, x = 0.0031, so 0.010-0.0031 = 0.007 (rounded to the correct number of significant figures). Certainly 0.007 is not the same as 0.010. in this problem, it was not safe

to assume that the initial concentration of $(C_2H_5)_2NH$ is the same as its equilibrium value.

 $0031\ M$ is about 30% of the initial value of 0.010 M, so it is certainly not negligible.

The next question, of course, is what do we do now? There are actually two choices. One is to expand the equation into a quadratic equation and apply the quadratic formula to it.

The quadratic formula:

$$x = \frac{-b \pm \sqrt{b2 - 4ac}}{2a}$$

Although tedious, the solution is relatively straightforward. It gives two values for x because of the "±" sign before the radical. These turn out to be

$$x = 2.7 \times 10^{-3}$$

 $x = -3.6 \times 10^{-3}$

we can discard the second value because the concentration of $(C_2H_5)_2NH_2^+$ and OH^- can't be negative and also because 0.010- (- 3.6 X 10^{-3}) = 0.014 (rounded), which is impossible. Therefore, we are left with $x = [OH^-] = 2.7 \times 10^{-3} M$. This gives a pOH of 2.57 and a pH of 11.43.

Buffers: the control of pH

If a solution contains <u>both</u> a weak acid and a weak base, it has the ability to absorb small additions of either a strong acid or strong base with very little change in pH. When a small amount of strong acid is added, its H_3O^+ is neutralized by the weak base, and when a small amount of strong base is added, its OH^- is neutralized by the weak acid. Such solutions are said to be **buffered** and the mixture of solutes that produces the effect is called a **buffer**.

Buffers usually consist of a weak acid and its conjugate base. An example is acetic acid and acetate ion, and a solution buffered with this pair is prepared by dissolving $HC_2H_3O_2$ and acetate salt such as $NaC_2H_3O_2$ in some appropriate amount of water. In this case, the buffer has pH lower than 7 because the acid, $HC_2H_3O_2$, is stronger than the base $C_2H_3O_2$. (For $HC_2H_3O_2$, $k_a = 1.6 \times 10^{-5}$ and for $C_2H_3O_2$, $k_b = 5.6 \times 10^{-10}$.) If a small amount of strong acid is added to this buffer, its H_3O_2 can react with acetate ion,

$$H_3O^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2 + H_2O_2^-$$

Or more simply,

$$H^{+} + C_{2}H_{3}O_{2}^{-} \rightarrow HC_{2}H_{3}O_{2}$$

Notice that this reaction removes H⁺ and changes the base into its conjugate acid. A similar reaction occurs if a strong base is added. The OH⁻ supplied by the strong base reacts with the acetic acid and converts it to its conjugate base.

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

Buffers with a ph higher than 7 can be prepared by using a base that is stronger than its conjugate acid. A common basic buffer is formed by mixing ammonia with an ammonium salt such as NH₄Cl and contains the conjugate acid-base pair NH₄⁺ and NH₃. If a strong acid is added to the buffer, it reacts as follows,

$$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$$

$$H^+ + NH_3 \rightarrow NH_4^+$$
 (simplified)

And if a strong base is added, the reaction is

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

Buffer calculations

Example: Calculating the pH of a buffer solution

Problem: What is the pH of buffer solution prepared by dissolving 0.10 mol of $NaC_2H_3O_2$ and 0.20 mol of $HC_2H_3O_2$ in enough water to give 1.00 L solution?

Solution: There is only one equilibrium here that we must concerned with

$$HC_2H_3O_2 + H_2O \implies H^+ + C_2H_3O_2^-$$

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

When NaC₂H₃O₂ dissolves, it is completely dissociated. It is important to remember that virtually all salts are 100% dissociated in solution. Therefore, 0.10 mol/ L of NaC₂H₃O₂ gives 0.10 mol/ L of Na⁺ and 0.10 mol/ L of C₂H₃O₂. We are interesting only in the C₂H₃O₂; the Na⁺ is simply a spectator ion and we ignore it. The initial concentration of the C₂H₃O₂ is therefore 0.10 M. As usual, we take the initial concentration of the weak acid to be the value specified in the problem; in this case [HC₂H₃O₂]_{initial} = 0.20 M. We also ignore the contribution that solvent makes to [H⁺], so we set this value to zero. These are the values that go into the first column of concentration table.

Next, we enter the changes in the center column. Since no H^+ is present, some $HC_2H_3O_2$ must ionize; so let's allow x to equal the number of moles per liter

of $HC_2H_3O_2$ that dissociates to give H^+ and $C_2H_3O^-$. This will increase $[H^+]$ and $[C_2H_3O_2^-]$ by x and decrease $[HC_2H_3O_2]$ by x. The equilibrium concentration are then found in the last column for our table.

	Initial Molar	Change	Equilibrium Molar
	Concentration		Concentration
H^{+}	0.0	x	x
$C_2H_3O_2$	0.10	x	$0.10 + x \approx 0.10$
HC ₂ H ₃ O ₂	0.20	- x	$0.20 - x \approx 0.20$

As before, we look at k_a and see that x will probably be small. We will therefore assume that $0.10 + x \approx 0.10$ and $0.20 - x \approx 0.20$. substituting into the expression for k_a gives

$$\frac{(x)(0.10)}{(0.20)} = 1.8 \times 10^{-5}$$
$$x = 3.6 \times 10^{-5}$$

Now let's check our assumption. If 3.6×10^{-5} is added to 0.10 and the result rounded to the correct number of significant figures, the sum is 0.10. If 3.6×10^{-5} is subtracted from 0.20, the difference is 0.20 when rounded correctly. This means that we were correct in our assumption that x was small compared to 0.10 and 0.20. the equilibrium concentrations are therefore

$$[H^{+}] = 3.6 \times 10^{-5} M$$

 $[C_2H_3O_2] = 0.10 M$
 $[HC_2H_3O_2] = 0.2 M$

Since we are interested in the pH, we use the H+ concentration.

$$pH = -log[H^+] = -log(3.6 \times 10^{-5})$$

= 4.44

Example: Preparing a buffer with a specified pH

<u>Problem:</u> What ratio of acetic acid to sodium acetate concentration is needed to form a buffer whose pH is 5.70?

Solution:

$$\frac{[HC_{2}H_{3}O_{2}]}{[C_{2}H_{3}O_{2}^{-}]} = \frac{[H^{+}]}{K_{a}}$$

The H+ concentration when the pH is 5.70 is

$$[H^+] = 2.0 \times 10^{-6} M$$

ACID-BASE TITRATIONS

Titration is useful way of determining the concentrations of solutions of acids and bases, provided that the equivalence point can be detected. The equivalence point, you should remember, occurs when equal numbers of equivalents of acid and base have been combined.

<u>Titration of a strong acid with a strong base</u>

The titration of 25.00 mL of 0.10 M with 0.10 M NaOH is a typical example of the titration of a strong acid with base. We can mathematically determine the ph throughout the titration by calculating the H^+ concentration present in the flask each time a quantity of NaOH is added to the HCl. For example, the number of moles of H^+ present in the mL of a 0.1 M HCl solution is

$$\left(\frac{0.10 \text{ mol}}{1000 \text{ mL}}\right) X 25 \text{ mL} = 2.5 \times 10^{-3} \text{ mol of H}^{+}$$

When 10 ml of the 0.10 M NaOH is added, we in fact have added

$$\left(\frac{0.10 \text{ mol}}{1000 \text{ mL}}\right) \text{X } 25 \text{ mL} = 2.5 \text{ X } 10^{-3} \text{ mol of OH}^{-}$$

The neutralization reaction

$$H^+ + OH^- \rightarrow H_2O$$

Table: Titration of 25 ml of 0.1 M HCl with a 0.1 M NaOH solution

Volume	volume	Total	Moles	Moles of OH	Molarity of Ions in	рН
of HCl	of	volume	of H ⁺		Excess	
(mL)	NaOH	(mL)				
	(mL)					
25.00	0.00	25.00	2.5×10^{-3}	0	$0.10~(\text{H}^{+})$	1.00
25.00	10.00	35.00	2.5×10^{-3}	1.0 X 10 ⁻³	$4.3 \times 10^{-2} (H^{+})$	1.37
25.00	24.99	49.99	2.5 X 10 ⁻³	2.499 X 10 ⁻³	$2.0 \times 10^{-5} (H^{+})$	4.70
25.00	25.00	50.00	2.5×10^{-3}	2.50 X 10 ⁻³	0	7.00
25.00	25.01	50.01	2.5×10^{-3}	2.501 X 10 ⁻³	2.0 X10 ⁻⁵ (OH ⁻)	9.30
25.00	26.00	51.00	2.5 X 10 ⁻³	2.60 X 10 ⁻³	2.0 X10 ⁻³ (OH ⁻)	11.30
25.00	50.00	75.00	2.5 X 10 ⁻³	5.0 X 10 ⁻³	3.3 X10 ⁻² (OH ⁻)	12.52

Occurs, and the amount of H⁺ remaining is

$$(2.5 \times 10^{-3}) - (1.0 \times 10^{-3}) = 1.5 \times 10^{-3} \text{ mol of H}^+$$

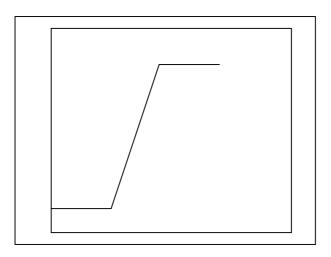
The molar concentration of H+ is now

$$[H^+] = \frac{1.5 \times 10^{-3} \text{ mol}}{0.035 \text{ L}} = 4.3 \times 10^{-2} M$$

And the pH is calculated to be 1.37. the concentrations of H^+ after further additions of NaOH have occurred are summarized in the previous table.

Our calculations show that the pH increases slowly at first, then rises rapidly near the equivalence point, and finally levels off gradually after the equivalence point is reached.

If a graph is drawn of pH versus the volume of base added, we obtain the plot shown in the <u>following figure</u>. The equivalence point occurs in this case, at a pH of 7. at the equivalence point the solution is neutral because neither of the ions of the salt that is left in solution (NaCl) undergoes hydrolysis.



Example: How many mL of $0.025 M H_2SO_4$ are required neutralize 525 mL of 0.06 M KOH. What is the pH of neutralized solution?

Solution:

N of KOH = n H = 1 X
$$0.06 = 0.06$$
 N
N of $H_2SO_4 = NH = 2 X 0.025 = 0.05$ N

$$\begin{aligned} N_a & X & V_a = N_b X & V_b \\ 0.05 & X & V_a = 0.06 X 525 \\ & V_a = 630 \text{ mL} \end{aligned}$$

Therefore, the pH of neutralized solution = 7

Acid-Base Indicators

Indicators are usually weak organic acids or bases that change color over a range of ph values. Not all indicators change color at the same ph, however.

If we denote an indicator by the general formula HIn, we have the dissociation reaction

 $HIn \longrightarrow H^+ + In^-$

Table: some common indicators

Indicator	Color change	pH Range in which color
		change occurs
Thymol blue	Red to yellow	1.2-2.8
Bromophenol blue	Yellow to blue	3.0-4.6
Congo red	Blue to red	3.0-5.0
Methyl orange	Red to yellow	3.2-4.4
Bromocresol green	Yellow to blue	3.8-5.4
Methyl red	Red to yellow	4.8-6.0
Bromocresol purple	Yellow to purple	5.2-6.8
Bromothymol blue	Yellow to blue	.0-7.6
Cresol red	Yellow to red	7.0-8.8
Thymol blue	Yellow to blue	8.0-9.6
phenolphthalein	Colorless to pink	8.2-10.2
Alizarin yellow	Yellow to red	10.1-12.0

Buffers and blood

- Oxygen is transported primarily by hemoglobin in the red blood cells
- CO₂ transported both in plasma and the red blood cells

$$CO_2 + 2H_2O \longrightarrow H_2CO_3$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$CO_2 \qquad \qquad H_3O^+ + HCO_3^-$$

The amount of CO₂ helps control blood pH

- Too much CO₂- Respiratory arrest (Hypoventilation)
- pH goes down, acid level goes up-acidosis
- Reduced in rate and depth of breathing
- Solution: ventilate and give bicarbonate via IV
- Too little CO₂-anxiety (hyperventilation)
- The pH goes up, acid level goes down-alkalosis
- Increase in rate and depth of breathing
- Solution: rebreath CO₂ in paper bag to raise level

Normal blood pH is from 7.35-7.45 Going outside of this range can be very dangerous or deadly

Acidosis and Alkalosis

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Metabolic acidosis

Can be caused by uncontrolled diabetes mellitus, diarrhea, aspirin overdose and after heavy exercise.

Metabolic alkalosis

Caused by prolonged vomiting, excessive use of bicarbonate for treating an upset stomach.