COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT

CHEM 101
LECTURES IN
GENERAL CHEMISTRY (1)

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1446 H – 2024/2025 G

TABLE OF CONTENTS

PERSONAL INFORMATION

اسم الطالب باللغة العربية →	
STUDENT UNIVERCIY NUMBER →	
MOBILE NUMBER →	
FIRST MIDTERM EXAM → (15 grades)	
SECONDMIDTERM EXAM → (15 grades)	
FINAL EXAM → (40 grades)	
مدرّس المقرّر →	**د. أحمد العويس** **CHEMISTRY DEPARTMENT** **OFFICE: 2A15** **COLLEDGE OF SCIENCE** **BUILDING: 5**

SYLLABUS

Text book: Raymond Chang, Chemistry, 14th edition, 2022		
Topics	**Page number**	**Lecture hours**
1 Chemistry: The Study of Change		
1.1 Chemistry: A Science for the Twenty-First Century	2	3
1.2 The scientific method	4	
1.3 Measurements	6	
1.4 Classification of matter		
1.5 Handling numbers	13	
1.6 Dimensional analysis in solving problems	20	
Review and Exercises		
2 Atoms, Molecules and Ions		
2.1 The Atomic Theory	41	5
2.2 The Structure of the Atom	43	
2.3 Atomic Number, Mass Number, and Isotopes	49	
2.4 The Periodic Table	51	
2.5 Molecules and Ions	54	
2.6 Chemical Formulas	55	
2.7 Naming Compounds	60	
Review and Exercises		
3 Mass Relationships in Chemical Reactions		
3.1 Atomic Mass	80	6
3.2 Avogadro’s Number and Molar Mass of an Element	82	
3.3 Molecular Mass	85	
3.4 The Mass Spectrometer	88	
3.5 Percent Composition of Compounds	90	
3.6 Experimental Determination of Empirical Formulas	93	
3.7 Chemical Reactions and Chemical Equations	95	
3.8 Amounts of Reactants and Products	100	
3.9 Limiting Reagents	104	
3.10 Reaction Yield and Atom Economy	108	
Review and Exercises		
4 Reactions in aqeueos solutions		
4.1 General Properties of Aqueous Solutions	125	6
4.2 Precipitation Reactions	127	
4.3 Acid-Base Reactions	132	
4.4 Oxidation-Reduction Reactions	138	
4.5 Concentration of Solutions	150	
4.6 Gravimetric Analysis	155	
4.7 Titrations	157	
Review and Exercises		
5 Gases		

5.1 Substances that Exist as gases	176	7
5.2 Pressure of a gas	178	
5.3 The gas laws	181	
5.4 The ideal gas law	188	
5.5 Gas stoichiometry	196	
5.6 Dalton's law of partial pressures	199	
5.7 The kinetic molecular theory of gases	206	
5.8 Deviation from ideal behavior	214	
Review and Exercises		
6 Thermochemistry		
6.1 The Nature of Energy and Types of Energy	231	**5**
6.2 Energy Changes in Chemical Reactions	232	
6.3 Introduction to Thermodynamics	234	
6.4 Enthalpy of Chemical Reactions	241	
6.5 Calorimetry	247	
6.6 Standard Enthalpy of Formation and Reaction	253	
6.7 Heat of Solution and Dilution	259	
Review and Exercises		
7 Quantum theory and the electronic structure of atoms		
7.1 From Classical Physics to Quantum Theory	274	**5**
7.2 The Photoelectric Effect	281	
7.3 Bohr’s Theory of the Hydrogen Atom	283	
7.4 The Dual Nature of the Electron	290	
7.5 Quantum Mechanics	294	
7.6 Quantum Numbers	297	
7.7 Atomic Orbitals	300	
7.8 Electron Configuration	305	
7.9 The Building-Up Principle	312	
Review and Exercises		
12 Solutions		
12.1 Types of Solutions	528	**7**
12.2 A Molecular View of the Solution Process	529	
12.3 Concentration Units	532	
12.4 The Effect of Temperature on Solubility	536	
12.5 The Effect of Pressure on the Solubility of Gases	538	
12.6 Colligative Properties of Nonelectrolyte Solutions	541	
12.7 Colligative Properties of Electrolyte Solutions	552	
Review and Exercises		
TOTAL HOURS		**42**

DISTRIBUTION OF GRADES

First theoretical midterm exam	15 grades
Second theoretical midterm exam	15 grades
Laboratory experiments	30 grades
Final theoretical midterm exam	40 grades
Total	100 grades

INTRODUCTION

The aims of this course are:

1) Acquiring the fundamental basic principles of the chemistry science
2) Comprehending the necessity of the basic mathematical arithmetic needed in chemistry
3) Understanding that the scientific conventions regarding symbols, names, units, numbering, …etc. are not personal choice but rather much closer to compulsory
4) Exercising how calculations should be accomplished in the world of chemistry
5) Questioning the so far acceptable hypothesis, theories, facts and laws in the field of chemistry

To achieve these aims, the following ought to be taken seriously in mind:

1) *Scientific methodology*: chemistry development has largely depended on the appreciation of the scientific methodology. therefore, it is highly important to follow this path to fulfill the greatest possible understanding of the contents of this course.
2) *Self-dependent*: when a person relies on his/her self, he/she will find reading the content, practicing exercises, questioning and criticizing are very fruitful means.
3) *Avoiding* c*arelessness*: avoiding carelessness regarding some aspects or subjects is a very crucial way to achieve these aims.

This course helps to understand the so many applications of chemistry findings in our life.

I, greatly, thank the Chemistry Department at King Saud University, I have a great appreciation to my students and colleagues previous and now a day.

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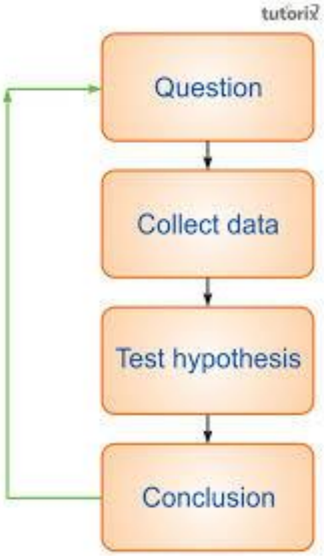
1. CHEMISTRY: THE STUDY OF CHANGE

1.1 Chemistry: A Science for the Twenty-First Century

- **CHEMISTRY** is the study of matter and the changes it undergoes
- It is **THE CENTRAL SCIENCE**, because it is essential for biology, physics, geology, ecology, and many other subjects
- Although it is an ancient science, its modern foundation was laid in the nineteenth century, when intellectual and technological advances enabled scientists to break down substances into ever smaller components and consequently to explain many of their physical and chemical characteristics
- The rapid development of technology throughout the twentieth century has given us even greater means to study things that cannot be seen with the naked eye
- Using computers and special microscopes, for example, chemists can analyze the structure of atoms and molecule and design new substances with specific properties, such as drugs and environmentally friendly consumer products.
- As we enter the twenty-first century, it is fitting to ask what part **the central science** will have in this century. Almost certainly, chemistry will continue to play a pivotal role in all areas of science and technology
- Whatever your reasons for taking general chemistry, a good knowledge of the subject will better enable you to appreciate its impact on society and on you as an individual

1.2 The Scientific Method

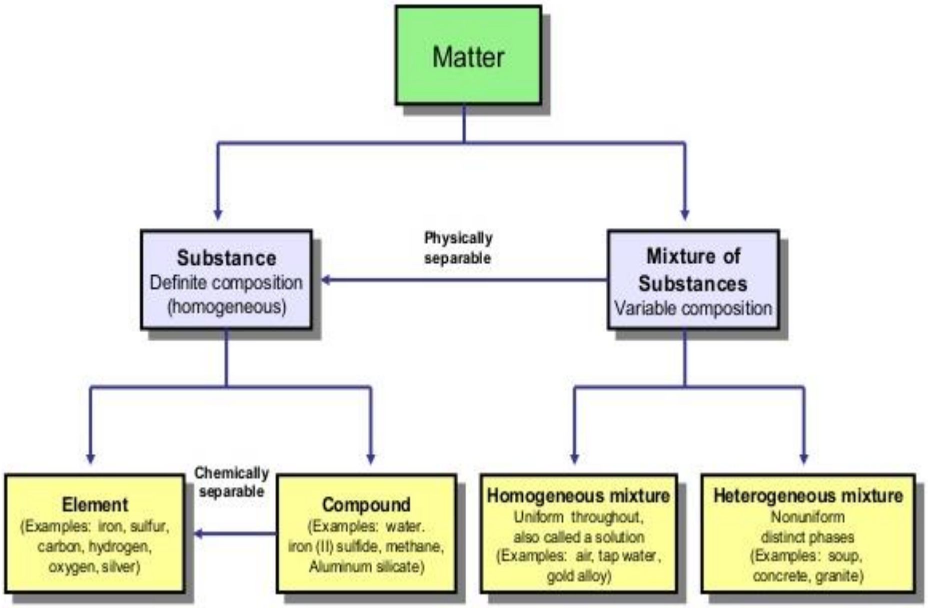
- The scientific method, a systematic approach to research
- All sciences employ various scientific methods
- For example, a chemist who is interested in measuring the heat given off when hydrogen gas burns in air would follows a scientific method in carrying out his investigations
- The first step is to carefully define the problem
- The next step includes performing experiments, making careful observations, and recording information, or data, about the system (*IN THE EXAMPLES JUST DISCUSSED*, *THE SYSTEMS IS A MIXTURE OF HYDROGEN AND AIR*)
- The data obtained in a research study may be both qualitative, consisting of general observations about the system, and quantitative, comprising numbers obtained by various measurements of the system
- Chemists generally use standardized symbols and equations in recording their measurements and observations. This form of representation not only simplifies the process of keeping records, but also provides a common basis for communication with other chemists
- When the experiments have been completed and the data have been recorded, the next step in the scientific method is interpretation (*THE SCIENTIST ATTEMPTS TO EXPLAIN THE OBSERVED PHENOMENON*)
- Based on the data that were gathered, the researcher formulates a hypothesis (*A TENTATIVE EXPLANATION FOR A SET OF OBSERVATIONS*)
- Further experiments are devised to test the validity of the hypothesis in as many ways as possible, and the process begins anew
- Figure 1.3 summarizes the main steps of the research process



- After a large amount of data has been collected, it is often desirable to summarize the information in a concise way, as a law (A *LAW* IS *A CONCISE VERBAL OR MATHEMATICAL STATEMENT OF A RELATIONSHIP BETWEEN PHENOMENA THAT IS ALWAYS THE SAME UNDER THE SAME CONDITIONS*)
- Hypotheses that survive many experimental tests of their validity may evolve into theories (*A THEORY IS A UNIFYING PRINCIPLE THAT EXPLAINS A BODY OF FACTS AND/OR THOSE LAWS THAT ARE BASED ON THEM*)
- Theories, too, are constantly being tested. If a theory is disproved by experiment, then it must be discarded or modified so that it becomes consistent with experimental observations
- Proving or disproving a theory can take years, even centuries, in part because the necessary technology may not be available (*IT TOOK ATOMIC THEORY MORE THAN 2000 YEARS TO WORK OUT THIS FUNDAMENTAL PRINCIPLE OF CHEMISTRY PROPOSED BY AN ANCIENT GREEK PHILOSOPHER "DEMOCRITUS"*)
- Scientific progress is seldom made in a rigid, step-by-step fashion. Sometimes a law precedes a theory; sometimes it is the other way around
- Two scientists may start working on a project with exactly the same objective but will end up taking drastically different approaches
- Scientists are human beings, and their modes of thinking and working are very much influenced by their background, training, and personalities
- The development of science has been irregular and sometimes even illogical
- Great discoveries are usually the result of the cumulative contributions and experience of many workers, even though the credit for formulating a theory or a law is usually given to only one individual
- There is, of course, an element of luck involved in scientific discoveries, but it has been said that "chance favors the prepared mind"
- It takes an alert and well-trained person to recognize the significance of an accidental discovery and to take full advantage of it
- More often the public learns only of spectacular scientific breakthroughs

- For every success story, there are hundreds of cases in which scientists have spent years working on projects that ultimately led to a dead end, and in which positive achievements came only after many wrong turns and at such a slow pace that they went unheralded. Yet even the dead ends contribute something to the continually growing body of knowledge about the physical universe
- It is the love of the search that keeps many scientists in the laboratory

1.3 Classifications of matter



- **<u>First: Substances:</u>** A ***substance*** is *a matter that has a definite (constant) composition and distinct properties. Substances differ in composition and can be identified by their appearance, smell, taste, and other properties.* Examples: water, ammonia, table sugar (sucrose), gold, and oxygen. Substances are either **elements** or **compounds**:
  - ✓ **Elements:** An element is a substance that cannot be separated into simpler substances by chemical means
    - ➢ **Symbols of elements:** Elements are given symbols that indicate their names. The periodic table contains the names and symbols of all elements
    - ➢ Most of the symbols of elements comes from their English names: symbol of carbon is "C" and of oxygen is "O". Some elements symboles are derived from their Latin names: gold, iron and sodium are "Au" and "Fe" and "Na" from Aurum, *ferrum* and *natrium*
    - ➢ Symbols either one or two letters. The first letter is *always* **"UPPERCASE"**. If the symbol is two letters, the second letter must be "**lowercase":** the symbol of cobalt is **Co**
  - ✓ **Compounds**: A compound is a substance composed of atoms of two or more elements chemically united in fixed proportions, water (H_2O) is an example
    - ➢ **Formulas of compounds:** Compounds are given formulas that consists of the symbols of the elements of the compound. For example: formulas of carbon monoxide and carbon dioxide are "CO" and "CO_2"

- **Second: Mixtures:** A ***mixture*** is *a combination of two or more substances in which the substances retain their distinct identities*. Mixtures do not have constant composition. They are two types:
  - ✓ **Homogeneous mixture:** A Homogeneous mixture is a mixture in which the composition of the mixture is the same throughout (*the composition is uniform*). Examples: air, soft drinks, milk, and cement
  - ✓ **Heterogeneous mixture:** A Heterogeneous mixture is a mixture in which the composition of the mixture is not the same throughout (*the composition is not uniform)*. Examples: the mixture of sand and iron filing
  - ✓ Any mixture can be separated to its components by physical means without changing the identities of the components

1.4 Measurement

- The measurements chemists make are often used in calculations to obtain other related quantities
- Different instruments enable us to measure a substance's properties:
  - ✓ The meterstick measures length or scale
  - ✓ The burette, the pipet, the graduated cylinder, and the volumetric flask measure volume
  - ✓ The balance measures mass
  - ✓ The thermometer measures temperature.

  These instruments provide measurements of ***macroscopic properties,*** which can be determined directly; ***Microscopic properties,*** *on the atomic or molecular scale*, must be determined by an indirect method
- A measured quantity is usually written as a number with an appropriate unit
- To say that the distance between Dammam and Jeddah is 1355 is meaningless, we must specify that the distance is 1355 kilometers. The same is true in chemistry; units are essential to stating measurements correctly

1.4.1 SI Units

- In 1960, the General Conference of Weights and Measures, the international authority on units, proposed a revised metric system called the ***International System of Units*** (abbreviated ***SI UNITS***)
- Physical quantities are two types: the base physical quantities that are given seven base SI units, and the derived physical quantities that are given derived SI units.

First: Base units

- The following table shows the seven base physical quantities and their SI base units:

Base quantity	SI base unit	
	Name	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
Thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

- The SI units of length and mass are in decimal fashion. The table below shows the prefixes used for their large and small quantities:

Prefixes used with SI Units		
Prefix (Symbol)	Power	Example
tera (T)	10^{12}	1 Tm = 1×10^{12} m
giga (G)	10^{9}	1 Gm = 1×10^{9} m
mega (M)	10^{6}	1 Mm = 1×10 m
kilo (k)	10^{3}	1 km = 1×10^{6} m
deci (d)	10^{-1}	1 dm = 1×10^{3} m
centi (c)	10^{-2}	1 cm = 1×10^{-1} m
milli (m)	10^{-3}	1 mm = 1×10^{-3} m
micro (μ)	10^{-6}	1 μm = 1×10^{-6} m
nano (n)	10^{-9}	1 nm = 1×10^{-9} m
pico (p)	10^{-12}	1 pm = 1×10^{-12} m

Second: Derived units

All the rest of physical quantities are derived from these seven quantities and their units are “derived units”.

1.4.2 Some important units

- **First: Mass and weight**
  - ✓ The SI unit of mass is the **kilogram** (kg). Smaller **gram** (g) is convenient sometimes:

    1 kg = 1000 g
  - ✓ Pound (lb), is a non- SI Unit of mass

    1 lb = 0.4536 kg

    1 kg = 2.2046 lb
- **Second: Volume**
  - ✓ The SI unit of volume is the **cubic meter** (m^3)

    $$1\ m^3 = 1 \times 10^3\ dm^3 = 1 \times 10^6\ cm^3$$
  - ✓ **Liter** (L), is a non- SI Unit of volume occupied by one cubic decimeter

    $$1\ L = 1\ dm^3 = 1000\ cm^3 = 1000\ mL$$
- **Third: Density**
  - ✓ The equation for density is

    $$\text{density} = \frac{\text{mass}}{\text{volume}}\ \textbf{OR}\ d = \frac{m}{V}$$

- ✓ The SI-derived unit for density is the **kilogram per cubic meter** ($\frac{\text{kg}}{\text{m}^3}$)
- ✓ **Gram per cubic centimeter** ($\frac{\text{g}}{\text{cm}^3}$) and its equivalent, **grams per milliliter** ($\frac{\text{g}}{\text{mL}}$) are commonly used for solid and liquid densities
- ✓ **Gram per liter** ($\frac{\text{g}}{\text{L}}$) and its equivalent, **grams per cubic decimeter** ($\frac{\text{g}}{\text{dm}^3}$) are commonly used for gas densities

$$1\ \frac{\text{kg}}{\text{m}^3} = 1 \times 10^{-3}\ \frac{\text{g}}{\text{cm}^3}$$

- ✓ The following table lists the densities of several substances

Material	Density ($\frac{\text{g}}{\text{cm}^3}$)
Gold	19.3
Mercury	13.6
Lead	11.3
Silver	10.5
Iron	7.86
Aluminum	2.7
Rubber	1.1
Water	1.0
Air	0.0013

EXAMPLE 1.1

A piece of gold with a mass of 301 g has a volume of 15.6 cm^3. Calculate the density of gold.

Solution

$$d = \frac{m}{V} = \frac{301\ \text{g}}{15.6\ \text{cm}^3} = 19.3\ \frac{\text{g}}{\text{cm}^3}$$

Practice Exercise 1.1

A piece of platinum with a density of 21.5 g/cm^3 has a volume of 4.49 cm^3. What is its mass?

EXAMPLE 1.2

The density of mercury is 13.6 $\frac{\text{g}}{\text{cm}^3}$. Calculate the mass of 5.50 mL of the liquid.

Solution

5.50 mL = 5.50 cm^3

$$m = d \times V = 13.6\ \frac{\text{g}}{\cancel{\text{cm}^3}} \times 5.5\ \cancel{\text{cm}^3} = 74.8\ \text{g}$$

Practice Exercise 1.2

The density of sulfuric acid solution in a certain car battery is 1.41 g/mL. Calculate the mass of 242 mL of this solution.

- **Fourth: Temperature**

  Temperature is an arbitrary measure of the degree of hotness or coldness of matter. There are three temperature scales, their units are **degrees Fahrenheit** (°F), **degrees Celsius** (°C), and **Kelvin** (K):

  - ✓ The **Celsius** scale, commonly used scale worldwide, divides the range between the normal freezing point (0°C) and boiling point (100°C) of water into 100 degrees, therefore it is sometimes called “the centigrade scale”

- ✓ The **Fahrenheit** scale, least used scale worldwide, defines the normal freezing and boiling points of water to be exactly 32 °F and 212 °F, respectively. The following equations are used to convert between degrees Celsius and degrees Fahrenheit:

$$\text{Temperature in °C} = (\text{Temperature in °F} - 32\ \text{°F}) \times \left(\frac{5\ \text{°C}}{9\ \text{°F}}\right)$$

$$\text{Temperature in °F} = (\text{Temperature in °C} \times \frac{9\ \text{°F}}{5\ \text{°C}}) + (32\ \text{°F})$$

- ✓ The **Kelvin** scale (also called the **absolute** temperature scale) is the SI base unit of temperature. By "absolute" we mean that the zero on the Kelvin scale, denoted by 0 K, is the lowest temperature that can be attained theoretically. The **Kelvin** scale defines the normal freezing and boiling points of water to be exactly 273.15 K and 373 K, respectively. The Celsius and the Kelvin scales have units of equal magnitude; that is, one degree Celsius is equivalent to one Kelvin:

$$0\ \text{K} = -273.15\text{°C} = -459.67\ \text{°F}$$

The following equations are used to convert between degrees Celsius and Kelvin:

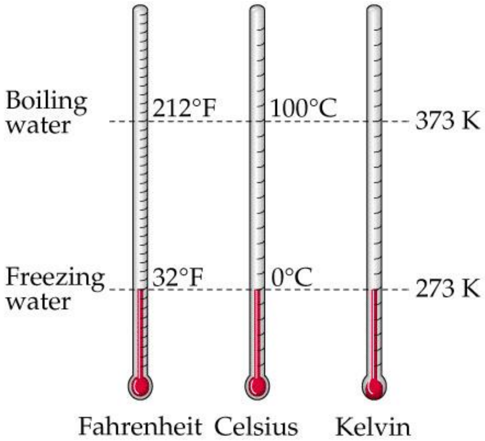
$$\text{Temperature in K} = (\text{Temperature in °C} + 273.15\ \text{°C})$$

$$\text{Temperature in °C} = (\text{Temperature in K} - 273.15\ \text{K})$$

The following equations are used to convert between degrees Fahrenheit and Kelvin:

$$\text{Temperature in K} = (\text{Temperature in °F} + 459.67\ \text{°F}) \times \frac{5\ \text{K}}{9\ \text{°F}}$$

$$\text{Temperature in °F} = (\text{Temperature in K} \times \frac{9\ \text{°F}}{5\ \text{K}}) - (459.67\ \text{°F})$$



EXAMPLE 1.3

A) Mercury melting point is − 38.9 °C. How much is it in Kelvin and °F?
B) Normal human temperature is 98.6 °F. How much is it in Kelvin and °C?
C) Iron boiling point is 3135.35 K. How much is it in °C and °F?

Solution

A) Temperature in K = (Temperature in °C + 273.15 °C)

$$\text{Temperature in K} = (-38.9\ \text{°C} + 273.15\ \text{°C}) = 234.3\ \text{K}$$

$$\text{Temperature in °F} = (\frac{9\ \text{°F}}{5\ \text{°C}} \times \text{Temperature in °C}) + 32\ \text{°F}$$

$$\text{Temperature in °F} = (\frac{9\ \text{°F}}{5\ \text{°C}} \times -38.9\ \text{°C}) + 32\ \text{°F} = -38.02\ \text{°F}$$

B) Temperature in K = (Temperature in °F + 459.67 °F) × $\frac{5}{9}$

Temperature in K = (98.6 °F + 459.67 °F) × $\frac{5\ \text{K}}{9\ °\text{F}}$ = 310.15 K

Temperature in °C = (Temperature in °F − 32 °F) × $\left(\frac{5\ °\text{C}}{9\ °\text{F}}\right)$

Temperature in °C = (98.6 °F − 32 °F) × $\left(\frac{5\ °\text{C}}{9\ °\text{F}}\right)$ = 37 °C

C) Temperature in °C = (Temperature in K − 273.15 K) × $\left(\frac{1\ °\text{C}}{1\ \text{K}}\right)$

Temperature in °C = (3135.35 K − 273.15 K) × $\left(\frac{1\ °\text{C}}{1\ \text{K}}\right)$ = 2862.20 °C

Temperature in °F = (Temperature in K × $\frac{9\ °\text{F}}{5\ \text{K}}$) – (459.67 °F)

Temperature in °F = (3135.35 K × $\frac{9\ °\text{F}}{5\ \text{K}}$) – (459.67 °F) = 5183.96 °F

Practice Exercise 1.3

A) Convert – 38.83 °C, (the freezing point of mercury) to °F and to K.
B) Convert 346 °F, (the freezing point of nitrogen) to °C and to K.
C) Convert 77 K, (the boiling point of nitrogen) to °C and to °F.

- **Fifth: Pressure**
  - ✓ Pressure is the force applied on unit area:

$$\text{Pressure SI Unit} = \frac{\text{Force SI Unit}}{\text{Area SI Unit}} = \left(\frac{\left(\frac{\text{kg m}}{\text{s}^2}\right)}{(\text{m}^2)}\right) = \frac{\text{kg}}{\text{m s}^2}$$

This unit "$\frac{\text{kg}}{\text{m s}^2}$", is called "Pascal" and abbreviated "Pa":

$$1\ \frac{\text{kg}}{\text{m s}^2} = 1\ \text{Pa}$$

  - ✓ Pressure is measured by other units:
    - ✓ The ***atmosphere*** unit, abbreviated "atm":

      1 atm = 101325 Pa
    - ✓ The ***centimeter mercury*** unit, abbreviated "cmHg":

      1 cmHg = 1333.22 Pa
    - ✓ The ***millimeter mercury*** unit, abbreviated "mmHg":

      1 mmHg = 0.1 cmHg = 133.322 Pa

      This unit "mmHg" is called "**Torricelli**" and abbreviated "Torr":

      1 Torr = 1 mmHg
    - ✓ The **pound per inch square** unit, abbreviated "psi":

      1 psi = 6894.76 Pa
    - ✓ The **bar** unit, abbreviated "bar":

      1 bar = 100,000 Pa

EXAMPLE 1.4

A) It is found, in a cold day, that the atmospheric pressure in Riyadh is 743 mmHg. How much this pressure in "atm" unit and in the SI Units?
B) If the pressure inside your car tire is 35 psi, how much is this pressure in bar unit and in the SI Units?
C) A balloon full of air at a pressure equals to 0.35 atm. What would its pressure be in "mmHg" unit and in the SI Units?

Solution

A) Pressure in atm = Pressure in mmHg × $\frac{1\ \text{atm}}{760\ \text{mmHg}}$ = 743 mmHg × $\frac{1\ \text{atm}}{760\ \text{mmHg}}$ = 0.978 atm

Pressure in Pa = Pressure in mmHg × $\frac{133.322\ \text{Pa}}{1\ \text{mmHg}}$ = 743 mmHg × $\frac{133.322\ \text{Pa}}{1\ \text{mmHg}}$ = 99058.2 Pa

B) Pressure in bar = Pressure in psi × $\frac{1\ \text{bar}}{14.504\ \text{psi}}$ = Pressure in Pa = 35 psi × $\frac{1\ \text{bar}}{14.504\ \text{psi}}$ = 2.41 bar

Pressure in Pa = Pressure in psi × $\frac{6894.76\ \text{Pa}}{1\ \text{psi}}$ = 35 psi × $\frac{6894.76\ \text{Pa}}{1\ \text{psi}}$ = 241316.6 Pa

C) Pressure in mmHg = Pressure in atm × $\frac{760\ \text{mmHg}}{1\ \text{atm}}$ = 0.35 atm × $\frac{760\ \text{mmHg}}{1\ \text{atm}}$ = 266 mmHg

Pressure in Pa = Pressure in atm × $\frac{101325\ \text{Pa}}{1\ \text{atm}}$ = 0.35 atm × $\frac{101325\ \text{Pa}}{1\ \text{atm}}$ = 35463.75 Pa

Practice Exercise 1.4

A) It is found, in a hot day, that the atmospheric pressure in Riyadh is 737 mmHg. How much is this pressure in “Pa” and in “bar” units?

B) If the pressure inside a gaseous cylinder is 4.6 atm, how much is it in “Pa” and in “Torr”.

C) If the pressure outside an airplane at 40000 ft-altitude reads 0.18 bar. What would this pressure be in “mmHg” unit and in the SI Unit of pressure

- **Sixth: Energy**
  - ✓ Energy is usually defined as the ability to do work:

    Work = force × distance
  - ✓ The SI Units of work is the SI Units of force times the the SI Unit of distance:

    The SI Units of work = $\frac{\text{kg m}}{\text{s}^2}$ × m = $\frac{\text{kg m}^2}{\text{s}^2}$ = J
  - ✓ This unit of work itself is the unit of energy. This SI Unit, $\frac{\text{kg m}^2}{\text{s}^2}$, is named “Joule” and abbreviated as “J”
  - ✓ The unit “calorie” abbreviated as “cal” is another unit for energy:

    1 cal = 4.184 $\frac{\text{kg m}^2}{\text{s}^2}$ = 4.184 J
  - ✓ It might be useful to mention that when the word “calorie” is written with capital “C” as “Calorie” its value changes:

    1 Cal = 1 kcal = 1000 cal = 4184 J
  - ✓ “Calorie” is used in the fields of food, nutrients and physical exercises. If there are 78 Calories in an average-mass apple (150 g), this equals 78000 calorie or 18642 J. And a moderate-speed waking for one kilometer burns 55 Calories which equals 55000 calorie or 230120 J. Therefore, we should not confuse calorie with Calorie.

1.5 Handling Numbers: Scientific notation and Significant figures

1.5.1 Scientific notation

- Chemists often deal with numbers that are either extremely large or extremely small. For example:
  - ✓ In 1 g of hydrogen there are 602,200,000,000,000,000,000,000 hydrogen atoms
  - ✓ The mass of a hydrogen atom is 0.00000000000000000000000166 g
- Consider the following multiplication:

  0.0000000056 × 0.00000000048 = 0.000000000000000002688

  It is easy to miss one zero or add one more zero after the decimal point
- When working with very large and very small numbers, we use a system called ***scientific notation***
- Regardless of their magnitude, all numbers can be expressed in the form

  $$N \times 10^{n}$$
  - ✓ N is a number between 1 and 10
  - ✓ n, the exponent, is a positive or negative integer (whole number)
- Any number expressed in this way is said to be written in **scientific notation**

- To express a number in scientific notation:
  - ✓ We must find *n*
  - ✓ We count the number of places that the decimal point must be moved to give the number *N* (which is between 1 and 10)
  - ✓ If the decimal point has to be moved to the left, then *n* is a positive integer; if it has to be moved to the right, *n* is a negative integer
  - ✓ The following examples illustrate the use of scientific notation:
    - ➢ $568.762 = 5.68762 \times 10^2$
      n = 2 because the decimal point is moved 2 places to the left
    - ➢ $0.00000772 = 7.72 \times 10^{-6}$
      n = – 6 because the decimal point is moved 6 places to the right
- Keep in mind the following two points:
  - ✓ n = 0 is used for numbers that are not expressed in scientific notation. For example, 74.6×10^0 (n = 0) is equivalent to 74.6
  - ✓ The superscript is omitted when n = 1. Thus, the scientific notation for 74.6 is 7.46×10 and not 7.46×10^1
- Addition and subtraction: To add or subtract using scientific notation:
  - ✓ Write each quantity, say N_1 and N_2, with the same exponent n
  - ✓ Combine N_1 and N_2; the exponents remain the same.
    - ➢ $(7.4 \times 10^3) + (2.1 \times 10^3) = 9.5 \times 10^3$
    - ➢ $(4.31 \times 10^4) + (3.9 \times 10^3) = (4.31 \times 10^4) + (0.39 \times 10^4) = 4.70 \times 10^4$
    - ➢ $(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) = (2.22 \times 10^{-2}) - (0.41 \times 10^{-2}) = 1.81 \times 10^{-2}$
- ✓ Multiplication and division: To multiply numbers expressed in scientific notation:
  - ✓ Multiply N_1 and N_2 in the usual way
  - ✓ Add the exponents together
    - ➢ $(8.0 \times 10^4) \times (5.0 \times 10^2) = (8.0 \times 5.0)\,(10^{4+2}) = 40 \times 10^6 = 4.0 \times 10^7$
    - ➢ $(4.0 \times 10^{-5}) \times (7.0 \times 10^3) = (4.0 \times 7.0)\,(10^{-5+3}) = 28 \times 10^{-2} = 2.8 \times 10^{-1}$
- To divide using scientific notation:
  - ✓ Divide N_1 and N_2 as usual
  - ✓ Subtract the exponents
    - ➢ $\frac{6.9 \times 10^7}{3.0 \times 10^{-5}} = \frac{6.9}{3.0} \times 10^{7-(-5)} = 2.3 \times 10^{12}$
    - ➢ $\frac{8.5 \times 10^4}{5.0 \times 10^9} = \frac{8.5}{5.0} \times 10^{4-9} = 1.7 \times 10^{-5}$

1.5.2 Significant figures

- Except when all the numbers involved are integers (for example, in counting the number of students in a class), it is often impossible to obtain the exact value of the quantity under investigation
- For this reason, it is important to indicate the margin of error in a measurement by clearly indicating the number of ***significant figures***
- ***Significant figures*** are *the meaningful digits in a measured or calculated quantity*
- When significant figures are used, the last digit is understood to be uncertain
  - ✓ we might measure the volume of a given amount of liquid using a graduated cylinder with a scale that gives an uncertainty of 1 mL in the measurement
    - ➢ If the volume is 6 mL, then the actual volume is in the range of 5 mL to 7 mL
    - ➢ We represent the volume of the liquid as (6 ± 1) mL

        - ➢ In this case, there is only one significant figure (the digit 6) that is uncertain by either plus or minus 1 mL
    - ✓ If we used a graduated cylinder that has finer divisions, so that the volume we measure is uncertain by only 0.1 mL
        - ➢ If the volume of the liquid is found to be 6.0 mL, we may express the quantity as (6.0 ± 0.1) mL
        - ➢ The actual value is somewhere between 5.9 mL and 6.1 mL
    - ✓ We can further improve the measuring device and obtain more significant figures, but in every case, the last digit is always uncertain; the amount of this uncertainty depends on the measuring device we use.
- Modern balances that measure the mass of objects to four or more decimal places are being used in many chemistry laboratories
- Tracking the number of significant figures in a measurement such as mass ensures that calculations involving the data will reflect the precision of the measurement.
- **Guidelines for Using Significant Figures:**

1. ***Any digit that is not zero is significant***
845 cm has three significant figures
1.234 kg has four significant figures
and so on

2. ***Zeros between nonzero digits are significant***
606 m contains three significant figures
40501 kg contains five significant figures
and so on

3. ***Zeros to the left of the first nonzero digit are not significant***
Their purpose is to indicate the placement of the decimal point
0.08 L contains one significant figure.
0.0000349 g contains three significant figures
and so on

4. ***If a number is greater than 1, then all the zeros written to the right of the decimal point count as significant figures***
2.0 mg has two significant figures
40.062 mL has five significant figures
3.040 dm has four significant figures
and so on

5. ***If a number is less than 1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant***.
0.090 kg has two significant figures.
0.3005 L has four significant figures.
0.00420 min has three significant figures.
and so on

6. Numbers that do not contain decimal points, the trailing zeros (zeros after the last nonzero digit) may or may not be significant
400 cm may have one significant figure (the digit 4), two significant figures (40), or three significant figures (400). We cannot know which is correct without more information. However, by using scientific notation we avoid this ambiguity:
We can express the number 400 in three different ways:

4×10^2 for one significant figure
4.0×10^2 for two significant figures
4.00×10^2 for three significant figures

EXAMPLE 1.5

Determine the number of significant figures in the following measurements:

a) 478 cm b) 6.01 g c) 0.825 m
d) 0.043 kg e) 1.310×10^{22} atoms f) 7000 mL

Solution

a) Three, because each digit is a nonzero digit
b) Three, because zeros between nonzero digits are significant
c) Three, because zeros to the left of the first nonzero digit do not count as significant figures
d) Two. Same reason as in (c)
e) Four, because the number is greater than one, so all the zeros written to the right of the decimal point count as significant figures
f) This is an ambiguous case. The number of significant figures may be four (7.000×10^3), three (7.00×10^3), two (7.0×10^3) or one (7×10^3). This example illustrates why scientific notation must be used to show the proper number of significant figures.

Practice Exercise 1.5

Determine the number of significant figures in each of the following measurements:

A) 24 mL B) 3001 g C) 0.0320 m^3
D) 6.4×10^4 molecules E) 560 kg

- ✓ A second set of rules specifies how to handle significant figures in calculations:

1. In addition, and subtraction

The answer cannot have more digits to the right of the decimal point than either of the original numbers:

89.332
+ 1.1 ← one digit after the decimal point
90.432 ← round off to 90.4

2.097 ← three digits after the decimal point
– 0.12 ← two digits after the decimal point
1.977 ← round off to 1.98

The rounding-off procedure is as follows:

- ✓ To round off a number at a certain point we simply drop the digits that follow if the first of them is less than 5:
  8.724 rounds off to 8.72 if we want only two digits after the decimal point. But if the first digit following the point of rounding off is equal to or greater than 5, we add 1 to the preceding digit:
  8.727 rounds off to 8.73
  0.425 rounds off to 0.43

2. In multiplication and division

The number of significant figures in the final product or quotient is determined by the original number that has the *smallest* number of significant figures. The following examples illustrate this rule:

$2.8 \times 4.5039 = 12.61092$ ← round off to 13

$\frac{6.85}{112.04}$ = 0.0611388789 ← round off to 0.0611

3. **Keep in mind**

   Keep in mind that *exact numbers* obtained from definitions or by counting numbers of objects can be considered to have an infinite number of significant figures. For example:

   - ✓ The inch is defined to be exactly 2.54 centimeters:

     1 in = 2.54 cm

     Thus, the "2.54" in the equation should not be interpreted as a measured number with three significant figures. In calculations involving conversion between "in" and "cm," we treat both "1" and "2.54" as having an infinite number of significant figures.
   - ✓ if an object has a mass of 5.0 g, then the mass of nine such objects is:

     5.0 g × 9 = 45 g

     The answer has two significant figures because 5.0 g has two significant figures. The number 9 is exact and does not determine the number of significant figures.

EXAMPLE 1.6

Carry out the following arithmetic operations to the correct number of significant figures in scientific notation:

a) 11,254.1 g + 0.1983 g b) 66.59 L – 3.113 L c) 8.16 m × 5.1355

d) 0.0154 kg ÷ 88.3 mL e) 2.64×10^3 cm + 3.27×10^2 cm.

Solution

a)
$$\begin{array}{r} 11{,}254.1\text{ g} \\ +\quad 0.1983\text{ g} \\ \hline 11{,}254.2983\text{ g} \end{array}$$
← round off to 11,254.3 g

b)
$$\begin{array}{r} 66.59\text{ L} \\ -\ 3.113\text{ L} \\ \hline 63.477\text{ L} \end{array}$$
← round off to 63.48 L

c) 8.16 m × 5.1355 = 41.90568 m ← round off to 41.9 m

d) $\frac{0.0154\text{ kg}}{88.3\text{ mL}}$ = 0.000174405436 kg/mL←round off to 0.000174 kg/mL

or 1.74×10^{-4} kg/mL

e) First we change 3.27×10^2 cm to 0.327×10^3 cm and then carry out the addition (2.64 cm + 0.327 cm) × 10^3. Following the procedure in (a), we find the answer is 2.97×10^3 cm.

Practice Exercise 1.6

Carry out the following arithmetic operations and round off the answers to the appropriate number of significant figures:

A) 26.5862 L + 0.17 L B) 9.1 g – 4.682 g C) 7.1×10^4 dm × 2.2654×10^2 dm

D) 6.54 g ÷ 86.5542 mL E) 7.55×10^4 m – 8.62×10^3 m

- ✓ The preceding rounding-off procedure applies to one-step calculations. In calculations involving more than one step, we can get a different answer depending on how we round off. The following is an example:

  First step: A × B = C

  Second step: C × D = E

- Let’s suppose that A = 3.66, B = 8.45, and D = 2.11.
- Depending on whether we round off C to three or four significant figures, we obtain a different number for E:

Method 1	Method 2
3.66 × 8.45 = 30.9	3.66 × 8.45 = 30.93
30.9 × 2.11 = 65.2	30.93 × 2.11 = 65.3

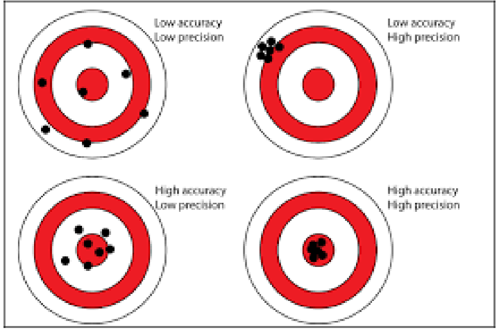
- However, if we had carried out the calculation as:

  3.66 × 8.45 × 2.11 = 65.3

  on a calculator without rounding off the intermediate answer, we would have obtained 65.3 as the answer for E
- Although retaining an additional digit past the number of significant figures for intermediate steps helps to eliminate errors from rounding, this procedure is not necessary for most calculations because the difference between the answers is usually quite small

1.6 Accuracy and precision

- Carefully, look at the following figure:



The distribution of darts on a dart board shows the difference between precise and accurate. The black dots show the positions of the darts.

Up left*: low accuracy and low precision.*
Up right *low accuracy and high precision.*
Down left*: high accuracy and low precision.*
Down right*: high accuracy and high precision.*

- **Accuracy** tells us how close a measurement is to the true value of the quantity that was measured.
- **Precision** refers to how closely two or more measurements of the same quantity agree with one another.
- Suppose, for example, that the true mass of a copper wire is 2.000 g
  - ✓ Three students are asked to determine the mass of this piece of copper wire.
  - ✓ The results of two successive weighing by each student are:

	Student A	Student B	Student C
1st weighing	1.964 g	1.972 g	2.000 g
2nd weighing	1.978 g	1.968 g	2.002 g
Average value	**1.971 g**	**1.970 g**	**2.001 g**

  - ✓ For student B, the deviation, on 1.972 g and 1.968 g from 1.970 g is less than the deviation of 1.964 g and 1.978 g from 1.971 g for student A. Therefore, we say: ***Results of Student B are more precise than the results of Student A***.
    but neither set of results is very *accurate*

- ✓ Because the average value of Student C is closest to the true value, we say:
  Results of Student C are the most precise and the most accurate
- ✓ Highly accurate measurements are usually precise too. On the other hand, highly precise measurements do not necessarily guarantee accurate results. For example, an improperly calibrated meterstick or a faulty balance may give precise readings that are in error

1.7 Dimensional analysis in solving problems (Conversion factors)

- Procedure we use to convert between units in solving chemistry problems is called ***dimensional analysis*** (also called the ***factor-label method***). It is based on the relationship between different units that express the same physical quantity. For example:
  - ✓ Because 1 cal = 4.184 J we can covert one to the other by the conversion factors:

    $$\frac{1\text{ cal}}{4.184\text{ J}} = 1 \text{ or } \frac{4.184\text{ J}}{1\text{ cal}} = 1$$
  - ✓ Because 1 atm = 101325 Pa we can covert one to the other by the conversion factors:

    $$\frac{1\text{ atm}}{101325\text{ Pa}} = 1 \text{ or } \frac{101325\text{ Pa}}{1\text{ atm}} = 1$$
  - ✓ Because 1 in = 2.54 cm we can covert one to the other by the conversion factors:

    $$\frac{1\text{ in}}{2.54\text{ cm}} = 1 \text{ or } \frac{2.54\text{ cm}}{1\text{ in}} = 1$$
- To apply dimensional analysis, we use the following relationship to cancel the given unit and to end up with the desired unit:

  $$\boxed{\cancel{\textbf{given unit}} \times \frac{\textbf{desired unit}}{\cancel{\textbf{given unit}}} = \textbf{desired unit}}$$
  - ✓ To convert 12 inches to centimeters:

    $$12\ \cancel{\text{in}} \times \frac{2.54\text{ cm}}{1\ \cancel{\text{in}}} = 30.48\text{ cm}$$
  - ✓ To convert 57.8 meters to centimeter:

    $$57.8\ \cancel{\text{m}} \times \frac{100\text{ cm}}{1 \times \cancel{\text{m}}} = 5780\text{ cm}$$

EXAMPLE 1.7

A person's average daily intake of glucose (a form of sugar) is 0.0833 pound (lb). What is this mass in milligrams (mg)? (1 lb = 453.6 g)

Solution

The sequence of conversions is

$\frac{453.6\text{ g}}{1\text{ lb}} = 1$	$\frac{1000\text{ mg}}{1\ \cancel{\text{g}}} = 1$

$$0.0833\ \cancel{\text{lb}} \times \frac{453.6\ \cancel{\text{g}}}{1\ \cancel{\text{lb}}} \times \frac{1000\text{ mg}}{1\ \cancel{\text{g}}} = 3.78 \times 10^{4}\text{ mg}$$

Practice Exercise 1.7

An aluminum foil has a mass of 1.07 kg. What is its mass in pounds?

EXAMPLE 1.8

An average adult has 5.2 L of blood. What is the volume of blood in m^3?

Solution

$$\boxed{\frac{1\text{ m}^3}{1000\text{ L}} = 1}$$

$$5.2\text{ L} = 5.2\ \cancel{\text{L}} \times \frac{1\text{ m}^3}{1000\ \cancel{\text{L}}} = 5.2 \times 10^{-3}\text{ m}^3$$

Practice Exercise 1.8

The volume of a room is 1.08 × 10^8 dm^3. What is the volume in m^3?

EXAMPLE 1.9

Liquid nitrogen is obtained from liquefied air and is used to prepare frozen goods and in low-temperature research. The density of liquid nitrogen at its boiling point (– 196 °C or 77 K) is 0.808 g/cm^3. Convert the density to units of kg/m^3.

Solution

$\frac{1000000\ cm^3}{1\ m^3} = 1$	$\frac{1\ kg}{1000\ g} = 1$

$$0.808\ \frac{\cancel{g}}{1\ \cancel{cm^3}} \times \frac{\frac{1\ kg}{1000\ \cancel{g}}}{\frac{1\ m^3}{1000000\ cm^3}} = 808\ \frac{1\ kg}{1\ m^3}$$

Practice Exercise 1.9

The density of the lightest metal, lithium (Li), is 5.34 × 10^2 kg/m^3. Convert the density to g/cm^3.

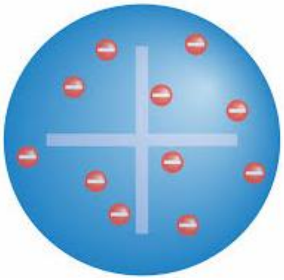
2. ATOMS, MOLECULES AND IONS

2.1 The atomic theory

- The word “atom” came from the Greek word “atomos” which means “indivisible”. It was chosen by **Democritus** about 2400 years ago. The theory of Democritus is that atoms are indivisible, infinite in number, uncreated, and eternal. Democritus attributed the properties of matter to the kind of its atoms
- The brilliant vision of Democritus was overlooked because the theory of the four elements (soil, water, air and fire) created by **Empedocles** was adopted by the greatest Greek philosopher **Aristotle**
- Our present understanding of the structure of matter began to take shape with the following Dalton’s atomic theory in 1808:
  1) Elements are composed of extremely small particles called atoms
  2) All atoms of a given element are identical, having the same size, mass, and chemical properties. The atoms of one element are different from the atoms of all other elements
  3) Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.
  4) A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in their creation or destruction

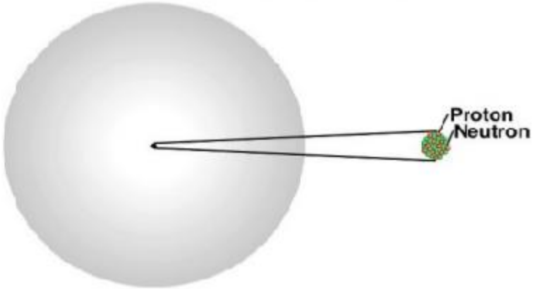
2.2 The structure of the atom

- After Dalton’s theory, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms possess internal structure made up of even smaller particles, which are called **subatomic particles**. This led to the discovery of the following well-known three subatomic particles:
- **The Electron**
  - ✓ Electron was discovered by an English physicist, J. J. Thomson in 1897
  - ✓ Electrons are negatively charged atomic particles
  - ✓ The electron mass and electric charge are 9.10×10^{-28} g and 1.6022×10^{-19} C
- **The Proton and the nucleus**
  - ✓ Because atoms are neutral, an atom must contain equal number of positive and negative charges
  - ✓ In 1904 Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded like raisins in a cake. This why Thomson model is called the “plum-pudding model” for “plum-pudding” is a kind of sweets originally offered in England at Christmas dinner. The following figures display Thompson’s model of the atom (left) and a typical “plum-pudding” (right):



- ✓ In 1909, **Ernest Rutherford** discovered that the positive particles of the atom constitute the center of the atom. These positive particles are called the "protons"
- ✓ The number of protons of any atom equals the number of its electrons and its electric charge equals that of the electron while its mass equals about **1840** times the mass of the electron
- ✓ The mass of the proton is 1.67262×10^{-24} g. Thus, the mass of a nucleus constitutes most of the mass of the entire atom
- ✓ Regarding the volume of the space that an atom occupies it is found that the nucleus occupies only about $\frac{1}{1013}$ of the entire volume of the atom
- ✓ A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is about 5×10^{-3} pm. If we imagine that the size of the nucleus is the same as that of a ping pong ball, then the first electron orbiting around it would be **666 m** away

- **The neutron**
  - ✓ In 1932, **James Chadwick** showed that atoms consist of a third type of subatomic particles, which he named **neutrons,** because they are electrically neutrals.
  - ✓ The mass of the neutron almost equals that of the proton.
  - ✓ The following figure shows the location of the elementary particles (protons, neutrons, and electrons) in an atom.
- The following figure shows that electrons are as "clouds" around the nucleus.



Particle	Mass (g)	Electric Charge (C)
Electron	9.10938×10^{-28}	-1.6022×10^{-19}
Proton	1.67262×10^{-24}	$+1.6022 \times 10^{-19}$
Neutron	1.67493×10^{-24}	0

2.3 Atomic number, mass number and isotopes

2.3.1 The atomic number (Z)

- The atomic number is the number of protons in the nucleus of each atom of an element
- In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in
- The chemical identity of an atom can be determined solely from its atomic number
- For example, the atomic number of oxygen is 8; this means that each oxygen atom has 8 protons and 8 electrons, this means that every atom in the universe that contains 8 protons is definitely an oxygen atom.

2.3.2 The mass number (A)

- The mass number is the total number of neutrons and protons in the nucleus of an atom of an element
- Except for the hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons

- The mass number is given by:

  mass number = number of protons + number of neutrons

  mass number = atomic number + number of neutrons
- Number of neutrons equals the difference between mass number and atomic number:

  number of neutrons = (A – Z)

  For example, if the mass number **(A)** of a boron atom is 12 and the atomic number **(Z)** is 5, then the number of neutrons is 7
- The conventional way to represent the atomic number (Z) and the mass number (A) of an atom of an element (X) is as follows:

$$\begin{array}{r}\text{mass number} \rightarrow \\ \text{atomic number} \rightarrow \end{array} {}^{A}_{Z}\mathrm{X}$$

  - ✓ Hydrogen which has 1 proton and no neutrons is written as:

$$^{1}_{1}\mathrm{H}$$

  - ✓ Uranium which has 92 protons and 143 neutrons is written as:

$$^{235}_{92}\mathrm{U}$$

- **Isotopes**
  - ✓ ***Isotopes*** *are atoms that have the same atomic number but different mass numbers*
  - ✓ Therefore, toms of a given element do not all have the same mass
  - ✓ Most elements have two or more isotopes. For example:
    - ➢ Hydrogen: There are three isotopes of hydrogen
      - ▪ ***Hydrogen***, "$^{1}_{1}H$", each atom has one proton and no neutrons
      - ▪ ***Deuterium***, "$^{2}_{1}H$", each atom has one proton and one neutron
      - ▪ ***Tritium***, "$^{3}_{1}H$", each atom has one proton and two neutrons
    - ➢ Uranium: There are two isotopes of uranium
      - ▪ ***Uranium-235***, "$^{235}_{92}U$", each atom has *92* protons and 143 neutrons
      - ▪ ***Uranium-238***, "$^{235}_{92}U$", each atom has *92* protons and 146 neutrons

EXAMPLE 2.1

Give the number of protons, electrons, and neutrons in each of the following:

A) $^{20}_{11}\mathrm{Na}$ B) $^{22}_{11}\mathrm{Na}$ C) $^{17}_{8}\mathrm{O}$ D) $^{14}_{6}\mathrm{C}$

Solution

A) number of protons = atomic number = number of electrons = 11
number of neutrons = mass number – number of protons = 20 – 11 = 9

B) number of protons = atomic number = number of electrons = 11
number of neutrons = mass number – number of protons = 22 – 11 = 11

C) number of protons = atomic number = number of electrons = 8
number of neutrons = mass number – number of protons = 17 – 8 = 9

D) number of protons = atomic number = number of electrons = 6
number of neutrons = mass number – number of protons = 14 – 6 = 8

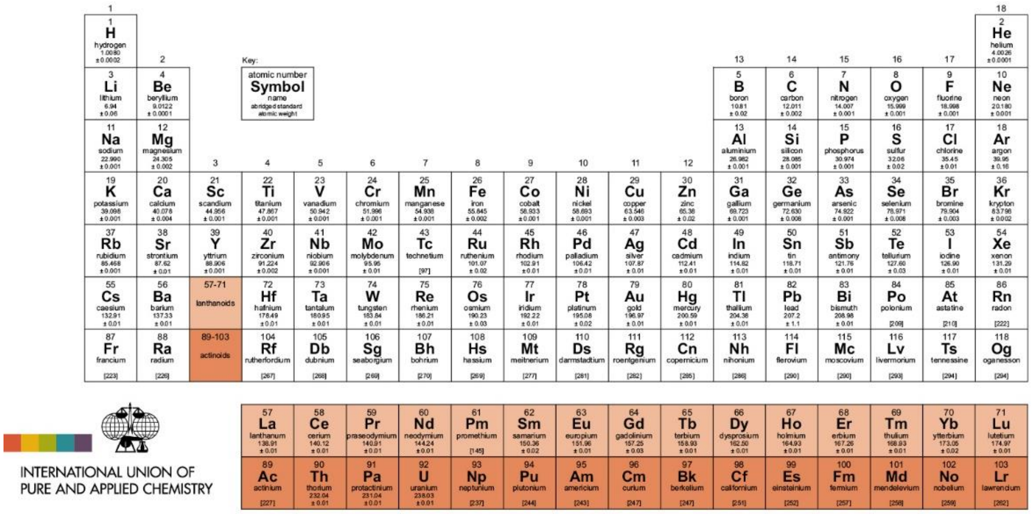
Practice Exercise 2.1

How many protons, neutrons, and electrons are in the isotope of copper: $^{63}_{29}\mathrm{Cu}$?

2.4 The periodic table of elements

- More than half of the elements known today were discovered between 1800 and 1900
- During this period, chemists noted that many elements show strong similarities to one another and there are periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elemental substances
- This led to the development of the ***periodic table,*** *a chart in which elements having similar chemical and physical properties are grouped together*
- The figure below shows the modern IUPAC periodic table

IUPAC Periodic Table of the Elements



For notes and updates to this table, see www.iupac.org. This version is dated 4 May 2022.
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- In the periodic table, the elements are arranged by atomic number (shown above the element symbol)
- *Horizontal rows* called ***periods*** and in *vertical columns* known as ***groups*** or ***families*** according to similarities in their ***chemical properties***
- The elements can be divided into three categories:
  - ✓ **Metals**: A ***metal*** is *a good conductor of heat and electricity*
  - ✓ **Nonmetal:** A ***nonmetal*** is usually *a poor conductor of heat and electricity*
  - ✓ **Metalloid:** A ***metalloid*** *has properties that are intermediate between those of metals and nonmetals*
  - ✓ The periodic table shows that the majority of its elements are metals; only 17 elements are nonmetals, and 8 elements are metalloids.
  - ✓ From left to right across any period, the physical and chemical properties of the elements change gradually from metallic to nonmetallic
  - ✓ There are 18 groups in the periodic table groups is 18 and they are numbered group 1, group 2, group 3 and so on to group 18
  - ✓ Some element groups are given special names.
    - ➢ *The Group 1 elements (Li, Na, K, Rb, Cs, and Fr)* are called ***alkali metals***
    - ➢ *The Group 2 elements (Be, Mg, Ca, Sr, Ba, and Ra)* are called ***alkaline earth metals***
    - ➢ *The Group 17 elements (F, Cl, Br, I, and At)* are called ***halogens***
    - ➢ *The Group 18 elements (He, Ne, Ar, Kr, Xe, Rn and Og)* are called ***noble gases***

2.5 Molecules

- A *molecule* is an *aggregate of at least two atoms in a definite arrangement held together by chemical forces* (also called *chemical bonds*)
- A molecule is the smallest particle of a substance that reflects the substance properties.
- A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio
- A molecule is not necessarily a compound, which, by definition, is made up of two or more elements
- Hydrogen gas, for example, is a pure element, but it consists of molecules made up of two H atoms each. Water, on the other hand, is a molecular compound that contains two hydrogen atoms and on oxygen in a ratio of two H atoms and one O atom
- Molecules are electrically neutral
- ***monatomic gases***

  Only the noble gases (group 18) in the periodic table (He, Ne, Ar, Kr, Xe, Rn, and Og) exist as single atoms. Therefore, they are called *monatomic* gases
- ***diatomic molecules***
  - ✓ Some elements normally exist as **diatomic molecules**, examples are: hydrogen (H_2) are nitrogen (N_2) oxygen (O_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2)
  - ✓ Of course, a diatomic molecule can contain atoms of different elements. Examples are hydrogen chloride (HCl) and carbon monoxide (CO)
- ***polyatomic molecules***
  - ✓ Most molecules contain more than two atoms
  - ✓ They can be atoms of the same element, as in ozone (O_3) and sulfur (S_8)
  - ✓ They can be combinations of two or more different elements like water (H_2O) and ammonia (NH_3) are polyatomic

2.6 Ions

2.6.1 Definition of ions

- **Ions:** An ion is an atom or a group of atoms that has an electric charge
  - ✓ **Positive ions (Cations):** Loss of electrons by an atom is the reason behind the positive charges of cations. Also, two or more atoms can combine to form cations and are classified as *polyatomic cations* such as H_3O^+, NH_4^+ and PH_4^+
  - ✓ **Negative ions (Anions):** Gain of electrons by an atom is the reason behind the negative charges of anions

Na atom	Na^+	Cl	Cl^-
11 protons	11 protons	17 protons	17 protons
11 electrons	10 electrons	17 electrons	18 electrons

2.6.2 Definition of ionic compounds

- The “ionic compounds” are the substances that are formed from positive and negative ions. Example: sodium chloride (NaCl) because it is formed from Na^+, and chloride Cl^-
- The cations in ionic compounds is mostly metals such as sodium, calcium, iron…etc
- Most positive ions are metals’ ions but there are some positive ions that are not metals such as H_3O^+ (hydronium), NH_4^+ (ammonium) and PH_4^+ (phosphonium)
- The anions are nonmetals such as nitride, oxide, fluoride…etc
- The following table shows the most common positive ions (CATIONS)

Hydrogen	H^+	Tin	Sn^{2+}
Lithium	Li^+	Chromium	Cr^{3+}
Sodium	Na^+	Manganese(II)	Mn^{2+}
Potassium	K^+	Iron(II)	Fe^{2+}
Cesium	Cs^+	Iron(III)	Fe^{3+}
Rubidium	Rb^+	Cobalt(II)	Co^{2+}
Magnesium	Mg^{2+}	Copper(I)	Cu^+
Manganese(II)	Mn^{2+}	Copper(II)	Cu^{2+}
Manganese(IV)	Mn^{4+}	Zinc	Zn^{2+}
Cobalt(III)	Co^{3+}	Silver	Ag^+
Calcium	Ca^{2+}	Cadmium	Cd^{2+}
Strontium	Sr^{2+}	Mercury(I)	Hg_2^{2+}
Barium	Ba^{2+}	Mercury(II)	Hg^{2+}
Aluminum	Al^{3+}	Hydronium	H_3O^+
Lead(II)	Pb^{2+}	Ammonium	NH_4^+
Lead(IV)	Pb^{4+}	Phosphonium	PH_4^+

- There are many nonmetals anions. Examples: CO_3^{2-} (carbonate), SO_4^{2-} (sulfate) and PO_4^{3-} (phosphate).
- The following table shows many anions ending with "-ide", "-ate" and "-ite"

Hydride	H^-
Carbide	C^{4-}
Nitride	N^{3-}
Oxide	O^{2-}
Peroxide	O_2^{2-}
Sulfide	S^{2-}
Selenide	Se^{2-}
Telluride	Te^{2-}
Fluoride	F^-
Chloride	Cl^-
Bromide	Br^-
Iodide	I^-
Hydroxide	OH^-
Cyanide	CN^-

Carbonate	CO_3^{2-}	Hydrogen carbonate (bicarbonate)	HCO_3^-
Phosphate	PO_4^{3-}	Hydrogen phosphate	HPO_4^{2-}
		Dihydrogen phosphate	$H_2PO_4^-$
Nitrate	NO_3^-	Nitrite	NO_2^-
Sulfate	SO_4^{2-}	Sulfite	SO_3^{2-}
		Hydrogen sulfate (bisulfate)	HSO_4^-
Chlorate	ClO_3^-	Chlorite	ClO_2^-
Chromate	CrO_4^{2-}	dichromate	$Cr_2O_7^{2-}$

2.7 Naming inorganic compounds

- Organic compounds have their special way to name them. Here we discuss naming inorganic compounds of only inorganic compounds
- These compounds are four types:
  1) Ionic compounds
  2) Molecular compounds
  3) Acids
  4) Bases
  5) Hydrates

2.7.1 Naming ionic compounds

- The tables given in section 2.6 provide the names of many cations and anions
- For ionic compounds formed from just two elements (**binary compounds**) the first word of its name is the metal name and the second word is the nonmetallic anion by taking the first part of its name with "**ide**" attached to it as a suffix. Examples are:
  - ✓ KBr is potassium bromide
  - ✓ ZnF_2 is zinc fluoride
  - ✓ Al_2O_3 is aluminum oxide
  - ✓ Na_3N is sodium nitride
  - ✓ KCN is potassium cyanide
  - ✓ Na_3N is sodium nitride
- Note that although OH^- and CN^- are not single-atomic anions their names end with the suffix "**ide**". Therefore, their ionic compounds with metal cations follows the previous rule
  - ✓ LiOH is lithium hydroxide
  - ✓ $Ca(CN)_2$ is calcium cyanide
- Cations of many transition metals can form more than one type of cation. Iron can form two cations: Fe^{3+} and Fe^{2+}.
  - ✓ **The old nomenclature system** assigns "-ic" the ending to the cation with more positive charges: **Fe^{3+} is ferric ion** as in ferric chloride, $FeCl_3$; and the ending "ous" to the cation with fewer positive charges: **Fe^{2+} is ferrous ion** as in ferrous chloride, $FeCl_2$.

    The new nomenclature system, done by the German chemist Stock, assigns the Roman numeral:
    - ➢ "I" means one positive charge
    - ➢ "II" means two positive charges
    - ➢ "III" means three positive charges
    - ➢ "IV" means four positive charges

    Therfore $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Other examples are:

    CuCl is copper(I)chloride
    $CuCl_2$ is copper(II)chloride
    $MnCl_2$ is manganese(II) chloride
    $MnCl_3$ is manganese(III) chloride
    $MnCl_4$ is manganese(IV) chloride

EXAMPLE 2.2

Name the following compounds:

A) $Cu(NO_3)_2$ B) KH_2PO_4 C) NH_4ClO_3

Solution

A) The nitrate anion (NO_3^-) has only one negative charge, so the copper cation must have two positive charges: the compound **copper(II) nitrate**.

B) The cation is potassium ion and the anion is dihydrogen phosphate: the compound is **potassium dihydrogen phosphate**.

C) The cation is ammonium ion and the anion is chlorate: the compound is **ammonium chlorate**.

Practice Exercise 2.2

Name the following compounds:

A) PbO B) Li_2SO_3 C) $Mn(SO_4)_2$

EXAMPLE 2.3

Write chemical formulas for the following compounds:

A) mercury(I) nitrite B) cesium sulfide C) calcium phosphate

Solution

A) The mercury ion has one positive charge, but it exists as diatomic (Hg_2^{2+}) and the anion is the nitrite ion (NO_2^-): the formula is **$Hg_2(NO_2)_2$**.

B) Sulfide ion has 2 negative charges, and cesium ion has 1 positive charge: the formula is **Cs_2S**.

C) The calcium ion has two positive charges (Ca^{2+}), and phosphate ion is PO_4^{3-}: the formula is **$Ca_3(PO_4)_2$**.

Practice Exercise 2.3

Write formulas for the following ionic compounds:

A) rubidium sulfate B)) barium hydride C) aluminum carbonate

2.7.2 Naming molecular compounds

- Molecular compounds consist of two or more different elements
  - ✓ Binary compounds consist of two different elements
  - ✓ Tertiary compounds consist of three different elements.
- Binary molecular compounds are named similarly as binary *ionic compounds* by placing the name of the first element in the formula first, and the second element is named by adding “ide” to the root of the element name
- There are some cases where two elements form several different compounds (C and O form CO and CO_2); in such cases Greek prefixes are used to denote the number of atoms of each element presents. The table below shows these Greek prefixes.

Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-
1	2	3	4	5	6	7	8	9	10

The following are some examples:

- ➢ “CO” is carbon monoxide and “CO_2” is carbon dioxide
- ➢ “SO_2” is sulfur dioxide and “SO_3” is sulfur trioxide
- ➢ “NO_2” is nitrogen dioxide and “N_2O_4” is dinitrogen tetroxide

- The following guidelines are helpful in naming molecular compounds with prefixes:
  - ✓ The prefix “mono-” may be omitted for the first element, this means that there is only one atom of that element in the molecule. For example, PCl_3 is phosphorus trichloride not monophosphorus trichloride
  - ✓ For oxides, the ending “a” in the prefix is usually omitted. For example, N_2O_4 is dinitrogen tetroxide rather than dinitrogen tetraoxide.

- ✓ Writing formulas for molecular compounds is usually straightforward. Thus, the name “arsenic trifluoride” means that there are three nonmetallic “F” atoms and one nonmetallic “As” atom in each molecule, and the molecular formula is “AsF_3”. Note that the order of elements in the formula is the same as in its name.
- ✓ Compounds containing hydrogen are named exceptionally. Many of them are called by their **common** and **nonsystematic** names or by names that do not indicate the number of hydrogen atoms. Also, in some formulas, hydrogen is written first not like other were it is written last. The following are some examples:
  - ➢ B_2H_6 is diborane not diboron hexahydride
  - ➢ CH_4 is methane not carbon tetrahydride
  - ➢ SiH_4 is silane not silicon tetrahydride
  - ➢ NH_3 is ammonia not nitrogen triahydride
  - ➢ PH_3 is phosphine not phosphorus triahydride
  - ➢ H_2O is water not dihydrogen oxide
  - ➢ H_2S is hydrogen sulfide not dihydrogen sulfide

EXAMPLE 2.4

Name the following molecular compounds:

A) $SiCl_4$ B) P_4O_{10}.

Solution

A) There are one silicon atom and four chlorine atoms: the compound is <u>**silicon tetrachloride**</u>.

B) There are four phosphorus atoms and ten oxygen atoms: the compound is <u>**tetraphosphorus decoxide**</u>.

Practice Exercise 2.4

Name the following molecular compounds:

A) SiF_4 b**)** Cl_2O_7

EXAMPLE 2.5

Write chemical formulas for the following molecular compounds:

A) carbon disulfide B) disilicon hexabromide

Solution

A) There are one carbon atom and two sulfur atoms: the formula is <u>**CS_2**</u>.

B) There are two silicon atoms and six bromine atoms: the formula is <u>**Si_2Br_6**</u>.

Practice Exercise 2.5

Write chemical formulas for the following molecular compounds:

A) sulfur tetrafluoride B) dinitrogen pentoxide

2.7.3 Naming acids

- An acid is a substance that has hydrogen atoms in its composition and give them as ions, H^+, when dissolved in water. Also, it is defined as substances that increases hydrogen ions concentration of water after it dissolves in it
- **Naming binary acids:**

  The following table gives the names anions which ends with the suffix “-ide”:

Sulfide	Fluoride	Chloride	Bromide	Iodide	Cyanide
S^{2-}	F^-	Cl^-	Br^-	I^-	CN^-

When one hydrogen ion (or more) is attached to any anion in the above table, the molecular compound formed is named as in the table below: (<u>***note: HCN is not a binary acid. However its name ends with the suffix “ide”***</u>)

Hydrogen sulfide	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide	Hydrogen cynide
H_2S	HF	HCl	HBr	HI	HCN

The ***aqueous* solution** of any one of the above compounds is a binary acid and it is named as in the following table:

Hydrosulfuric acid	Hydrofluoric acid	Hydrochloric acid	Hydrobromic acid	Hydroiodic acid	Hydrocyanic acid
H_2S	HF	HCl	HBr	HI	HCN

- **Naming oxoacids:**
  - ✓ **The reference oxacids and the derived oxacids**
    - ➢ **The reference oxacids:** When one or more hydrogen ion is attached to an anion ending with the suffix “ate”, the product is an oxoacid named as follows:

Nitrate	Carbonate	Sulfate	Phosphate	Fluorate	Chlorate	Bromate	Iodate
NO_3^-	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}	FO_3^-	ClO_3^-	BrO_3^-	IO_3^-
Nitric acid	Carbonic acid	Sulfuric acid	Phosphoric acid	**Fluoric acid**	**Chloric acid**	**Bromic acid**	**Iodic acid**
HNO_3	H_2CO_3	H_2SO_4	H_3PO_4	$\mathbf{HFO_3}$	$\mathbf{HClO_3}$	$\mathbf{HBrO_3}$	$\mathbf{HIO_3}$

These above acids are called “***the reference oxoacids***” because some other oxoacids are derived from them. The last four acids are called “**halic acids**

- ➢ **The derived oxacids**
  - ❖ **Addition of one “O” atom to a halic acid**

The addition of one “O” atom to a “halic acid” gives a “perhalic acid”:

Perfluorate	Perchlorate	Perbromate	Periodate
FO_4^-	ClO_4^-	BrO_4^-	IO_4^-
Perfluoric acid	**Perchloric acid**	**Perbromic acid**	**Periodic acid**
$\mathbf{HFO_4}$	$\mathbf{HClO_4}$	$\mathbf{HBrO_4}$	$\mathbf{HIO_4}$

- ❖ **Removal of one “O” atoms from the reference acids except $\mathbf{H_2CO_3}$**

Removal of one “O” atom from any reference acid except H_2CO_3 changes the suffix “ic” to “ous” and the oxoions suffixes changes from “ate” to “ite”:

Nitrite	Sulfite	Phosphite	**Fluorite**	**Chlorite**	**Bromite**	**Iodite**
NO_2^-	SO_3^{2-}	PO_3^{3-}	$\mathbf{FO_2^-}$	$\mathbf{ClO_2^-}$	$\mathbf{BrO_2^-}$	$\mathbf{IO_2^-}$
Nitrous acid	Sulfurous acid	Phosphorous acid	**Fluorous acid**	**Chlorous acid**	**Bromous acid**	**Iodous acid**
HNO_2	H_2SO_3	H_3PO_3	$\mathbf{HFO_2}$	$\mathbf{HClO_2}$	$\mathbf{HBrO_2}$	$\mathbf{HIO_2}$

- ❖ **Removal of two “O” atoms from the reference acids except $\mathbf{H_2CO_3}$,**

Removal of two “O” atoms from any reference acid except H_2CO_3 and HNO_3 adds a “hypo” prefix and changes the suffix “ic” to “ous”:

Hyposulfite ion	Hypophosphite ion	**Hypofluorite ion**	**Hypochlorite ion**	**Hypobromite ion**	**Hypoiodite ion**
SO_2^{2-}	PO_2^{3-}	$\mathbf{FO^-}$	$\mathbf{ClO^-}$	$\mathbf{BrO^-}$	$\mathbf{IO^-}$
Hyposulfurous acid	hypophosphorous acid	**hypofluorous acid**	**hypochlorous acid**	**Hypobromous acid**	**hypoiodous acid**
H_2SO_2	H_3PO_2	**HFO**	**HClO**	**HBrO**	**HIO**

- **Removal of hydrogen ions from some oxoacids**

  The names of anions in which one or more but not all the hydrogen ions have been removed must indicate the number of remaining hydrogen ions. For example:

  - H_3PO_4: The removal of one hydrogen ion produces dihydrogen phosphate ion, $H_2PO_4^-$, and the removal of two hydrogen ions produces hydrogen phosphate ion HPO_4^{2-}
  - H_2SO_4: the removal of one hydrogen ion produces hydrogen sulfate ion, HSO_4^-

EXAMPLE 2.6

Name the following oxoacid and oxoanion:

A) H_3PO_3 B) IO_4^-

Solution

A) The reference acid is phosphoric acid (H_3PO_4). Because H_3PO_3 has one fewer O atom, it is **phosphorous acid**.

B) The reference acid is chloric acid (HIO_3). Because the acid HIO_4 has one more O atom than our reference acid, it is called periodic acid and its oxanion, IO_4^-, is **periodate ion**.

Practice Exercise 2.6

Name the following oxoacid and oxoanion:

A) HBrO B) HSO_4^-.

2.7.4 Naming bases

- A base is a substance that yields hydroxide ions (OH^-) when dissolved in water. Some examples are NaOH, KOH and $Ba(OH)_2$. These compounds are named as ionic compounds are named. The name starts with metal name and ends with the anion name which is hydroxide. Therefore, the names of the previous three bases are sodium hydroxide, potassium hydroxide and barium hydroxide respectively.
- Ammonia (NH_3) is a very famous base but it does not have OH^- in its formula. It is a molecular compound in its gaseous state or when it is a pure. When NH_3 is dissolved in water, it reacts partially with water to yield NH_4^+ and OH^- ions:

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

  Thus, its aqueous solution is properly classified as a base.

2.7.5 Naming hydrates

- Hydrates are compounds that have a specific number of water molecules attached to them. For example, in its normal state, each unit of copper(II) sulfate has five water molecules associated with it
- The systematic name for this compound is copper(II) sulfate pentahydrate and its formula is written as:

$$CuSO_4{\cdot}5H_2O$$

- The water molecules can be driven off by heating. When this occurs, the resulting compound is $CuSO_4$, which is named copper sulfate and sometimes called anhydrous copper(II) sulfate. The word “anhydrous” means that the compound no longer has water molecules associated with it
- Other examples are:
  - ✓ Barium chloride dihydrate, $BaCl_2{\cdot}2H_2O$
  - ✓ Lithium chloride monohydrate, $LiCl{\cdot}H_2O$
  - ✓ Magnesium sulfate heptahydrate, $MgSO_4{\cdot}7H_2O$

- ✓ Strontium nitrate tetrahydrate, $Sr(NO_3)_2·4H_2O$

2.8 Common and systematic names of some compounds

There are several compounds acquired their names since remote human history or have names that are so common among people worldwide and among chemists. These compounds kept their common names. The following table gives the formula and their common and systematic names.

Formula	Common name	Systematic name
H_2O	water	Dihydrogen monoxide
NH_3	Ammonia	Trihydrogen nitride
CO_2	Dry ice	Solid carbon dioxide
NaCl	Table salt	Sodium chloride
N_2O	Laughing gas	Dinitrogen monoxide
$CaCO_3$	Marble, chalk, limestone	Calcium carbonate
CaO	Quicklime	Calcium oxide
$Ca(OH)_2$	Slaked lime	Calcium hydroxide
$NaHCO_3$	Baking soda	Sodium hydrogen carbonate
$Na_2CO_3 \cdot 10H_2O$	Washing soda	Sodium carbonate decahydrate
$MgSO_4 \cdot 7H_2O$	Epsom salt	Magnesium sulfate heptahydrate
$Mg(OH)_2$	Milk og magnesia	Magnesium hydroxide
$CaSO_4 \cdot 2H_2O$	Gupsum	Calcium sulfate dihydrate

3. MASS RELATIONSHIPS IN CHEMICAL REACTIONS

3.1 Atomic mass and average atomic mass

- The mass of an atom depends on the number of protons and neutrons it contains
- Atoms are extremely small particles. The smallest speck of dust that our eyes can detect contains as many as 1×10^{16} atoms
- It is possible to determine the mass of one atom relative to another experimentally
- ***Atomic mass is the mass of the atom in atomic mass units (amu)***
- 1 amu is the mass which equals one-twelfth the mass of one carbon-12 atom which equals 1.993×10^{-23} g
- The mass of one carbon-12 atom is exactly 12 amu
- Hydrogen atom is 8.4% as massive as the carbon-12 atom. Thus, the atomic mass of hydrogen is 0.084 × 12.00 amu = 1.008 amu
- Similar calculations show that the atomic mass of oxygen is 15.999 amu and that of iron is 55.845 amu
- The atomic mass of carbon in the periodic table of elements, is not 12.00 amu but 12.0111 amu
- The reason for the difference is that most naturally occurring elements (including carbon) have more than one isotope
- This means that when we measure the atomic mass of an element, we must generally settle for the *average atomic mass* of the naturally occurring mixture of isotopes using the following equation:

  Average atomic mass = ∑percent of isotope × atomic mass of isotope
- For example, 98.90% is carbon-12 (The atomic mass of carbon-12 = 12.0000 amu) and 1.10% is carbon-13 (The atomic mass of carbon-13 = 13.0033 amu):

  average atomic mass = aam

  aam an element = ∑percent of isotope × atomic mass of isotope

  aam of carbon = {(0.9890) × (12.0000 amu)} + {(0.0110) × (13.0033 amu)}

  aam of carbon = 12.011 amu
- It is important to understand that when we say that the atomic mass of carbon is 12.011 amu, we are referring to the ***average*** value. But for simplicity, the word "**average**" is usually omitted when discussing the atomic masses

EXAMPLE 3.1

The abundance of the copper isotope ${}^{63}_{29}\mathrm{Cu}$ is 69.09% and of the copper isotope ${}^{65}_{29}\mathrm{Cu}$ is 30.91%. Calculate the average atomic mass of copper.

Solution

Average atomic mass = ∑percent of isotope × atomic mass of isotope

Average atomic mass = (0.6909) × (63 amu) + (0.3091) × (65 amu) = 63.62 amu

Practice Exercise 3.1

The abundance of the boron isotope, ${}^{10}_{5}\mathrm{B}$ is 19.78% and of the boron isotope ${}^{11}_{5}\mathrm{B}$ is 80.22%. Calculate the average atomic mass of boron.

3.2 Avogadro's number and the molar mass of an element

- The idea of a unit to denote a certain number of objects is not new. For examples of familiar units are: the pair = 2 items, the dozen = 12 items

- In 1811, the Italian scientist, **Avogadro** introduced the idea that if we express the atomic mass of an element in the unit of "gram" rather than in the unit of "amu" we will have the same number of atoms regardless of the type of the element we chose
- Avogadro died before achieving his goal to determine this number
- The value was first determined in 1865 by the Austrian scientist Josef Loschmidt. This number was named "***Avogadro's number***" by the French scientist Jean Perrin
- Now, **Avogadro's number, N_A, is the number of carbon-12 atoms in 0.012 kg of carbon-12 isotope. Its currently accepted value is:**

$$N_A = 6.0221415 \times 10^{23} = 6.022 \times 10^{23}$$

- Avogadro's number is enormous: For example, spreading 6.022×10^{23} oranges over the entire surface of Earth would produce a layer of no less than 14 km into space!
- The symbol "N" is given for the number of particles we have
- The value of "N" may equal Avogadro's number, more than Avogadro's number or less than Avogadro's number
- The mole is the SI unit for the "amount of substance"
- The IUPAC definition of the mole is that ***the mole is the amount of substance* of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12**
- The molar mass is discussed below

3.3 Molecular mass

"Atomic mass, molecular mass, formula mass and the molar mass"

- "**Molar mass**" of the substance is the mass of one mole of it
- Substances are either atoms, molecules of the same element, molecular compound or ionic compounds
- When the compound is molecular compound the mass of one mole of it is called "molecular mass" and when the compound is ionic compound the mass of one mole of it is called "formula mass"

1) **"Atomic mass" and "Molar mass":**
   The periodic table shows that the atomic masses H is 1.008 amu, therefore the mass of one mole of atomic hydrogen (H) using SI UNITS is 1.008 $\frac{\mathrm{g}}{\mathrm{mol}}$. This mass is called the **atomic mass** of H; it is also called **the molar mass** of H
2) **"Molecular mass" and "Molar mass":**
   The periodic table shows that the atomic masses oxygen, O, is 16 amu, therefore the mass of one mole of molecular oxygen, ($\mathrm{O_2}$), using SI UNITS is 32 $\frac{\mathrm{g}}{\mathrm{mol}}$. This mass is called the **molecular mass** of $\mathrm{O_2}$; it is also called **the molar mass** of $\mathrm{O_2}$. Another example: the periodic table shows that the atomic masses carbon, C, is 12.01 amu and the atomic masses oxygen, O, is 16 amu. Therefore, the mass of one mole of $\mathrm{CO_2}$, using SI UNITS is 44.01 $\frac{\mathrm{g}}{\mathrm{mol}}$. This mass is called the **molecular mass** of $\mathrm{CO_2}$; it is also called **the molar mass** of $\mathrm{CO_2}$
3) **"Formula mass" and "Molar mass":**
   The periodic table shows that the atomic masses sodium, Na, is 22.99 amu and of chlorine, Cl, is 35.45 amu. Therefore, the mass of one mole of NaCl, using SI UNITS is 58.44 $\frac{\mathrm{g}}{\mathrm{mol}}$. This mass is the **formula mass** of NaCl; it is also called **the molar mass** of carbon NaCl

- The above examples show that the mass of one mole of any substance is called its “**molar mass**” regardless whether it consists of atoms, molecules or ions
- **Relations between M**”, “**m**”, “**n**”, and “**N**”
- It is important to know the relations between “**M**”, “**m**”, “**n**”, “**N**” and “$\mathbf{N_A}$”
  M = Molar mass of a substance in g/mole units (or kg/mole units)
  m =Mass of a substance in g units (or kg units)
  n = Number of moles of a substance
  N = Number of particles (atoms, molecules or ions) of a substance
  N_A = Avogadro’s number
- The relations between M”, “m”, “n”, and “N” are:

$\mathbf{n = \frac{m}{M}}$	$\mathbf{n = \frac{N}{N_A}}$	$\mathbf{\frac{m}{M} = \frac{N}{N_A}}$

EXAMPLE 3.2
How many moles of He atoms are in 6.46 g of He?
Solution
$n = \frac{m}{M} = \frac{6.46\ g}{4.003\ \frac{g}{mol}} = 1.61$ mol
Practice Exercise 3.2
How many moles of magnesium (Mg) are there in 87.3 g of Mg?

EXAMPLE 3.3
How many grams of Zn are in 0.356 mole of Zn?
Solution
m = n × M = 0.356 mole × 65.39 g/mol = 23.3 g
Practice Exercise 3.3
Calculate the number of grams of lead (Pb) in 12.4 moles of lead.

EXAMPLE 3.4
How many atoms are in 16.3 g of S?
Solution

$$\frac{m}{M} = \frac{N}{N_A}$$

$$\frac{16.3\ g}{32.07 \frac{g}{mol}} = \frac{N}{6.022 \times 10^{23}\ \frac{atoms}{mol}}$$

$$N = \frac{16.3\ g \times 6.022 \times 10^{23}\ \frac{atoms}{mol}}{32.07 \frac{g}{mol}} = 3.06 \times 10^{23} \text{ atoms}$$

Practice Exercise 3.4
Calculate the number of atoms in 0.551 g of potassium (K).

EXAMPLE 3.5
How many hydrogen atoms are present in 25.6 g of urea [$(NH_2)_2CO$], which is used as a fertilizer, in animal feed, and in the manufacture of polymers? The molar mass of urea is 60.06 g/mol.
Solution

$\frac{\mathrm{m}}{\mathrm{M}} = \frac{\mathrm{N}}{\mathrm{N_A}}$

$\mathrm{N} = \frac{\mathrm{m} \times \mathrm{N_A}}{\mathrm{M}}$

$\mathrm{N_{hydrogen\ atoms}} = 4 \times \mathrm{N_{urea\ molecules}}$

$\mathrm{N_{hydrogen\ atoms}} = 4 \times \frac{\mathrm{m} \times \mathrm{N_A}}{\mathrm{M}} = 4 \times \frac{25.6\ \mathrm{g} \times 6.022 \times 10^{23}\ \frac{\mathrm{atoms}}{\mathrm{mol}}}{60.06 \frac{\mathrm{g}}{\mathrm{mol}}} = 1.03 \times 10^{24}$ H atoms

Practice Exercise 3.5

How many H atoms are in 72.5 g of isopropanol (rubbing alcohol), C_3H_8O?

EXAMPLE 3.6

Methane (CH_4) is the principal component of natural gas. How many moles of CH_4 are present in 6.07 g of CH_4?

Solution

$\mathrm{n} = \frac{\mathrm{m}}{\mathrm{M}} = \frac{6.07\ \mathrm{g}}{1 \times 12.01 \frac{\mathrm{g}}{\mathrm{mol}} + 4 \times 1.008 \frac{\mathrm{g}}{\mathrm{mol}}} = 0.378\ \mathrm{mol}$

Practice Exercise 3.6

Calculate the number of moles of chloroform ($CHCl_3$) in 198 g of $CHCl_3$.

EXAMPLE 3.7

Calculate the molar masses (in $\frac{\mathrm{g}}{\mathrm{mol}}$) of the following compounds:

A) Sulfur dioxide (SO_2) B) Caffeine ($C_8H_{10}N_4O_2$).

Solution

A) $\mathrm{M_{SO_2}} = 1 \times 32.07 \frac{\mathrm{g}}{\mathrm{mol}} + 2 \times 16.00 \frac{\mathrm{g}}{\mathrm{mol}} = 64.07 \frac{\mathrm{g}}{\mathrm{mol}}$

B) $\mathrm{M_{C_8H_{10}N_4O_2}} = (8 \times 12.01 \frac{\mathrm{g}}{\mathrm{mol}}) + (10 \times 1.008 \frac{\mathrm{g}}{\mathrm{mol}}) + (4 \times 14.01 \frac{\mathrm{g}}{\mathrm{mol}}) + 2 \times 16.00 \frac{\mathrm{g}}{\mathrm{mol}} = 194.20 \frac{\mathrm{g}}{\mathrm{mol}}$

Practice Exercise 3.7

Calculate the molar mass (in $\frac{\mathrm{g}}{\mathrm{mol}}$) of methanol ($CH_4O$).

3.4 The mass spectrometer

- The most direct and accurate method for determining atomic and molecular masses is mass spectrometry
- In a *mass spectrometer,* a gaseous sample is bombarded by a stream of high-energy electrons
- Collisions between the electrons and the gaseous atoms (or molecules) produce positive ions by dislodging an electron from each atom or molecule
- These positive ions (of mass *m* and charge *e*) are accelerated by two oppositely charged plates as they pass through the plates
- The emerging ions are deflected into a circular path by a magnet
- The radius of the path depends on the charge-to-mass ratio (that is, $\frac{\mathrm{e}}{\mathrm{m}}$)
- Ions of smaller $\frac{\mathrm{e}}{\mathrm{m}}$ ratio trace a wider curve than those having a larger $\frac{\mathrm{e}}{\mathrm{m}}$ ratio, so that ions with equal charges but different masses are separated from one another
- The mass of each ion (and hence its parent atom or molecule) is determined from the magnitude of its deflection
- Eventually the ions arrive at the detector, which registers a current for each type of ion

- The amount of current generated is directly proportional to the number of ions, so it enables us to determine the relative abundance of isotopes
- The first mass spectrometer, developed in the 1920s by the English physicist F. W. Aston, was crude by today's standards. Nevertheless, it provided indisputable evidence of the existence of isotopes—neon-20 (atomic mass 19.9924 amu and natural abundance 90.92%) and neon-22 (atomic mass 21.9914 amu and natural abundance 8.82%)
- When more sophisticated and sensitive mass spectrometers became available, scientists were surprised to discover that neon has a third stable isotope with an atomic mass of 20.9940 amu and natural abundance 0.257 percent
- This example illustrates how important experimental accuracy is to a quantitative science like chemistry. Early experiments failed to detect neon-21 because its natural abundance is just 0.257%. In other words, only 26 in 10,000 Ne atoms are neon-21
- The masses of molecules can be determined in a similar manner by the mass spectrometer

3.5 Percent composition of elements in compounds

- Any compound is composed of two elements or more
- The mass percent of any element in the compound is called the "**percent composition of the element in a compound**" and is obtained by dividing the mass of the element in 1 mole of the compound by the molar mass of the compound and multiplying by 100:

$$\text{percent composition of an element} = \frac{\text{n} \times \text{molar mass of element}}{\text{molar mass of compound}} \times 100$$

- Where "n" is the number of moles of the element in 1 mole of the compound. For example, in 1 mole of hydrogen peroxide (H_2O_2) there are 2 moles of H atoms and 2 moles of O atoms. The molar masses of H_2O_2, H, and O are 34.02 $\frac{\text{g}}{\text{mol}}$, 1.008 $\frac{\text{g}}{\text{mol}}$, and 16.00 $\frac{\text{g}}{\text{mol}}$, respectively. Therefore, the percent composition of H and O in H_2O_2 is calculated as follows:

$$\text{percent composition of H} = \frac{2 \times 1.008\,\frac{\text{g}}{\text{mol}}}{34.016\,\frac{\text{g}}{\text{mol}}} \times 100 = 5.927\%$$

$$\text{percent composition of O} = \frac{2 \times 16.00\,\frac{\text{g}}{\text{mol}}}{34.02\,\frac{\text{g}}{\text{mol}}} \times 100 = 94.073\%$$

EXAMPLE 3.8

Phosphoric acid (H_3PO_4) is a colorless liquid used in detergents, fertilizers, toothpastes, and in carbonated beverages. Calculate the percent composition of H, P, and O in this compound.

Solution

The molar mass of H_3PO_4 is 97.99 g/mol

$$\text{percent composition of H} = \frac{3 \times 1.008\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}} \times 100 = 3.086\%$$

$$\text{percent composition of P} = \frac{1 \times 30.97\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}} \times 100 = 31.61\%$$

$$\text{percent composition of O} = \frac{4 \times 16.00\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}} \times 100 = 65.31\%$$

Practice Exercise 3.8

Calculate the percent composition by mass of each of the elements in sulfuric acid (H_2SO_4).

3.6 Experimental determination of empirical formula
(Empirical and molecular formulas)

First: The empirical formulas

The empirical formula of a compound is the formula which tells us the numerical ratios of the elements in the formula. Usually we seek the ratios that consists of the simplest (smallest) whole numbers. The procedure to determine the empirical formula is as follows.

- The procedure to determine the empirical formula is as follows
  - ✓ **First**, from qualitative chemical analysis we know the elements of the compound
  - ✓ **Second**, from quantitative chemical analysis, we know the mass of each element present in a given mass of the compound (or the mass percent of each element)
  - ✓ **Third**, we convert the masses to number of moles of each element
  - ✓ **Forth**, we obtain the mole ratio of elements to each other
  - ✓ **Finally**, we find the empirical formula of the compound

EXAMPLE 3.9

Ascorbic acid is composed of 40.92 percent carbon (C), 4.58 percent hydrogen (H), and 54.50 percent oxygen (O) by mass. Determine its empirical formula.

Solution

$$\begin{array}{ccccc} \mathrm{C} & : & \mathrm{H} & : & \mathrm{O} \\ \frac{40.92\ \mathrm{g}}{12.01\ \frac{\mathrm{g}}{\mathrm{mol}}} & : & \frac{4.58\ \mathrm{g}}{1.008\ \frac{\mathrm{g}}{\mathrm{mol}}} & : & \frac{54.50\ \mathrm{g}}{16.00\ \frac{\mathrm{g}}{\mathrm{mol}}} \\ 3.407 & : & 4.54 & : & 3.406 \\ \frac{3.407}{3.406} & : & \frac{4.54}{3.406} & : & \frac{3.406}{3.406} \\ 1 & : & 1.33 & : & 1 \\ 3 & : & 4 & : & 3 \end{array}$$

The result indicates that C, H and O are in the ratio 3:4:3 and the simplest (smallest) empirical formula for ascorbic acid $C_3H_4O_3$ is.

Practice Exercise 3.9

Determine the empirical formula of a compound having the following percent composition by mass: K: 24.75%; Mn: 34.77%; O: 40.51%.

Second: The molecular formulas

- The **molecular formula** shows the exact number of atoms of each element in the molecule
- Any multiple of the simplest (smallest) empirical formula is an empirical formula
- The molecular formula is the empirical formula with the actual number of each element's atom in the compound
- To determine which empirical formula is the molecular formula we need, in addition to its simplest empirical formula, to know the ***actual*** or the ***approximate molar mass*** of the compound
- The molar mass of a compound must be the molar mass of the simplest (smallest) empirical formula or its multiples

EXAMPLE 3.10

A sample of a compound contains 1.52 g of nitrogen (N) and 3.47 g of oxygen (O). The molar mass of this compound is between 90 g and 95 g. Determine the molecular formula and the accurate molar mass of the compound.

Solution

$n = \frac{m}{M}$

$n_N = \frac{1.52\ g}{14.01\ \frac{g}{mol}} = 0.108$ mol

$n_O = \frac{3.47\ g}{16.00\ \frac{g}{mol}} = 0.217$ mol

$$\begin{array}{ccc} N & : & O \\ 0.108 & : & 0.217 \\ \frac{0.108}{0.108} & : & \frac{0.217}{0.108} \\ 1 & : & 2 \end{array}$$

NO_2 is the simplest (smallest) empirical formula for compound.

Empirical formula molar mass = 1 × 14.01 + 2 × 16.00 = 46 $\frac{g}{mol}$

$\frac{\text{actual molar mass}}{\text{emperical molar mass}} \quad : \quad \frac{90\ \frac{g}{mol}}{46\ \frac{g}{mol}} \approx 2$

The actual molar mass is twice the empirical molar mass. This means that molecular formula is 2 × NO_2

The molecular formula is N_2O_4.

Practice Exercise 3.10

A sample of a compound consisting of boron (B) and hydrogen (H) contains 6.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

3.7 Chemical reactions and chemical equations

- A **chemical reaction** is a process in which a substance (or substances) is changed into one or more new substances
- The **chemical-reaction equation**, or simply the **chemical equation** is the chemists' way to represent what happens to atoms and molecules in a chemical reaction
- The **chemical equation** uses symbols and formulas to show what happens during a chemical reaction
- **Writing chemical equations:** The chemical equation consists of three parts. The first part is the most important and, unfortunately, the most to be forgotten and ignored.
  - ✓ The first part is the arrow "→"
  - ✓ The second part is "**the reactants**" at the left of the arrow "→"
  - ✓ The third part is the "**products**" at the right of the arrow "→"
  - ✓ The arrow is the "official speaker" or the "narrator" of the equation. It tells us what and how much we had at the beginning and what and how much we had at the end
  - ✓ Producing water from the combustion of hydrogen gas (H_2) in oxygen (O_2) of air is represented by the chemical equation as:

    $$H_2 + O_2 \rightarrow H_2O$$

    The "plus" sign means "reacts with" and the arrow tells us the story as follows: "water is produced on the expense of consuming hydrogen and oxygen" or "Molecular hydrogen reacts with molecular oxygen to produce water"
  - ✓ looking at the previous equation reveals that it violates the law of conservation of matter. However, this violation can be simply prevented by ensuring that number of atoms of any element on the right and on the left sides of the arrow are equal. This is done by balancing the equation. The *balanced* equation of the previous reaction is:

    $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

- ✓ Usually, we prefer that equation is balanced in a way that gives whole correct numbers without fractions. So, although the last equation is correct, we prefer the following:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- ✓ To provide additional information, chemists often indicate the physical states of the reactants and products by using the letters g, *l*, and s to denote gas, liquid, and solid, respectively. For example:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

- ✓ To represent what happens when the solid sodium chloride (NaCl) is added to liquid water, we write:

$$NaCl(s) \xrightarrow{H_2O} NaCl(aq)$$

- ✓ where "aq" denotes the aqueous environment. ("aqua" means "water"). Writing H_2O above the arrow symbolizes the physical process of dissolving a substance in water, although it is sometimes left out for simplicity.

EXAMPLE 3.11

When aluminum metal is exposed to air, a protective layer of aluminum oxide (Al_2O_3) forms on its surface. This layer prevents further reaction between aluminum and oxygen, and it is the reason that aluminum beverage cans do not corrode. Write a balanced equation for the formation of Al_2O_3.

Solution

- The unbalanced equation is:

$$Al + O_2 \rightarrow Al_2O_3$$

- We see that there is one Al atom on the reactants side and there are two Al atoms on the product side. We can balance the Al atoms by placing a coefficient of 2 in front of Al on the reactants side:

$$2Al + O_2 \rightarrow Al_2O_3$$

- There are two O atoms on the reactants, and three O atoms on the product of the equation. We can balance the O atoms by placing a coefficient of $\frac{3}{2}$ in front of O_2 on the reactants side:

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$$

- This is a balanced equation. However, we prefer equations with the smallest set of *whole* number. Multiplying both sides of the equation by 2 gives whole number coefficients:

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

Practice Exercise 3.11

Balance the equation representing the reaction between iron(III)oxide, Fe_2O_3, and carbon monoxide (CO) to yield iron (Fe) and carbon dioxide (CO_2).

3.8 Amounts of reactants and products in chemical reactions (Stoichiometry)

- The word "stoichiometry" came from two Greek words: "stoikhein" which means "element" and "metron" which means "measure"
- stoichiometry concerns with measuring and calculating quantities of substances consumed and produced in chemical reactions
- **Stoichiometry** answers questions such as:

  - ✓ “How much product will be formed as a result of the reaction of a specific amount of a reactant?”
  - ✓ “How much reactant must be used in a reaction to obtain a specific amount of a product?”
- To interpret a reaction quantitatively, we need to apply our knowledge of molar masses and the mole concept

  Whether the units given for reactants (or products) are grams, liters, or any other units, we only use the “**mole method**” in which the “**mole**” is the unit used to carry out calculations in any reaction

- For example, industrially ammonia is synthesized as follows:

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

  The stoichiometric coefficients show that 1 mole of N_2 reacts with 3 moles of H_2 to produce 2 moles of NH_3

- Suppose 16.0 g of H_2 reacted completely with N_2 to form NH_3, and we need to know number of grams of NH_3 formed.
  - ✓ We do this calculation using the “**mole method**”. So, we need to convert grams of H_2 to moles of H_2

$$n = \frac{m}{M}$$

$$\text{number of moles of } H_2 = \frac{16\text{ g}}{2.016\frac{\text{g}}{\text{mol}}} = 7.94 \text{ mol } H_2$$

  - ✓ Then we construct a table as follows:

Equation	$N_2(g)$	+	$3H_2(g)$	→	$2NH_3(g)$
Equation moles			3 mol		2 mol
Question moles			7.94 mol		X

  - ✓ Then we do our calculations:

$$X = 2 \text{ mol } NH_3 \times \frac{7.94 \text{ mol } H_2}{3 \text{ mol } H_2} = 5.29 \text{ mol } NH_3$$

$$m = n \times M$$

$$\text{mass of } NH_3 = 5.29 \text{ mol} \times 17.03\frac{\text{g}}{\text{mol}} = 90.1 \text{ g } NH_3$$

  - ✓ Similarly, we can calculate the mass in grams of N_2 consumed
  - ✓ The general approach for the table of solving stoichiometry problems is as follows:
    1) Write a balanced equation for the reaction
    2) Write number of moles as appeared in the equation
    3) Write number of moles as given or as calculated
    4) Carry on your calculation using the mole method
    5) Convert your result to any other unit you like

EXAMPLE 3.12

The food we eat is degraded in our bodies to provide energy. The degradation of glucose ($C_6H_{12}O_6$) to carbon dioxide (CO_2) and water (H_2O) is as follows:

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

If 856 g of $C_6H_{12}O_6$ is consumed what is the mass of CO_2 produced?

Solution

$$\text{Number of moles of } C_6H_{12}O_6 = \frac{m}{M} = \frac{856\text{ g}}{180.2\frac{\text{g}}{\text{mol}}} = 4.750 \text{ mol } C_6H_{12}O_6$$

	$C_6H_{12}O_6$	+	$6O_2$	→	$6CO_2$	+	$6H_2O$
Equation moles	1 mole				6 mol		

Question moles	4.750 mol	X

$X = n_{CO_2} = 6 \times n_{C_6H_{12}O_6} = 6 \times 4.750\ \text{mol} = 28.50\ \text{mol}$

$m_{CO_2} = n_{CO_2} \times M_{CO_2} = 28.50\ \text{mol} \times 44.01\ \frac{\text{g}}{\text{mol}} = 1.25 \times 10^3\ \text{g}$

Practice Exercise 3.12

Methanol (CH_3OH) burns in air according to the equation

$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$

If 209 g of methanol are a combusted, what is the mass of H_2O produced?

EXAMPLE 3.13

A typical reaction of alkali metals with water is that between lithium and water:

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

How many grams of Li are needed to produce 9.89 g of H_2?

Solution

Number of moles of $H_2 = \frac{m}{M} = \frac{9.89\ \text{g}}{2 \times 1.008\ \frac{\text{g}}{\text{mol}}} = 5\ \text{mol}\ H_2$

	$2Li$	+	$2H_2O$	$\rightarrow$	$2LiOH$	+	H_2
Equation moles	2 mol						1 mol
Question moles	X						5 mol

$X = n_{Li} = 2\ \text{mol of Li} \times \frac{5\ \text{mol}\ H_2}{1\ \text{mol}\ H_2} = 10\ \text{mol}$

$m_{Li} = n_{Li} \times M_{Li} = 10\ \text{mol} \times 6.941\ \frac{\text{g}}{\text{mol}} = 69.41\ \text{g}$

Practice Exercise 3.13

A key step in photochemical smog formation is the following reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO_2):

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

How many grams of O_2 are consumed to produce 2.21 g of NO_2?

3.9 Limiting reactants (reagents)

- Let’s imagine that a person has 11 toast breads and 4 slices of cheese.
- To make a sandwich two toasts and one cheese slice is needed.
- If we symbolize the toast as “Ts” and the cheese as “Ch”, the formula of the sandwich will be “Ts_2Ch”:

$$2Ts + Ch \rightarrow Ts_2Ch$$

- We know that number “Ch” available is enough to produce only 4 “Ts_2Ch” while some of the “Ts” will remain “unreacted” because it is present in access.
- We say that “Ch” is the “reactant” which **limits** the quantity of “products” because it is the one which is consumed completely, and we call it “**the limiting reactant**”.
- We say that “Ts” is the “**in-access reactant**” because some of it will be will remain “**unreacted**”.
- When a chemist carries out a reaction, the reactants are usually not present in exact **stoichiometric amounts** as the balanced equation requires.
- Frequently a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted to the desired product. Consequently, some reactant will be left over at the end of the reaction.

- In a reaction, the reactant consumed totally with no left over is called the **limiting reactant** or the **limiting reagent** because the maximum amount of product formed is limited by its amount, and once this reactant is used up, no more product can be formed.
- Any reactant presents in a quantity greater than necessary to react with the quantity of the limiting reactant is called **excess reactant** or **excess reagent**
- To determine which reactant is the limiting reactant we follow the steps below for the industrial synthesis of methanol (CH_3OH) from 4 moles of carbon monoxide and 6 moles hydrogen:
  1) Write the balanced chemical equation of the reaction

     $$CO + 2H_2 \rightarrow CH_3OH$$

  2) Divide the number of moles of each reactant by its coefficient in the chemical equation:

     For CO: $\frac{4}{1}$ = 4 and For H_2: $\frac{6}{2}$ = 3
  3) The reactant with the least quotient is the limiting reactant, the other is the excess reactant. Therefore, in this reaction H_2 is the limiting reactant, and CO is the excess reactant.
  4) After the limiting reagent has been identified, the rest of the problem can be solved.

EXAMPLE 3.14

637.2 g of NH_3 are treated with 1142 g of CO_2 to produce urea $(NH_2)_2CO$:

$$2NH_3\,(g) + CO_2(g) \rightarrow (NH_2)_2CO(aq) + H_2O(l)$$

A) Which reactants is the limiting reagent?
B) Calculate the mass of $(NH_2)_2CO$ formed
C) How much excess reagent (in grams) is left at the end of the reaction?

Solution

A) number of moles of NH_3 = $\frac{m}{M} = \frac{637.2\ g}{17.03\ \frac{g}{mol}}$ = 37.416 mol

number of moles of CO_2 = $\frac{m}{M} = \frac{1142\ g}{44.02\ \frac{g}{mol}}$ = 25.943 mol

	$2NH_3$	+	CO_2	→	$(NH_2)_2CO(_3)$	+	H_2O
Equation moles	2		1				
Question moles	37.416		25.943				
$\frac{\text{Question moles}}{\text{Equation moles}}$	18.708		25.943				

B) It is clear from the above that **NH_3** is the limiting reagent.

	$2NH_3$	+	CO_2	→	$(NH_2)_2CO$	+	H_2O
Equation moles	2 mol				1mol		
Question moles	37.416 mole				X		

X = number of moles of $(NH_2)_2CO$ = $\frac{37.416\ mol \times 1\ mol}{2\ mol}$ = 18.708 mol

mass of $(NH_2)_2CO$ = n × M = 18.708 mol × 60.06 g/mol = 1123.6 g

C) It is clear from the above that **CO_2** is the excess reagent.

	$2NH_3$	+	CO_2	→	$(NH_2)_2CO(_3)$	+	H_2O

Equation moles	2 mol	1 mol
Question moles	37.416 mole	Y

Y = number of moles of CO_2 reacted = $\frac{37.416 \text{ mol} \times 1 \text{ mol}}{2 \text{ mol}}$ = 18.708 mol

number of moles of CO_2 remains = 25.943 mol – 18.708 mol = 7.235 mol

mass of CO_2 remains = n × M = 7.235 mol × 44.02 g/mol = 318.5 g

Practice Exercise 3.14

The reaction between **Al** and **Fe_2O_3** can generate temperatures approaching 3000 °C and is used in welding metals:

$2Al(g) + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

In one process, 124 g of Al are reacted with 601 g of Fe_2O_3. (a) Calculate the mass (in grams) of Al_2O_3 formed. (b) How much of the excess reagent is left at the end of the reaction?

3.10 Reaction yield (Yield percentage)

- The amount of a product that should be produced in a chemical reaction can be calculated theoretically.
- This calculated amount of product is called "**the theoretical yield**" of the reaction.
- The theoretical yield is, *the amount of product that would result if all the limiting reagent reacted*. It is the *maximum* obtainable yield and is known by calculations on the balanced equation.
- The amount of a product that is really (not theoretically) produced is different from the theoretical yield and is called "**the actual yield**".
- For many reasons, the actual yield is always less than **the theoretical yield**.
- Chemists have created a criterion that could be a measure of their efficiency and success in production of chemicals. This criterion is called "**the yield percent**", or "**the yield percentage**"

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

EXAMPLE 3.15

In an industrial operation 3.54×10^7 g of $TiCl_4$ reacted with 1.13×10^7 g of Mg:

$$TiCl_4(g) + 2Mg(g) \rightarrow Ti(s) + 2MgCl_2(l)$$

A) Calculate the theoretical yield of Ti

B) Calculate the percent yield if 7.91×10^6 g of Ti actually are obtained

Solution

A) $n_{TiCl_4} = \frac{m_{TiCl_4}}{M_{TiCl_4}} = \frac{3.54 \times 10^7 \text{ g}}{189.9 \frac{\text{g}}{\text{mol}}} = 1.87 \times 10^5$ mol **AND** $n_{Mg} = \frac{m_{Mg}}{M_{Mg}} = \frac{1.13 \times 10^7 \text{ g}}{24.31 \frac{\text{g}}{\text{mol}}} = 4.65 \times 10^5$ mol

$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

	$TiCl_4$	2Mg	Ti	$2MgCl_2$
Equation moles	1 mol	2 mol		
Question moles	1.87×10^5	4.65×10^5		
$\frac{\text{Question moles}}{\text{Equation moles}}$	1.87×10^5	2.325×10^5		

It is clear from the last row that $TiCl_4$ is the limiting reagent.

$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

	$TiCl_4$	2Mg	Ti	$2MgCl_2$
Equation moles	1 mol		1 mol	
Question moles	1.87×10^5 mole		n	

Theoretical yield of Ti = $\frac{1.87 \times 10^5 \text{ mol} \times 1 \text{ mol}}{1 \text{ mol}} = 1.87 \times 10^5$ mol

$m = n \times M = 1.87 \times 10^5 \text{ mol} \times 47.88 \text{ g/mol} = 8.95 \times 10^6 \text{ g}$

C) $\%\text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{7.91 \times 10^6 \text{ g}}{8.95 \times 10^6 \text{ g}} \times 100 = 88.37\%$

Practice Exercise 3.15

Industrially, vanadium metal, which is used in steel alloys, can be obtained by reacting vanadium(V) oxide with calcium at high temperatures:

$5Ca + V_2O_5 \rightarrow 5CaO + 2V$

In one process, 1.54×10^3 g of V_2O_5 react with 1.96×10^3 g of Ca. (a) Calculate the theoretical yield of V. (b) Calculate the percent yield if 803 g of V are obtained.

4. REACTIONS IN AQUEOUS SOLUTIONS

4.1 General properties of aqueous solutions

- A **solution** is a homogeneous mixture of two or more substances
- The **solute** is the substance present in a smaller amount, and the **solvent** is the substance present in a larger amount
- We will discuss only **aqueous solutions** of a liquid or a solid

4.2 Electrolytic properties

- All solutes that dissolve in water are either electrolytes or nonelectrolytes
- An ***electrolyte*** is *a substance that, when dissolved in water, results in a solution that can conduct electricity*
- A ***nonelectrolyte*** *does not conduct electricity when dissolved in water*
- A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated. Thus, we can represent dissolving 0f sodium chloride in water as:

$$\mathrm{NaCl\ (s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

- Electrolytes are two kinds
  - ✓ **strong** (i.e. ionic compounds that are 100% dissociated into its ions when dissolved in water). NaCl is an example:
    This equation says that all dissolved sodium chloride ends up as $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions and no undissociated NaCl units in solution:

$$\mathrm{NaCl\ (s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

  - ✓ Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid ($\mathrm{HNO_3}$) are strong electrolytes: These acids are assumed to ionize completely in water:

$$\mathrm{HCl\ (g)} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

  - ✓ **weak** (i.e. molecular compounds that partially ionized into cations and anions when dissolved in water). Acetic acid is an example:

$$\mathrm{CH_3COOH(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{CH_3COO^-(aq)}$$

    This equation says that some dissolved acetic acid ends up as $\mathrm{H^+}$ and $\mathrm{CH_3COO^-}$ ions and the rest of it remains as $\mathrm{CH_3COOH}$ units in solution
  - ✓ Strong acids (bases) and weak acids (and bases) are the most common types of electrolytes. The following table shows that:

Electrolyte		Nonelectrolyte
Strong	Weak	
HCl	HF	$\mathrm{(NH_2)_2CO}$, urea
$\mathrm{HNO_3}$	$\mathrm{HNO_2}$	$\mathrm{CH_3OH}$, methanol
$\mathrm{HClO_4}$	$\mathrm{NH_3}$	$\mathrm{CH_3CH_2OH}$ ethanol
$\mathrm{H_2SO_4}$	$\mathrm{H_2O}$ (extremely weak)	$\mathrm{C_6H_{12}O_6}$, glucose
NaOH	HCOOH	$\mathrm{C_{12}H_{22}O_{11}}$, sucrose
$\mathrm{BaOH_2}$	$\mathrm{CH_3COOH}$	$\mathrm{C_3H_5OH_3}$, glycerol

4.3 Precipitation reactions

4.3.1 Solubility

- **Precipitation reaction** is the formation of an insoluble product, or precipitate
- A **precipitate** is an insoluble solid that separates from the solution

- Precipitation reactions usually involve ionic compounds.
- Example: Adding an aqueous solution of lead(II) nitrate, to an aqueous solution of potassium iodide, a yellow precipitate of lead(II) iodide ,PbI_2, is formed:

  $$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

  This reaction is an example of a ***metathesis reaction*** (also called a double-displacement reaction), ***a reaction that involves the exchange of parts between the two compounds***
- **Solubility: predicting** whether a precipitate will form when a compound is added to a solution or when two solutions are mixed depends on the ***solubility*** of the solute
- The ***solubility*** of the solute is *the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature*
  - ✓ A **soluble substance** is the substance if a fair amount of it visibly dissolves in water
  - ✓ A **slightly soluble** or an **insoluble** substance that a fair amount of it is not visibly dissolves in water
  - ✓ All ionic compounds are strong electrolytes, but they are not equally soluble
  - ✓ The following table classifies common ionic compounds as soluble or insoluble

SOLUBLE COMPOUND	**INSOLUBLE EXEPTIONS**
Compounds containing alkali metals ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and mmonium (NH_4^+)	
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-),	
Halides (Cl^-, Br^-, l^-)	Halides of Ag^+, Hg_2^{2-}, Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+, Cu^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2-}, Pb^{2+}

INSOLUBLE COMPOUND	**SOLUBLE EXEPTIONS**
Carbonates (CO_3^{2-}), Phosphates (PO_4^{3-}), Chromates (CrO_4^{2-}), Sulfides (S^{2+})	Compounds containing alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+), and ammonium (NH_4^+)
Hydroxides (OH^-)	Compounds containing alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+), and barium ion (Ba^{2+})

  - ***We must memorize*** that all ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, we need to look up in references

Example 4.1

Classify the following ionic compounds as soluble or insoluble:

A) silver sulfate (Ag_2SO_4), B) calcium carbonate $CaCO_3$, C) sodium phosphate Na_3PO_4)

Solution

A) According to the previous table Ag_2SO_4 is insoluble

B) Calcium isn’t an alkali and chromate compounds are insoluble, so it is insoluble

C) Sodium is an alkali metal, so it is soluble

Practice exercise 4.1

Classify the following ionic compounds as soluble or insoluble:

A) CuS, B) $Ca(OH)_3$, C) $Zn(NO_3)_2$

4.3.2 Molecular equations, ionic Equations, and net ionic equations

- The equation written in the section 5.3.1 is:

$$\mathrm{Pb(NO_3)_2(aq)} + \mathrm{2KI(aq)} \rightarrow \mathrm{PbI_2(s)} + \mathrm{2KNO_3(aq)}$$

- This equation called a **molecular equation** because the formulas of the compounds are written as though all species existed as molecules or whole units
- A molecular equation is useful because it identifies the reagents (lead(II) nitrate and potassium iodide)
- However, a molecular equation does not describe in detail what really is happening in solution
- When ionic compounds dissolve in water, they break apart into their component cations and anions
- The equations should show the dissociation of dissolved ionic compounds into ions. Therefore, it's better to write it as follows:

$$\mathrm{Pb^{2+}} + \mathrm{2NO_3^-} + \mathrm{2K^+} + \mathrm{2I^-} \rightarrow \mathrm{PbI_2(s)} + \mathrm{2K^+} + \mathrm{2NO_3^-}$$

- This preceding equation is an example of an **ionic equation,** which shows dissolved species as free ions
- To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is, $\mathrm{PbI_2}$ and $\mathrm{KNO_3}$
  - ✓ The table given in section 5.3.1 shows that $\mathrm{PbI_2}$ is an insoluble compound and $\mathrm{KNO_3}$ is soluble
  - ✓ Therefore, $\mathrm{KNO_3}$ remains in solution as separate $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ ions, which are called **spectator ions,** or ions that are not involved in the overall reaction
  - ✓ Spectator ions can be eliminated from both sides of the ionic equation to be:

$$\mathrm{Pb^{2+}(aq)} + \mathrm{2I^-(aq)} \rightarrow \mathrm{PbI_2(s)}$$

- Another example is:

$$\mathrm{BaCl_2(aq)} + \mathrm{Na_2SO_4(aq)} \rightarrow \mathrm{BaSO_4(s)} + \mathrm{2NaCl(aq)}$$

$$\mathrm{Ba^{2+}(aq)} + \mathrm{2Cl^-(aq)} + \mathrm{2Na^+(aq)} + \mathrm{SO_4^{2-}(aq)} \rightarrow \mathrm{BaSO_4(s)} + \mathrm{2Na^+} + \mathrm{2Cl^-(aq)}$$

$$\mathrm{Ba^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)} \rightarrow \mathrm{BaSO_4(s)}$$

- The following steps summarize the procedure for writing ionic and net ionic equations:
  1) Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds and specify which product is a precipitate
  2) Rewrite the equation as ionic equation (The compound that is not a precipitate should be shown as free ions
  3) Identify and cancel the spectator ions on both sides of the equation then write the net ionic equation for the reaction
  4) Check that the charges and number of atoms are balanced in the net ionic equation

Example 4.2

Predict what happens when a potassium phosphate ($\mathrm{K_3PO_4}$) solution is mixed with a calcium nitrate ($\mathrm{Ca(NO_3)_2}$) solution. Write a net ionic equation for the reaction.

Solution

A) $\mathrm{2K_3PO_4(aq)} + \mathrm{3Ca(NO_3)_2(aq)} \rightarrow \mathrm{Ca_3(PO_4)_2(s)} + \mathrm{6KNO_3(aq)}$

B) $\mathrm{6K^+(aq)} + \mathrm{PO_4^{3-}(aq)} + \mathrm{3Ca^{2+}(aq)} + \mathrm{6NO_3^-(aq)} \rightarrow$

$\mathrm{Ca(PO_4)_2(s)} + \mathrm{6K^+(aq)} + \mathrm{6NO_3^-(aq)}$

C) $\mathrm{PO_4^{3-}(aq)} + \mathrm{3Ca^{2+}(aq)} \rightarrow \mathrm{Ca(PO_4)_2(s)}$

D) The net ionic equation is balanced in the number of atoms and in the number of positive and negative charges

Practice exercise 4.2

Write the net ionic equation for the reaction of $Al(NO_3)_3$ solution with a NaOH solution.

4.4 Acid-base reactions

- Acids and bases are as familiar as acetylsalicylic acid (aspirin) and magnesium hydroxide (milk of magnesia)
- Acid-base chemistry is important in industrial processes and essential in sustaining biological systems

4.4.1 General properties of acids and bases

- **Definitions**
  - ✓ **Arrhenius Acids and Bases:** Arrhenius defined acids as substances that ionize in water to produce H^+ ions and bases as substances that ionize in water to produce OH^- ions
  - ✓ **Brønsted Acids and Bases:** Brønsted defined acids as substances that donates H^+ ions and bases as substances that accepts H^+ ions (Note: Brønsted's definitions do not require acids and bases to be in aqueous solution)
- Acids have a sour taste; vinegar owes its sourness to acetic acid, and lemons and other citrus fruits contain citric acid
- Acids cause color changes in plant dyes, they change the color of litmus from blue to red
- Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:
$$2H^+(aq) + 2Cl^-(aq) + Mg(s) \rightarrow MgCl_2(s) + H_2(g)$$
- Aqueous acid solutions conduct electricity
- Bases have a bitter taste
- Bases feel slippery; soaps, which contain bases, exhibit this property
- Bases cause color changes in plant dyes; they change the color of litmus from red to blue
- Aqueous base solutions conduct electricity
- Hydrochloric acid is a Brønsted acid because it donates a proton in water:
$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$
- $H^+(aq)$ ion is just a bare proton. This exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole of H_2O to form hydronium ion $H_3O^+(aq)$
- For convenience, we generally use $H^+(aq)$ to represent the hydrated proton, but $H_3O^+(aq)$ is closer to reality
- Keep in mind that both notations represent the same species in aqueous solution
- Acids commonly used in the laboratory are hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4).
  - **Monoprotic acids:** is an acid that when each unit yields one hydrogen ion upon ionization it examples are:
$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
    Because the ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason, it is called a weak acid. On the other hand, HCl and HNO_3 are strong acids that completely ionized in solution (single arrows)

- **Diprotic acids:** is an acid that when each unit yields two hydrogen ions upon ionization it example is:

  $$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
  $$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

  H_2SO_4 is a strong electrolyte or strong acid (the first step of ionization is complete), but HSO_4^- is a weak acid or weak electrolyte, and we need a double arrow to represent its incomplete ionization

- **Triprotic acids,** is an acid that when each unit yields three hydrogen ions upon ionization it examples is:

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

  $H_2PO_4^-$ and $H_2PO_4^-$ are weak acids (the double arrows represent its incomplete ionization) found in aqueous solutions of phosphates such as NaH_2PO_4 and Na_2HPO_4

- The following table lists several common strong and weak acids:

Strong acids		Weak acids	
Hydrochloric acid	HCl	Hydrofluoric acid	HF
Hydrobromic acid	HBr	Nitrous acid	HNO_2
Hydroiodic acid	HI	Phosphoric acid	H_3PO_4
Nitric acid	HNO_3	Acetic acid	CH_3COOH
Sulfuric acid	H_2SO_4		
Perchloric acid	$HClO_4$		

- Some hydroxides, such as NaOH, are strong electrolytes. they are completely ionized in water:

  $$NaOH(g) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

  The OH^- ion can accept a proton as follows:

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

  Thus, OH^- is a Brønsted base
- After ammonia gas, ($NH_3(g)$) dissolves in water it is classified as a Brønsted base because it can accept H^+ from H_2O:

  $$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) + OH^-(aq)$$

- Ammonia is a weak base) because only a small fraction of dissolved NH_3(g molecules react with water to form NH_4^+ and ions OH^-.
- All the alkali metal hydroxides are soluble, the most commonly used strong base in the laboratory is the cheap and soluble NaOH
- The most commonly used weak base is aqueous ammonia solution, it is sometimes erroneously called ammonium hydroxide. The species NH_4OH do not exists
- All the alkali earth metal hydroxides elements form hydroxides. $Ba(OH)_2$. Magnesium and calcium hydroxides are used in medicine and industry
- Hydroxides of other metals, such as $Al(OH)_3$ and $Zn(OH)_2$ are insoluble and are not used as bases

Example 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:

A) HBr B) NO_2^- C) HCO_3^-

Solution

A) $HBr(aq) \rightarrow H^+(aq) + Br^-(aq)$
HBr is a Brønsted acid

B) $NO_2^-(aq) + H^+(aq) \rightarrow HNO_2(aq)$
NO_2^- is a Brønsted base

C) $HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq)$
HCO_3^- is a Brønsted acid
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$
$HCO_3^-(aq)$ is a Brønsted base
$HCO_3^-(aq)$ is an amphoteric substance
An amphoteric substance a substance that has the ability to act either as an acid or a base

Practice exercise 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:

A) SO_4^{2-} B) HI

4.4.2 Acid-Base Neutralization

- A neutralization reaction is a reaction between an acid and a base
- Generally, aqueous acid-base reactions produce water and a salt, which is an ionic compound made up of a cation other than H^+ and an anion other than OH^- or O^{2-}:
$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$
- The following example is the typical neutralization reaction:
$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
$Na^+(aq)$ and $Cl^-(aq)$ are spectator ions
- If the molar amounts of acid and the base are equal we would have only a salt and no leftover acid or base. This is a characteristic of acid-base **neutralization reactions**
- A reaction between a weak acid such as HCN and a strong base such as NaOH is:
$$HCN(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + CN^-(aq) + H_2O(l)$$
$$HCN(aq) + OH^-(aq) \rightarrow CN^-(aq) + H_2O(l)$$
$Na^+(aq)$ is the only spectator ion
- The following are examples of acid-base neutralization reactions, represented by molecular equations:
$$HF(aq) + KOH(aq) \rightarrow KF(aq) + H_2O(l)$$
$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$
$$HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq)$$
The last equation looks different because it does not show water as a product. However, if we express $NH_3(aq)$ as $NH_4^+(aq)$ and $OH^-(aq)$, then the equation becomes:
$$HNO_3(aq) + NH_4^+(aq) + OH^-(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

4.4.3 Acid-base reactions leading to gas formation

- Certain salts like carbonates (containing the CO_3^{2-} ion), bicarbonates (containing the HCO_3^- ion), sulfites (containing the SO_3^{2-} ion), and sulfides (containing the S^{2-} ion) react with acids to form gaseous products
- For example, the molecular equation for the reaction between sodium carbonate (Na_2CO_3) and HCl(aq) is:
$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2CO_3(aq)$$

Carbonic acid is unstable and if present in solution in sufficient concentrations decomposes as follows:

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

Other examples are:

$$NaHCO_3(aq) + HCl(aq) \rightarrow CO_2(g) + H_2O(l) + NaCl(aq)$$
$$Na_2SO_3(aq) + 2HCl(aq) \rightarrow SO_2(g) + H_2O(l) + 2NaCl(aq)$$
$$K_2S(aq) + 2HCl(aq) \rightarrow H_2S(g) + 2KCl$$

4.5 Oxidation-reduction reactions

4.5.1 The concept

- Let us **carefully** see and inspect the following equation:

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

- MgO is an ionic compound made up of one Mg^{2+} ion and one O^{2-} ion
- Forming one MgO compound is a result of transferring two electrons from an Mg atom to an O atom. This transfer usually is split into two steps each of which is called half-reaction:

$$2Mg \rightarrow 2Mg^{2+} + 4e^-$$
$$2O + 4e^- \rightarrow 2O^{2-}$$

- The sum of these two halves is:

$$2Mg(s) + O_2(g) + 4e^- \rightarrow 2MgO(s) + 4e^-$$
$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

- **NOTE:** *From the previous points we may think that transfer of electrons is limited to the formation of ionic compounds. However, the truth is not; formation of some nonionic compound involves this transfer, in other words involves oxidation and reduction. These cases will be discussed in the next section titled "**Oxidation numbers**"*

4.5.2 Terminology

- **The oxidation reaction** is the half reaction "$2Mg \rightarrow 2Mg^{2+} + 4e^-$" which involves electron loss (or donation). The substance that loses (donates) electrons is called **the reductant** (or the reducing agent)
- **The reduction reaction** is the half reaction "$2O + 4e^- \rightarrow 2O^{2-}$" which involves electron gain (or acceptance). The substance that gains (accepts) electrons is called **the oxidant** (or the oxidizing agent)
- The reducing agent is **oxidized**, and "the oxidizing agent is **reduced**
- Other examples of oxidation-reduction reactions are:
  - ✓ $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

    Its half-reactions are
    - ➢ $Zn \rightarrow Zn^{2+} + 2e^-$ (Here, zinc is oxidized)
    - ➢ $Cu^{2+} + 2e^- \rightarrow Cu$ (Here, copper is reduced)
  - ✓ $Cu(s) + 2AgNO_3(aq) \rightarrow CU(NO_3)_2(aq) + 2Ag(s)$

    Its half-reactions are
    - ➢ $Cu \rightarrow Cu^{2+} + 2e^-$ (Here, copper is oxidized)
    - ➢ $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ (Here, silver is reduced)

4.5.3 Oxidation number

- The formation of nonionic compounds such as hydrogen chloride (HCl) and sulfur dioxide (SO_2):

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

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

- Because HCl and SO_2 are molecular compounds, no electrons are transferred in their formation of these compounds
- Chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from H to Cl in HCl and from S to O in SO_2)
- To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's ***oxidation number,*** also called ***oxidation state,*** signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred* completely

  For example, we can rewrite the previous equations for the formation of HCl and SO_2 as follows:

$$\overset{0}{H_2}(g) + \overset{0}{Cl_2}(g) \rightarrow 2\overset{+1}{H}\overset{-1}{Cl}(g)$$

$$\overset{0}{S}(s) + \overset{0}{O_2}(g) \rightarrow \overset{+4}{S}\overset{-2}{O_2}(g)$$

- The numbers above the element symbols are the oxidation numbers
- In both reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero
- For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons.
- The oxidation numbers reflect the number of electrons "transferred"
- Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance
- The elements that show an increase in oxidation number, hydrogen and sulfur are oxidized, so their oxidation numbers increase
- The elements that show a decrease in oxidation number, chlorine and oxygen are reduced, so their oxidation numbers decrease
- Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and −1) is zero and the sum of the oxidation numbers of S and two atoms of O [+4 and 2 × (−2)] is zero

4.5.4 Rules to assign oxidation numbers

1) In free elements (that is, in the uncombined state), each atom has an oxidation number of zero
2) For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion
3) All metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers
4) All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds
5) The oxidation number of oxygen in most compounds (for example, MgO and H_2O) is +2, but −1 in hydrogen peroxide (H_2O_2) and peroxide ion (O_2^{-2})
6) The oxidation number of hydrogen is +1, but −1 when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH_2)
7) Fluorine has an oxidation number of −1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their

compounds. When combined with oxygen, for example in oxoacids and oxoanions, they have positive oxidation numbers

8) In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH_4^+, the oxidation number of N is −3 and that of H is +1. Thus, the sum of the oxidation numbers is (– 3) + (4 × + 1) = + 1
9) Oxidation numbers do not have to be integers. For example, in the superoxides ion, O_2^-, the oxidation number of O is $\frac{1}{2}$

Example 4.4

Assign oxidation numbers to all the elements in the following compounds and ion:

A) Li_2O B) HNO_3 C) $Cr_2O_7^{2-}$

Solution

A) Li = + 1 and O = − 2

B) We can write HNO_3 as $H^{+1}N^{x}O_3^{-2}$

$(+1) + (x) + (3 \times -2) = 0$

The oxidation number of N = x = + 5

C) We can write $Cr_2O_7^{2-}$ as $[Cr_2^{x}O_7^{-y}]^{-2}$

The oxidation number of O = y = − 2

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

The oxidation number of Cr = x = + 6

Practice exercise 4.4

Assign oxidation numbers to all the elements in the following compound and ion: (a) PF 3 , (b) MnO4:

A) PF_3 B) MnO_4^-

4.5.6 Types of redox reactions

- **Combination reactions:** A *combination reaction* is *a reaction in which two or more substances combine to form a single product*. For example:

$$\overset{0}{S}(s) + \overset{0}{O}_2(g) \rightarrow \overset{+4}{S}\overset{-2}{O}_2(g)$$

$$2\overset{0}{Al}(s) + 3\overset{0}{Br}_2(l) \rightarrow 2\overset{+3}{Al}\overset{-1}{Br}_3(s)$$

- **Decomposition reactions:** A *decomposition reaction* is *the breakdown of a compound into two or more components*. Thy are the opposite of combination reaction. For exampl:

$$2\overset{+2}{Hg}\overset{-2}{O}(s) \rightarrow 2\overset{0}{Hg} + \overset{0}{O}_2(g)$$

$$2\overset{+1}{K}\overset{+7}{Cl}\overset{-2}{O}_4(s) \rightarrow 2\overset{+1}{K}\overset{-1}{Cl}(s) + 4\overset{0}{O}_2(g)$$

$$2\overset{+1}{Na}\overset{-1}{H}(s) \rightarrow 2\overset{0}{Na}(s) + \overset{0}{H}_2(g)$$

- **Combustion reactions:** A combustion reaction is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane (C_3H_8), a component of natural gas that is used for domestic heating and cooking:

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

- **Displacement reactions:** A displacement reaction is a reaction in which an ion (or atom) in a compound is replaced by an ion (or atom) of another element. Displacement reactions are several subcategories:

1) Hydrogen displacement: All alkali metals and some alkaline earth metals (Ca, Sr, and Ba), which are the most reactive of the metallic elements, displace hydrogen from cold water:

$$\overset{0}{2Na}(s) + 2\overset{+1}{H_2}\overset{-1}{O}(l) \rightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H_2}(g)$$

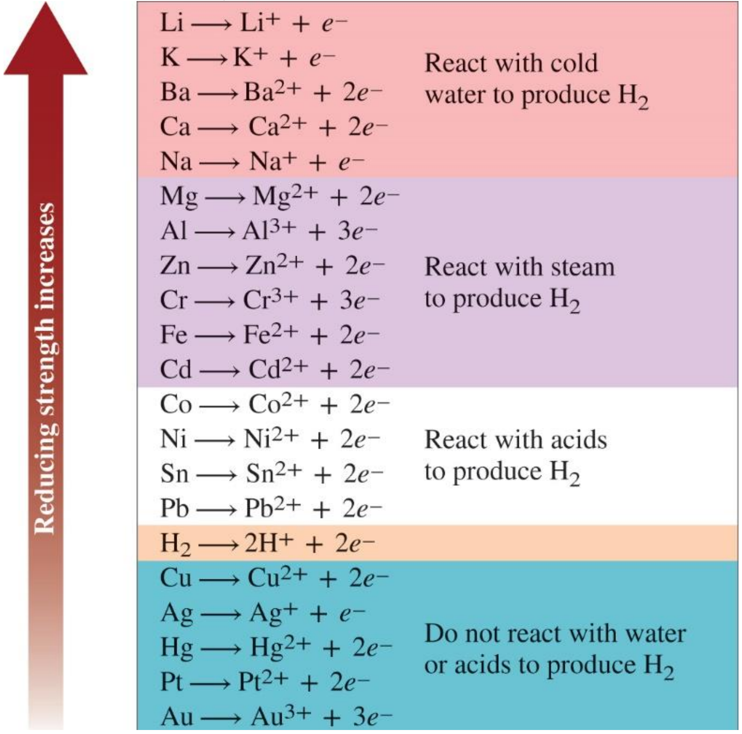
$$\overset{0}{Ca}(s) + 2\overset{+1}{H_2}\overset{-1}{O}(l) \rightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(s) + \overset{0}{H_2}(g)$$

Also, many metals displace hydrogen from acids:

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Mg}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Mg}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

2) Metal displacement: A metal in a compound can be displaced by another metal in the elemental state. An easy way to predict whether a metal or hydrogen displacement reaction will occur is to refer to an **activity series** (the electrochemical series):



$Li \longrightarrow Li^+ + e^-$	React with cold water to produce H_2
$K \longrightarrow K^+ + e^-$	
$Ba \longrightarrow Ba^{2+} + 2e^-$	
$Ca \longrightarrow Ca^{2+} + 2e^-$	
$Na \longrightarrow Na^+ + e^-$	
$Mg \longrightarrow Mg^{2+} + 2e^-$	React with steam to produce H_2
$Al \longrightarrow Al^{3+} + 3e^-$	
$Zn \longrightarrow Zn^{2+} + 2e^-$	
$Cr \longrightarrow Cr^{3+} + 3e^-$	
$Fe \longrightarrow Fe^{2+} + 2e^-$	
$Cd \longrightarrow Cd^{2+} + 2e^-$	
$Co \longrightarrow Co^{2+} + 2e^-$	React with acids to produce H_2
$Ni \longrightarrow Ni^{2+} + 2e^-$	
$Sn \longrightarrow Sn^{2+} + 2e^-$	
$Pb \longrightarrow Pb^{2+} + 2e^-$	
$H_2 \longrightarrow 2H^+ + 2e^-$	
$Cu \longrightarrow Cu^{2+} + 2e^-$	Do not react with water or acids to produce H_2
$Ag \longrightarrow Ag^+ + e^-$	
$Hg \longrightarrow Hg^{2+} + 2e^-$	
$Pt \longrightarrow Pt^{2+} + 2e^-$	
$Au \longrightarrow Au^{3+} + 3e^-$	

According to this series, any metal above hydrogen will displace it from water or from an acid, but metals below hydrogen will not react with either water or an acid. In fact, any metal listed in the series will react with any metal (in a compound) below it. For example, Zn is above Cu, so zinc metal will displace copper ions from copper sulfate. For example:

✓ Vanadium is obtained by treating vanadium oxide with metallic calcium:

$$\overset{+5}{V_2}\overset{-2}{O_5}(s) + 5\overset{0}{Ca}(l) \rightarrow 2\overset{0}{V}(l) + 5\overset{+2}{Ca}\overset{-2}{O}(s)$$

Ca is above V. Ca reduces V^{+5} in V_2O_5 to V

- ✓ Titanium is obtained from titanium(IV) chloride according to the reaction

$$\overset{+4}{\mathrm{Ti}}\overset{-1}{\mathrm{Cl}}_4(s) + 2\overset{0}{\mathrm{Mg}}(l) \rightarrow \overset{0}{\mathrm{Ti}}(s) + 2\overset{+2}{\mathrm{Mg}}\overset{-1}{\mathrm{Cl}}_2(l)$$

Mg is above Ti. Mg reduces Ti^{+4} in $TiCl_4$ to Ti

3) Halogen displacement: The halogens as a group are the most reactive of the nonmetallic elements. They are all strong oxidizing agents. As a result, they are found in nature in the combined state (with metals) as halides and never as free elements. Activity series of the halogens' in halogen displacement reactions is as follows:

$$F_2 > Cl_2 > Br_2 > I_2$$

F_2 is the strongest oxidizing halogen and I_2 is the weakest oxidizing halogen. For example, F_2 can replace Cl^-, Br^- or I^- in their solutions as shown below:

$$\overset{0}{\mathrm{Cl}}_2(g) + 2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{Br}}(aq) \rightarrow 2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{Cl}}(aq) + \overset{0}{\mathrm{Br}}_2(l)$$

$$\overset{0}{\mathrm{Cl}}_2(g) + 2\overset{-1}{\mathrm{Br}}{}^-(aq) \rightarrow 2\overset{-1}{\mathrm{Cl}}{}^-(aq) + \overset{0}{\mathrm{Br}}_2(l)$$

$$\overset{0}{\mathrm{Cl}}_2(g) + 2\overset{+1}{\mathrm{Na}}\overset{-1}{\mathrm{I}}(aq) \rightarrow 2\overset{+1}{\mathrm{Na}}\overset{-1}{\mathrm{Cl}}(aq) + \overset{0}{\mathrm{I}}_2(s)$$

$$\overset{0}{\mathrm{Cl}}_2(g) + 2\overset{-1}{\mathrm{I}}{}^-(aq) \rightarrow 2\overset{-1}{\mathrm{Cl}}{}^-(aq) + \overset{0}{\mathrm{I}}_2(s)$$

$$\overset{0}{\mathrm{Br}}_2(l) + 2\overset{-1}{\mathrm{I}}{}^-(aq) \rightarrow 2\overset{-1}{\mathrm{Br}}{}^-(aq) + \overset{0}{\mathrm{I}}_2(s)$$

4) Disproportionation reactions: In a disproportionation reaction, an element in one oxidation state is simultaneously oxidized and reduced. One reactant in a disproportionation reaction always contains an element that can have at least three oxidation states. The element itself is in an intermediate oxidation state; that is, both higher and lower oxidation states exist for that element in the products. The following are examples:

$$2\overset{+1}{\mathrm{H}}_2\overset{-1}{\mathrm{O}}_2(aq) \rightarrow 2\overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(l) + \overset{0}{\mathrm{O}}_2(g)$$

$$\overset{0}{\mathrm{Cl}}_2(g) + 2\overset{-2}{\mathrm{O}}\overset{+1}{\mathrm{H}}{}^-(aq) \rightarrow 2\overset{+1}{\mathrm{Cl}}\overset{-2}{\mathrm{O}}{}^-(aq) + \overset{-1}{\mathrm{Cl}}{}^-(aq) + \overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(s)$$

Example 4.5

Classify the following redox reactions and indicate changes in the oxidation numbers of the elements:

A) $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$
B) $6Li(g) + N_2(g) \rightarrow 2Li_3N(s)$
C) $Ni(s) + Pb(NO_3)_2(aq) \rightarrow Pb + Ni(NO_3)_2(aq)$
D) $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

Solution

A) This is a decomposition reaction because one reactant is converted to two different products. The oxidation number of N changes from +1 to 0, while that of O changes from −2 to 0.
B) This is a combination reaction (two reactants form a single product). The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to −3.
C) This is a metal displacement reaction. The Ni metal replaces (reduces) the Pb^{2+} ion. The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.
D) The oxidation number of N is +4 in NO_2 and it is +3 in HNO_2 and +5 in HNO_3.Because the oxidation number of the same element both increases and decreases, this is a disproportionation reaction**Practice exercise 4.5**

Identify the following redox reactions by type:
A) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
B) $S + 3F_2(aq) \rightarrow SF_6$
C) $2CuCl \rightarrow Cu + CuCl_2(aq)$
D) $2Ag + PtCl_2 \rightarrow 2AgCl + Pt$

4.6 Concentration of solutions

- The **concentration of a solution** is the amount of solute present in a given amount of solvent, or a given amount of solution
- The concentration of a solution can be expressed in different ways
- Here we will consider one of the most commonly used units in chemistry, **molarity (M),** or **molar concentration,** *which is the number of moles of solute per liter of solution*:

$$\text{moloarity} = \frac{\text{moles of solute}}{\text{volume of solution in liter unit}}$$

$$M = \frac{n_{\text{solte}}}{V_{\text{solution}}\,(L)}$$

- A 1.46 molar glucose ($C_6H_{12}O_6$) solution, written as 1.46 M $C_6H_{12}O_6$, contains 1.46 moles of glucose in 1 L of the solution. Of course, we do not always work with solution volumes of 1 L. Thus, a 500-mL solution containing 0.73 mole of glucose also has a concentration of 1.46 M

$$M = \frac{0.73 \text{ mole of glucose}}{0.5 \text{ L}} = 1.46 \text{ M } C_6H_{12}O_6$$

- When a sample of (KCl) is dissolved in enough water to make a 1 M solution:

$$KCl(s) \xrightarrow{H_2O} K^+(aq) + Cl^-(aq)$$

  Because KCl is a strong electrolyte, it is completely dissociated in solution. Thus, a 1 M KCl solution contains 1 mole of K^+ and 1 mole of Cl^-, and no KCl units are present. The molarity can be expressed using square brackets [ ]. Therefore, $[K^+]$ = 1 M and $[Cl^-]$ = 1 M.

- When a sample of ($Ba(NO_3)_2$) is dissolved in enough water to make a 1 M solution:

$$Ba(NO_3)_2 \xrightarrow{H_2O} Ba^{2+}(aq) + 2NO_3^-(aq)$$

  Because $Ba(NO_3)_2$ is a strong electrolyte, it is completely dissociated in solution. Thus, a 1 M $Ba(NO_3)_2$ solution contains 1 mole of K^+ and 2 moles of NO_3^-, and no $Ba(NO_3)_2$ units are present. The molarity can be expressed using square brackets [ ]. Therefore, $[Ba^{2+}]$ = 1 M and $[NO_3^-]$ = 2 M.

- The procedure for preparing a solution of known molarity is as follows:
  - ✓ First, the solute is weighed and transferred to a volumetric flask through a funnel.
  - ✓ Next, water is added to the flask the is carefully swirled to dissolve the solid
  - ✓ After all the solid has dissolved, more water is added slowly to bring the level of solution exactly to the volume mark
  - ✓ Knowing the volume of the solution in the flask and the number of moles dissolved, we can calculate the molarity of the solution

Example 4.6

Calculate the mass, in grams, of potassium dichromate $K_2Cr_2O_7$ required to prepare a 250 mL of a its solution in water whose concentration is 2.16 M?

Solution

$M = \frac{n_{solte}}{V_{solution}\ (L)}$

$n_{K_2Cr_2O_7} = M \times V_{solution}\ (L) = 2.16\ M \times 0.25\ L = 0.54\ mol\ K_2Cr_2O_7$

$m_{K_2Cr_2O_7} = n_{K_2Cr_2O_7} \times M_{K_2Cr_2O_7} = 0.54\ mol \times 294.2\ \frac{g}{mol} = 159\ g$

Practice exercise 4.6

Calculate the molarity of an 85.0-mL ethanol (C_2H_5OH) solution containing 1.77 g of ethanol?

Example 4.7

Calculate the volume, in mL, of a solution of 3.81 g of glucose in water if the solution molarity equals 2.53 M. (molar mass og glucose = 180.2 $\frac{g}{mol}$)

Solution

$$V = \frac{n_{solte}}{M} = \frac{\frac{m_{solte}}{M_{solte}}}{M} = \frac{\frac{3.81\ g}{180.2\ \frac{g}{mol}}}{2.53\ \frac{mol}{L}} = 0.00836\ L = 8.36\ mL$$

Practice exercise 4.7

Calculate the volume, in mL, of a 0.315 M NaOH solution containing 6.22 g of NaOH?

- **Dilution law:**

$$\text{initial moles of slute} = \text{final moles of slute}$$
$$M_{initial} \times V_{initial} = M_{final} \times V_{final}$$

  - ✓ Solutions stored in laboratories stock rooms are very concentrated solutions. We dilute these “stock” solutions to perform experiments
  - ✓ **Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one
  - ✓ Suppose that we want to prepare 1 L of a 0.400 M $KMnO_4$ solution from a solution of 1.00 M $KMnO_4$

$$M_{initial} \times V_{initial} = M_{final} \times V_{final}$$
$$1\ M \times V_{initial} = 0.4\ M \times 1\ L$$
$$V_{initial} = \frac{0.4\ M \times 1\ L}{1\ M} = 0.4\ L$$

  - ✓ We need to take 0.400 mL of the 1.00 m $KMnO_4$ and dilute it to 1000 mL by water
  - ✓ This method gives us 1 L of the desired solution of 0.400 M $KMnO_4$

Example 4.8

Describe how you would prepare 500 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4.

Solution

$M_{initial} \times V_{initial} = M_{final} \times V_{final}$

$8.61\ M \times V_{initial} = 1.75\ M \times 500\ mL$

$V_{initial} = \frac{1.75\ M \times 500\ mL}{8.61\ M} = 102\ mL$

Thus, we must take 102 mL of the 8.61 M H_2SO_4 solution and dilute it with water to 500 mL.

Practice exercise 4.8

How would you prepare 200 mL of a 0.866 M NaOH solution, starting with a 5.07 M stock solution?

4.7 Gravimetric analysis

- **Gravimetric analysis** is an analytical technique based on the measurement of mass

- One of the famous gravimetric analysis experiment involves the formation, isolation, and mass determination of a precipitate of an ionic compound
  - ✓ A sample an ionic compound of unknown composition is dissolved in water and allowed to react with another ionic compound to form a precipitate
  - ✓ The precipitate is filtered off, dried, and weighed
  - ✓ Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of the particular chemical component (the anion or cation) of the original sample
  - ✓ From the mass of the component and the mass of the original sample, we can determine the percent composition by mass of the component in the original compound
- A reaction that is often studied in gravimetric analysis is:

$$\mathrm{AgNO_3} + \mathrm{NaCl(aq)} \rightarrow \mathrm{NaNO_3} + \mathrm{AgCl(s)}$$
$$\mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} \rightarrow \mathrm{AgCl(s)}$$

- Let us imagine that we know that the elements which constitute table salt are Na and Cl but we do not know their mass percentage and consequently do not know how many Na atom and Cl atom in each unit of the table salt. This means that we imagine that we do not know that the chemical formula of table salt is NaCl or $\mathrm{Na_2Cl_2}$ or any other
  - ✓ If we add an excess mass of $\mathrm{AgNO_3}$ to a table salt solution we insure that all Cl in table salt solution will produce silver chloride as a precipitate (solid)
  - ✓ We know that formula of silver chloride is AgCl. Therefore, the mass percent of Ag in AgCl can be simply calculated, then the mass of Ag in AgCl can be calculated
  - ✓ Subtraction of Ag mass from the mass of AgCl gives the mass of Cl present in the original mass of table salt, and subtraction of this mass of Cl from the original mass of table salt gives us the mass of Na in the reacted table salt
- Knowing masses of Na and Cl in a given mass of table salt enables us to calculate the mass percentage of both Na and Cl in the salt

Example 4.9

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of $\mathrm{AgNO_3}$. If 1.0882 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

Solution

Molar $\mathrm{mass_{Cl}} = 35.45\ \frac{\mathrm{g}}{\mathrm{mol}}$ and Molar $\mathrm{mass_{AgCl}} = 143.4\ \frac{\mathrm{g}}{\mathrm{mol}}$

Therefore, the percent by mass of Cl in AgCl is given by:

$$\mathrm{Cl\%\ in\ AgCl} = \frac{35.45\ \frac{\mathrm{g}}{\mathrm{mol}}}{143.4\ \frac{\mathrm{g}}{\mathrm{mol}}} \times 100 = 24.72\%$$

$$\mathrm{mass\ of\ Cl\ in\ AgCl} = 0.2472 \times 1.0882\ \mathrm{g} = 0.2690\ \mathrm{g}$$

$$\mathrm{Cl\%\ in\ the\ compound} = \frac{0.2690\ \mathrm{g}}{0.5662\ \mathrm{g}} \times 100 = 47.51\%$$

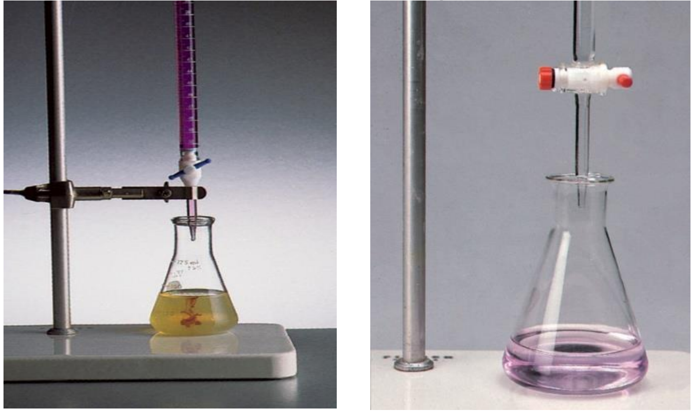
Practice exercise 4.9

A sample of 0.3220 g of an ionic compound containing the bromide ion ($\mathrm{Br^-}$) is dissolved in water and treated with an excess of $\mathrm{AgNO_3}$. If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

4.8 Acid-base titration

- Acid-base titration is a technique used for quantitative studies of acid-base neutralization reactions

- In ***titration,*** *a solution of accurately known concentration,* called a ***standard solution,*** *is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete*
- If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution
- The procedure for the titration is shown in the figure below



- In acid-base titrations, ***indicators*** are *substances that have distinctly different colors in acidic and basic media*
- One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions
- At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless
- However, if we add just one more drop of NaOH solution from the burette, the solution will immediately turn pink because the solution is now basic. Example 4.10 illustrates
- Suppose we wanted to use a diprotic acid such as H_2SO_4 for the titration:

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

- Because $2NaOH(aq) \equiv H_2SO_4(aq)$, we need twice as much NaOH to react completely with a H_2SO_4 solution of the same molar concentration. On the other hand, we would need twice the amount of HCl to neutralize a $Ba(OH)_2$ solution compared to a NaOH solution having the same concentration and volume because 1 mole of $Ba(OH)_2$ yields 2 moles of OH^- ions:

$$2HCl(aq) + Ba(OH)_2(aq) \rightarrow Ba(Cl)_2(aq) + 2H_2O(l)$$

- In calculations involving acid-base titrations, regardless of the acid or base that takes place in the reaction, keep in mind that the total number of moles of H^+ ions that have reacted at the equivalence point must be equal to the total number of moles of OH^- ions that have reacted.

Example 4.10

How many milliliters (mL) of a 0.610 M NaOH solution are needed to neutralize 20.0 mL of a 0.245 M H_2SO_4 solution?

Solution

$$n_{H_2SO_4} = \frac{0.245\ \text{mol} \times 20\ \text{mL,solution}}{1000\ \text{mL,solution}} = 4.90 \times 10^{-3}\ \text{mol}$$

Because 1 mol $H_2SO_4 \equiv$ 2 mol NaOH, there must be $2 \times 4.90 \times 10^{-3}$ mol of NaOH

$$\text{volume of NaOH} = \frac{9.80 \times 10^{-3}\ \text{mol}}{0.610\ \frac{\text{mol}}{1\ \text{L,solution}}} = 0.0161\ \text{L} = 16.1\ \text{mL}$$

Practice exercise 4.10

Calculate the volume of a 1.28 M H_2SO_4 solution needed to neutralize 60.2 mL of a 0.427 M KOH solution.

4.9 Redox titration

- We can titrate a solution containing an oxidizing agent by a solution containing a reducing agent
- *Two common oxidizing agents are potassium permanganate (*$KMnO_4$*) and potassium dichromate (*$K_2Cr_2O_7$*)*
- The following is an example

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + H_2O$$

Example 4.11

A 16.42-mL volume of 0.1327 M $KMnO_4$ solution is needed to oxidize 25.00 mL of $FeSO_4$ solution in an acidic medium. What is the concentration of the $FeSO_4$ solution in molarity? The net ionic equation is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + H_2O$$

Solution

$$n_{KMnO_4} = \frac{0.1327\ \text{mol} \times 16.42\ \text{mL,solution}}{1000\ \text{mL,solution}} = 2.179 \times 10^{-3}\ \text{mol}$$

Because 5 mol $FeSO_4$ ≡ 1 mol MnO_4^-, n_{FeO_4} can be calculated:

$$n_{FeO_4} = \frac{2.179 \times 10^{-3}\ \text{mol}\ KMnO_4 \times 5\ \text{mol}\ FeSO_4}{1\ \text{mol}\ KMnO_4} = 1.090 \times 10^{-2}\ \text{mol}\ FeSO_4$$

$$\text{molarity}_{FeO_4} = \frac{1.090 \times 10^{-2}\ \text{mol}\ FeSO_4}{25\ \text{mL,solution} \times \frac{1000\ \text{mL,solution}}{1\ \text{L,solution}}} = 0.340\ \text{M}$$

Practice exercise 4.11

How many milliliters of a 0.206 M HI solution are needed to reduce 22.5 mL of a 0.374 M $KMnO_4$ solution according to the following equation:

$$10HI + 2KMnO_4 + 3H_2SO_4 \rightarrow 5I_2 + 2MnSO_4 + 2K_2SO_4 + 8H_2O$$

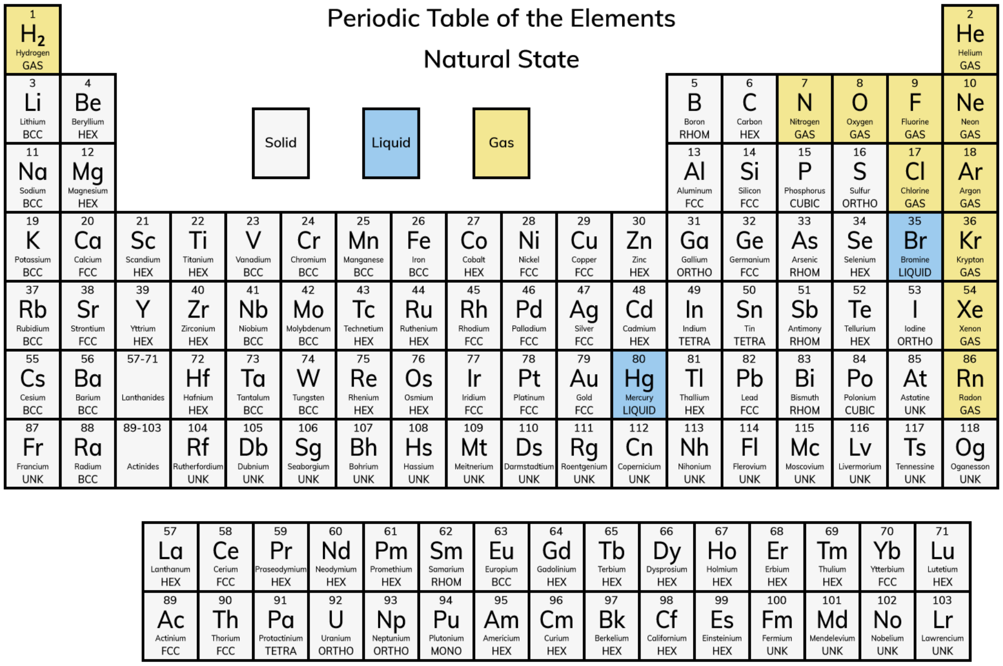
5. GASES

5.1 Substances that exist as gases

- We live at the bottom of an ocean of air whose composition by volume is roughly 78% N_2, 21 percent O_2, and 1 percent of CO_2 and other gases
- We will focus on the behavior of substances that exist as gases under **normal atmospheric conditions** which are defined as **25 °C and 1 atm (atmosphere)**

5.1.1 Elements that exist as gases

- All the elements in Group 18, the noble gases except Og, exist as **monatomic** gases: He, Ne, Ar, Kr, Xe, Rn
- The elements of hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as **diatomic** molecules: H_2, N_2, O_2, F_2, and Cl_2
- Ozone is another form of oxygen that exist as **triatomic** molecules, O_3



Periodic Table of the Elements

Natural State

Solid

Liquid

Gas

1 H_2 Hydrogen GAS																	2 He Helium GAS
3 Li Lithium BCC	4 Be Beryllium HEX											5 B Boron RHOM	6 C Carbon HEX	7 N Nitrogen GAS	8 O Oxygen GAS	9 F Fluorine GAS	10 Ne Neon GAS
11 Na Sodium BCC	12 Mg Magnesium HEX											13 Al Aluminum FCC	14 Si Silicon FCC	15 P Phosphorus CUBIC	16 S Sulfur ORTHO	17 Cl Chlorine GAS	18 Ar Argon GAS
19 K Potassium BCC	20 Ca Calcium FCC	21 Sc Scandium HEX	22 Ti Titanium HEX	23 V Vanadium BCC	24 Cr Chromium BCC	25 Mn Manganese BCC	26 Fe Iron BCC	27 Co Cobalt HEX	28 Ni Nickel FCC	29 Cu Copper FCC	30 Zn Zinc HEX	31 Ga Gallium ORTHO	32 Ge Germanium FCC	33 As Arsenic RHOM	34 Se Selenium HEX	35 Br Bromine LIQUID	36 Kr Krypton GAS
37 Rb Rubidium BCC	38 Sr Strontium FCC	39 Y Yttrium HEX	40 Zr Zirconium HEX	41 Nb Niobium BCC	42 Mo Molybdenum BCC	43 Tc Technetium HEX	44 Ru Ruthenium HEX	45 Rh Rhodium FCC	46 Pd Palladium FCC	47 Ag Silver FCC	48 Cd Cadmium HEX	49 In Indium TETRA	50 Sn Tin TETRA	51 Sb Antimony RHOM	52 Te Tellurium HEX	53 I Iodine ORTHO	54 Xe Xenon GAS
55 Cs Cesium BCC	56 Ba Barium BCC	57-71 Lanthanides	72 Hf Hafnium HEX	73 Ta Tantalum BCC	74 W Tungsten BCC	75 Re Rhenium HEX	76 Os Osmium HEX	77 Ir Iridium FCC	78 Pt Platinum FCC	79 Au Gold FCC	80 Hg Mercury LIQUID	81 Tl Thallium HEX	82 Pb Lead FCC	83 Bi Bismuth RHOM	84 Po Polonium CUBIC	85 At Astatine UNK	86 Rn Radon GAS
87 Fr Francium UNK	88 Ra Radium BCC	89-103 Actinides	104 Rf Rutherfordium UNK	105 Db Dubnium UNK	106 Sg Seaborgium UNK	107 Bh Bohrium UNK	108 Hs Hassium UNK	109 Mt Meitnerium UNK	110 Ds Darmstadtium UNK	111 Rg Roentgenium UNK	112 Cn Copernicium UNK	113 Nh Nihonium UNK	114 Fl Flerovium UNK	115 Mc Moscovium UNK	116 Lv Livermorium UNK	117 Ts Tennessine UNK	118 Og Oganesson UNK

57 La Lanthanum HEX	58 Ce Cerium FCC	59 Pr Praseodymium HEX	60 Nd Neodymium HEX	61 Pm Promethium HEX	62 Sm Samarium RHOM	63 Eu Europium BCC	64 Gd Gadolinium HEX	65 Tb Terbium HEX	66 Dy Dysprosium HEX	67 Ho Holmium HEX	68 Er Erbium HEX	69 Tm Thulium HEX	70 Yb Ytterbium FCC	71 Lu Lutetium HEX
89 Ac Actinium FCC	90 Th Thorium FCC	91 Pa Protactinium TETRA	92 U Uranium ORTHO	93 Np Neptunium ORTHO	94 Pu Plutonium MONO	95 Am Americium HEX	96 Cm Curium HEX	97 Bk Berkelium HEX	98 Cf Californium HEX	99 Es Einsteinium HEX	100 Fm Fermium UNK	101 Md Mendelevium UNK	102 No Nobelium UNK	103 Lr Lawrencium UNK

5.1.2 Compounds that exist as gases

- Poisonous compounds such as H_2S) and HCN and many others such as CO, NO_2, O_3, and SO_2 are gases under ***normal atmospheric conditions***.
- The following is a list of the most famous gaseous compounds.

Name	Formula	Name	Formula
Hydrogen fluride	HF	Carbon monoxide	CO
Hydrogen chloride	HCl	Carbon dioxide	CO_2
Hydrogen bromide	HBr	Nitrogen monoxide	NO
Hydrogen iodide	HI	Nitrogen dioxide	NO_2
Hydrogen cyanide	HCN	Dinitrogen tetroxide	N_2O_4
Hydrogen sulfide	H_2S	Sulfur dioxide	SO_2
Ammonia	NH_3	Sulfur trioxide	SO_3

5.2 Pressure of the gas

Pressure of a gas is one of the following four important properties of any gas

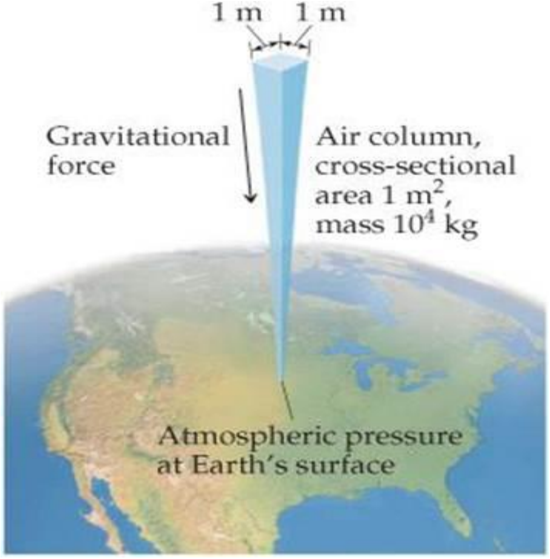
5.2.1 The four important properties in studying gases

The following table gives the four properties of gases that are so important to know while studying or dealing with gases:

PROPERTY	SYMBOL	UNITS	
		SI Units	Non-SI Units
Amount	n	Mole (mol)	--------------
Temperature	T	Kelvin (K)	--------------
Pressure	P	Pascal (Pa)	atm
Volume	V	Cubic meter (m^3)	Liter (L)

5.2.2 Atmospheric pressure and standard atmospheric pressure and temperature (STP)

- **Atmospheric pressure**
  - ✓ The pressure of the earth atmosphere is the effect of the force (weight) of the Earth's atmosphere on a specified area of the Earth's surface
  - ✓ If the chosen area on the surface of our Earth that equals 1 m^2, there will be above it a column of air extending all the way up to the far end of the Earth atmosphere
  - ✓ Its height from the sea level is more than from Everest peak (8850 m above sea level) and less than from the level of the dead sea (423 m below sea level)



- **Standard atmospheric pressure**

  The pressure of the atmosphere at sea level at 273 K is called "**standard atmospheric pressure**". Its value is 101,325 Pa

- **Standard temperature and pressure (STP)**

  Standard **T**emperature and **P**ressure (**STP**) is 273 K and 101325 Pa

5.3 The gas laws

Although the most famous law known as "the ideal or the perfect gas law" was derived from other gas laws, we will start with it and show how the other older gas laws can ve derived from it.

5.3.1 The ideal gas law (The relation between n, P, V and T of an ideal gas) and the gas constant "R"

- The mathematical relation between the gas quantity (n), pressure(P), volume (V) and temperature (T) is given by a famous expression called "**the ideal gas law**" or simply the **gas law**. The gas law is written as follow:

$$\mathbf{P \times V = n \times R \times T}$$

R is the gas constant

$$\frac{P \times V}{n \times T} = R$$

- This means that:

$$R = \frac{P_1 \times V_1}{n_1 \times T_1} = \frac{P_2 \times V_2}{n_2 \times T_2} = \frac{P_3 \times V_3}{n_3 \times T_3} = \ldots$$

- If we have a gas with **n = 1 mole, T = 273 K, P = 101325 Pa = 1 atm** it will occupy a volume (V) that equals **22.4×10^{-3} m^3 = 22.4 L**. We calculate the value of R as follows:
  1) **Using the SI units:**

  $$R = \frac{101325 \text{ Pa} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \frac{\text{Pa m}^3}{\text{mol K}}$$

  Knowing here that:

  Pascal unit × Cubic meter unit = Joule unit

  The value of R is as follows:

  $$\boxed{\mathbf{R = 8.314 \frac{J}{mol\ K}}}$$

  2) **Using the non-SI units:**

  $$R = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.0821 \frac{\text{atm L}}{\text{mol K}}$$

  $$\boxed{\mathbf{R = 0.0821 \frac{atm\ L}{mol\ K}}}$$

- The main conclusion here is that **the numerical value of the gas constant, R, depends on the units of the gas pressure and volume**

5.3.2 Boyle's law

Boyle's law is the gas law at constant <u>quantity and temperature</u>: Boyle studied the relation between the gas pressure and volume when its quantity and temperature are kept constant ($n_1 = n_2$ and $T_1 = T_2$):

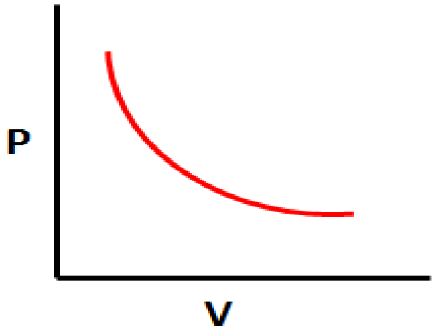
$$\frac{P_1 \times V_1}{n_1 \times T_1} = \frac{P_2 \times V_2}{n_2 \times T_2}$$

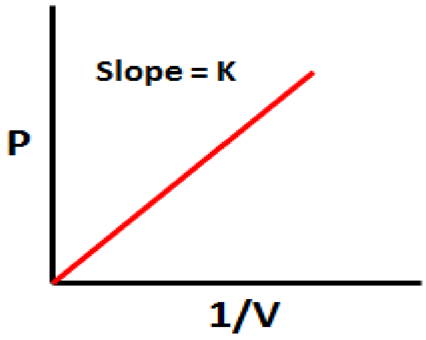
$$P_1 \times V_1 = P_2 \times V_2$$

$$P \times V = \text{constant}$$

$$P \propto \frac{1}{V}$$

The figures below show the relationship between the gas P and V at constant n and T.





5.3.3 Charles's and Gay-Lussac's law

Charles's and Gay-Lussac's law is the gas law at constant <u>quantity and pressure</u>: ($n_1 = n_2$ and $T_1 = T_2$):

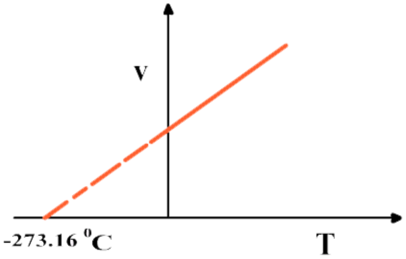
$$\frac{P_1 \times V_1}{n_1 \times T_1} = \frac{P_2 \times V_2}{n_2 \times T_2}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{T} = \text{constant}$$

$$V \propto T$$

The figure below shows this relation and that the minimum temperature that can be reached is – 273.16 °C which equals 0 K



5.3.4 Avogadro's law

Avogadro's law is the gas law at constant temperature and pressure: ($T_1 = T_2$ and $P_1 = P_2$)

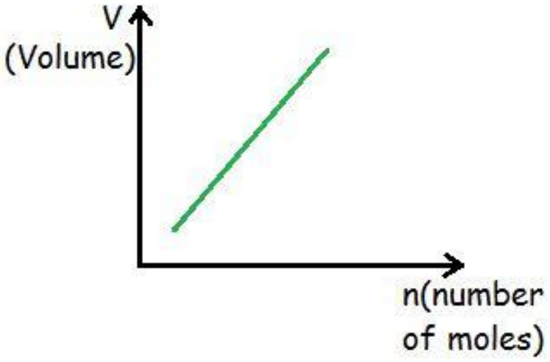
$$\frac{P_1 \times V_1}{n_1 \times T_1} = \frac{P_2 \times V_2}{n_2 \times T_2}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{V}{n} = \text{constant}$$

$$V \propto n$$

The figure below shows, the relation between the gas n and V at constant T and P:



5.3.5 The combined gas law

The cmbined gas law is the gas law at constant amount: ($n_1 = n_2$)

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

$$\frac{P \times V}{T} = \text{constant}$$

If 1 mole of a gas is at STP its volume is called the **molar volume** at STP which equals 22.41 L:

$$V = \frac{n \times R \times T}{P} = \frac{1.0\ \text{mol} \times 0.0821 \frac{\text{L atm}}{\text{K mol}} \times 273\ \text{K}}{1.0\ \text{atm}} = 22.41\ \text{L}$$

5.3.6 Other gas laws

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \text{(at constant n and V)}$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2} \qquad \text{(at constant T and V)}$$

$n_1 \times T_1 = n_2 \times T_2$ (at constant P and V)

$\frac{P_1 \times V_1}{n_1} = \frac{P_2 \times V_2}{n_2}$ (at constant T)

$\frac{P_1}{n_1 \times T_1} = \frac{P_2}{n_2 \times T_2}$ (at constant V)

$\frac{V_1}{n_1 \times T_1} = \frac{V_2}{T_2}$ (at constant P)

EXAMPLE 5.1

Calculate the pressure (in atm) exerted by 1.82 moles of sulfur hexafluoride gas (SF_6) in a steel vessel of volume 5.43 L at 69.5 °C.

Solution

$$P = \frac{n \times R \times T}{V} = \frac{1.82 \text{ mol} \times 0.0821 \frac{\text{L atm}}{\text{K mol}} \times (69.5\ °\text{C} + 273)\text{ K}}{5.43 \text{ L}} = 9.42 \text{ atm}$$

Practice Exercise 5.1

Calculate the volume, in L, occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76 °C.

EXAMPLE 5.2

Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Solution

$$n = \frac{m}{M} = \frac{7.4 \text{ g}}{17.03 \frac{\text{g}}{\text{mol}}} = 0.435 \text{ mol}$$

$$V = \frac{n \times R \times T}{P} = \frac{0.435 \text{ mol} \times 0.0821 \frac{\text{L atm}}{\text{K mol}} \times 273 \text{ K}}{1 \text{ atm}} = 9.75 \text{ L}$$

Practice Exercise 5.2

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

EXAMPLE 5.3

An inflated helium balloon with a volume of 0.55 L at sea level (1.0 atm) is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

Solution

$P_1 \times V_1 = P_2 \times V_2$

$1 \text{ atm} \times 0.55 \text{ L} = 0.4 \text{ atm} \times V_2$

$V_2 = 1.4 \text{ L}$

Practice Exercise 5.3

A sample of $Cl_2(g)$ occupies 946 mL at a pressure of 726 mmHg. Calculate the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL.

EXAMPLE 5.4

A certain lightbulb containing argon gs (Ar) at 1.20 atm and 18 °C is heated to 85 °C at constant volume. Calculate its final pressure.

Solution

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{1.2 \text{ atm}}{(18\ °\text{C} + 273\ °\text{C}) \times \frac{1 \text{ K}}{1\ °\text{C}}} = \frac{P_2}{(85\ °\text{C} + 273\ °\text{C}) \times \frac{1 \text{ K}}{1\ °\text{C}}}$$

$P_2 = 1.48 \text{ atm}$

Practice Exercise 5.4

A sample of $O_2(g)$ initially at 0.97 atm is heated from 21 °C to 268 °C at constant volume. What is its final pressure?

EXAMPLE 5.5

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8 °C and 6.4 atm, to the water's surface, where the temperature is 25 °C and the pressure is 1.0 atm. Calculate the final volume of the bubble if its initial volume was 2.1 mL.

Solution

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

$$\frac{6.4\ \text{atm} \times 2.1\ \text{mL}}{(8\ °\text{C} + 273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}} = \frac{1\ \text{atm} \times V_2}{(25\ °\text{C} + 273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}}$$

$$V_2 = \frac{6.4\ \text{atm} \times 2.1\ \text{mL} \times 298\ \text{K}}{281\ \text{K} \times 1\ \text{atm}}$$

$V_2 = 14.3$ mL

Practice Exercise 5.5

A gas initially at 4.0 L, 1.2 atm, and 66 °C undergoes a change so that its final volume and temperature are 1.7 L and 42 °C. What is its final pressure? Assume the number of moles remains unchanged.

5.4 The relation between the gas density and molar mass

- From the gas law, $P \times V = n \times R \times T$, and from the equation "$m = n \times M$" we can relate the gas density to its molar mass:

$$P \times V = \frac{m}{M} \times R \times T \qquad \text{and} \qquad P \times M = \frac{m}{V} \times R \times T$$

$$P \times M = d \times R \times T$$

- Unlike molecules in liquids and solids, gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very small and are expressed in grams per liter ($\frac{g}{L}$) rather than in grams per milliliter ($\frac{g}{mL}$)

EXAMPLE 5.6

Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55 °C.

Solution

$P \times M = d \times R \times T$

0.99 atm × 44.1 g/mol = d × 0.0821 atm L/mol K × (55 °C + 273) K

d = 1.62 g/L

Practice Exercise 5.6

What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62 °C?

EXAMPLE 5.7

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36 °C and 2.88 atm. Calculate the molar mass of the compound.

Solution

To calculate gas molar mass, we need the density, temperature and pressure.

$P \times M = d \times R \times T$

2.88 atm × M = 7.71 g/L × 0.0821 atm L/mol K × (36 °C + 273) K

M = 67.9 g/mol

Practice Exercise 5.7

The density of a gaseous compound is 3.38 g/L at 40 °C and 1.97 atm. What is its molar mass?

EXAMPLE 5.8

Chemical analysis of a gaseous compound showed that it contained 33.0% by mass silicon (Si) and 67.0% by mass fluorine (F). At 35 °C, 0.210 L the compound pressure is 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Solution

First, we find the empirical formula and its molar mass

$$\text{Si} \quad : \quad \text{F}$$

$$\frac{33\ \text{g}}{28.09\,\frac{\text{g}}{\text{mol}}} : \frac{67\ \text{g}}{19\,\frac{\text{g}}{\text{mol}}}$$

$$1.17\ \text{mol} : 3.53\ \text{mol}$$

$$\frac{1.17\ \text{mol}}{1.17\ \text{mol}} : \frac{3.53\ \text{mol}}{1.17\ \text{mol}}$$

$$1 \quad : \quad 3$$

Therefore, the empirical formula is **SiF_3**

Molar mass of the empirical formula SiF_3 = 85.09 g/mol

Second, we find the actual molar mass (molar mass of molecular formula)

$$P \times M = \frac{m}{V} \times R \times T$$

$$1.7\ \text{atm} \times M = \frac{2.38\ \text{g}}{0.21\ \text{L}} \times 0.0821\ \text{atm L/mol K} \times (35\ °\text{C} + 273)\ \text{K}$$

M = 169 g/mol

Third, we divide actual molar mass by the empirical molar mass,

$$\frac{m}{V} = \frac{169\,\frac{\text{g}}{\text{mol}}}{85.09\,\frac{\text{g}}{\text{mol}}} = 1.99 = 2$$

The molecular formula = 2 × The empirical formula = 2 × SiF_3 = Si_2F_6

Practice Exercise 5.8

A gaseous compound is, by mass, 78.14% boron (B) and 21.86% hydrogen (H) and its pressure at 27 °C, 74.3 mL is 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

5.5 Gas stoichiometry

- We show in chapter 3 , (section 3.3), that the method used for calculations on chemical equations is the "**mole method**"
- Here, we show that, if the reactants and/or products are gases, calculations on chemical equations can use the "**volume method**"
- Justification for using the volume method for reactions involving gases comes from the relationship between "**V**" of the gas and its "**n**" at constant T and P, "$\mathbf{V} = \frac{\mathbf{R \times T}}{\mathbf{P}}$," which that **V** is becomes constant and is proportional to its number of moles "**n**":

$$\mathbf{V} = \mathbf{n} \times \frac{R \times T}{P} \text{ AND } \mathbf{V} \propto \mathbf{n}$$

Example 5.9

Calculate the volume of O_2 (in liters) required for the complete combustion of 7.64 L of acetylene (C_2H_2) measured at the same T and P.

$2C_2H_2\,(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$

Solution

$2C_2H_2\,(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$

2 L	5 L
7.64 L	V_{oxyg}

$V_{oxyg} = \frac{5\ L \times 7.64\ L}{2\ L} = 19.1\ L$

Practice exercise 5.9

The equation of the reaction between nitric oxide and oxygen is:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

If 9.0 L of NO reacted with excess O_2 at certain T and P, calculate the volume and the number of moles of the NO_2 produced?

Example 5.10

Assuming no change in T and P, calculate the V_{O_2} (in liters) required for the complete combustion of 14.9 L of butane (C_4H_{10}):

$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

Solution

$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

2 L 13 L

14.9 L V_{oxyg}

$V_{oxyg} = \frac{13\ L \times 14.9\ L}{2\ L} = 96.85\ L$

Practice exercise 5.10

Sodium azide (NaN_3), used in some automobile air bags, decomposes as follows:

$2NaN_3(g) \rightarrow 2Na(s) + 3N_2(g)$

The nitrogen gas produced quickly inflates the bag. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3.

Example 5.11

The equation for the metabolic breakdown of glucose ($C_6H_{12}O_6$) is:

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

Calculate the volume of CO_2 produced at 37 °C and 1.00 atm when 5.60 g of glucose is used up in the reaction.

Solution

$n_{CO_2} = 6 \times n_{C_6H_{12}O_6} = 6 \times \frac{5.6\ g}{180.156\ \frac{g}{mol}} = 0.1865\ mol$

$V = \frac{n \times R \times T}{P} = \frac{0.1865\ mol \times 0.0821\ \frac{atm\ L}{mol\ K} \times (37 + 273) K}{1\ atm} = 4.75\ L$

Practice exercise 5.11

The combustion equation of methane is:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

If 15.0 moles of methane are reacted, calculate the volume of CO_2 produced at 23.0 °C and 0.985 atm?

5.6 Dalton’s law of partial pressures

MOLE FRACTION

Before we discuss this law, we need to know what the term “*mole fraction*” means.

- When more than one substance (for example, two substances “A” and “B”) are present together, and we know the number of moles of each “n_A and n_B”, this means that we know the total number of moles “n_{Total}”.
- Now, if we divide n_A or n_B by n_{Total} the quotient will have no unit

- This quotient is the mole fraction of each “X_A and X_B”.
- Therefore, we write:

$$\mathbf{X_A} = \frac{\mathbf{n_A}}{\mathbf{n_{Total}}} \text{ and } \mathbf{X_B} = \frac{\mathbf{n_B}}{\mathbf{n_{Total}}}$$

1) In mixtures of gases, the total gas pressure is related to their **partial pressures**
2) **partial pressure** is the pressures of individual gas components in the mixture
3) In 1801, Dalton formulated a law, now known as **Dalton’s law of partial pressures,** which states that the total pressure of a mixture of gases is the sum of the pressures that each gas would exert if it were present alone
4) Consider a case in which two gases, A and B, are in a container of volume V at temperature T
5) According to the ideal gas equation, the pressure exerted by gas are:

$$P_A = n_A \times \frac{RT}{V} \textbf{ AND } P_B = n_B \times \frac{RT}{V}$$

6) Because the two gases are mixed in the same container at the same temperature, the total pressure P_{Total} is:

$$P_{Total} = P_A + P_B$$

$$P_{Total} = (n_A \times \frac{RT}{V}) + (n_B \times \frac{RT}{V}) = (n_A + n_B) \times \frac{RT}{V} = n_{Total} \times \frac{RT}{V}$$

$$\frac{P_A}{P_{Total}} = \frac{n_A}{n_{Total}} = X_A \textbf{ AND } \frac{P_B}{P_{Total}} = \frac{n_B}{n_{Total}} = X_B$$

$$P_A = X_A \times P_{Total} \textbf{ AND } P_B = X_B \times P_{Tota}$$

EXAMPLE 5.12

A mixture of 4.46 mol of Ne gas, 0.74 mol of Ar gas, and 2.15 mol of Xe gas has a total pressure of 2.00 atm. What are the partial pressures of each?

Solution

number of total moles of all substances = 4.46 mol + 0.74 mol + 2.15 mol = 7.35 mol

$$\text{Mole fraction of a substance} = \frac{\text{number of moles of the substance}}{\text{number of total moles of all substances}}$$

$$X_{Ne} = \frac{4.46 \text{ mol}}{7.35 \text{ mol}} = 0.607,\ X_{Ar} = \frac{0.74 \text{ mol}}{7.35 \text{ mol}} = 0.1,\ X_{Xe} = \frac{2.15 \text{ mol}}{7.35 \text{ mol}} = 0.29$$

Pressure of any gas in the mixture = its mole fraction × total pressure

$P_{Ne} = 0.607 \times 2$ atm = 1.21 atm

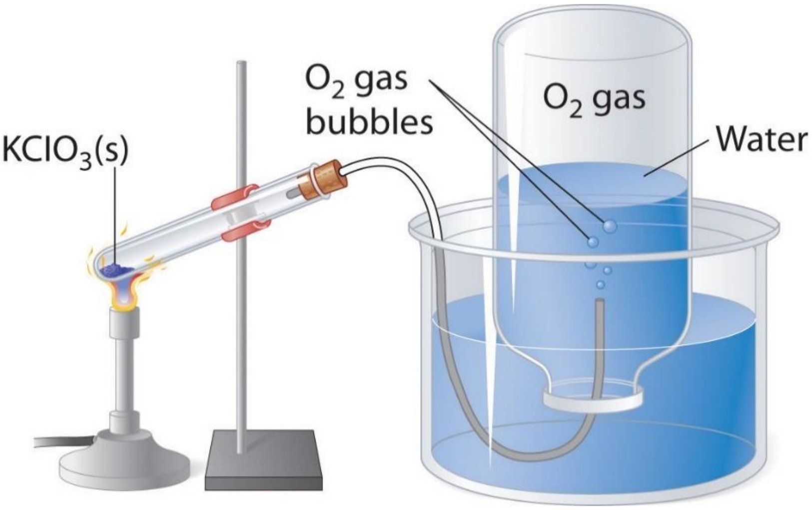
$P_{Ar} = 0.1 \times 2$ atm = 0.2 atm

$P_{Xe} = 0.29 \times 2$ atm = 0.586 atm

Practice Exercise 5.12

A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the mixture is 1.37 atm, what are the partial pressures of each gas?

7) **Collecting a gas over water**
   - ✓ Frequently, chemists need to collect gases over water
   - ✓ They use a devise like the one below in which oxygen gas is produced from the decomposition of potassium chlorate ($KClO_3$):



- ✓ Potassium chlorate ($KClO_3$) is thermally decomposed:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

- ✓ The produced oxygen escapes through the hose immersed in water and a flask is rises above water surface as shown in the figure
- ✓ Of course, oxygen will not be alone in the space above water surface; water vapor too is occupying this space, (**They become roommates**) and the pressure above water is the pressure of both:

$$P_{\text{Total}} = P_{\text{oxygen}} + P_{\text{water vapor}}$$

EXAMPLE 5.13

$O_2(g)$ generated from potassium chlorate is collected as shown in the previous figure. The volume above surface became128 mL at 297 K and pressure of 762 mmHg is. Calculate the mass of $KClO_3$ consumed. The pressure of the water vapor at 297 K is 22.4 mmHg.

Solution

$P_{\text{oxygen}} = P_{\text{Total}} - P_{\text{water vapor}} = 762 \text{ mmHg} - 22.4 \text{ mmHg} = 740 \text{ mmHg}$

$$n = \frac{P \times V}{R \times T} = \frac{740 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times 128 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}{0.0821 \frac{\text{atm L}}{\text{mol K}} \times 297 \text{ K}} = 5.11 \times 10^{-5} \text{ mol}$$

		$2KClO_3$	$\rightarrow$	$2KCl$	$+$	$3O_2$
Equation moles	⇒	2				3
Question moles	⇒	X				5.11×10^{-5}

$X = \text{number of mol } KClO_3 = 2 \text{ mol} \times \frac{5.11 \times 10^{-5} \text{ mol}}{3 \text{ mol}} = 3.41 \times 10^{-5} \text{ mol}$

$\text{Mass of } KClO_3 = n \times M = 3.41 \times 10^{-5} \text{ mol} \times 123.427 \frac{\text{g}}{\text{mol}} = 4.21 \times 10^{-5} \text{ g}$

Practice Exercise 5.13

Hydrogen gas generated when calcium metal reacts with water is collected as shown in the previous figure. The volume of gas collected at 30°C and 988 mmHg is 641 mL. What is the mass of the $H_2(g)$ obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

5.7 The kinetic molecular theory of gases

- The gas laws help us to predict their behavior, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world
- It became so clear to physicists and chemists that this macroscopic and sensible behavior of gases is a reflect of the behavior of its atomic and molecular microscopic behavior

- In the nineteenth century, several physicists, notably Ludwig Boltzmann and James Clerk Maxwell, found that the physical properties of gases can be explained in terms of the motion of individual molecules
- This molecular movement is a kinetic energy (KE)
- Maxwell, Boltzmann, and others concluded several generalizations about gas behavior that have since been known as the **kinetic molecular theory of gases,** or simply the **kinetic theory of gases**

5.7.1 The five hypotheses of the theory

1) A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be "points"; that is, they possess mass, but their **volume is negligible**
2) Attractive or repulsive forces on one another gas molecule is **negligible**
3) Gas molecules are in constant motion in random directions
4) Gas molecules collide with one another and with the walls of the container they occupy. These collisions are perfectly elastic, this means that energy is transferred from one molecule to another but the total energy of all the molecules remains the same
5) The average kinetic energy of the molecules is proportional to its absolute temperature. This means that any two equal-quantity gases at the same temperature will have the same average kinetic energy

- The average kinetic energy of a molecule with a mass equals "m" is given by the following equation:

$$\overline{KE} = \frac{1}{2}\,m\,\overline{U^2}$$

- U is the speed of the molecule but $\overline{U^2}$ is the mean square speed; the bar over U^2 means that it is the average of the square of the speeds of all the molecules and is usually given the symbol U_{rms} which means the **r**oot-**m**ean-square **s**peed of all molecules. The value of U_{rms} can be obtained using the following equation:

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

Example 5.14

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in $\frac{m}{s}$ at 25°C.

Solution

$$U_{rms,He} = \sqrt{\frac{3RT}{M_{He}}} = \sqrt{\frac{3 \times 8.314\,\frac{J}{mol\,K} \times 298\ K}{4.003\frac{g}{mol} \times \frac{1\ kg}{1000\ g}}} = 1362.6\ \frac{m}{s}$$

$$U_{rms,N_2} = \sqrt{\frac{3RT}{M_{N_2}}} = \sqrt{\frac{3 \times 8.314\,\frac{J}{mol\,K} \times 298\ K}{28.014\,\frac{g}{mol} \times \frac{1\ kg}{1000\ g}}} = 515.1\ \frac{m}{s}$$

Practice exercise 5.14

It is found that the value of U_{rms} of an unknown gas is 1.5 times the value of U_{rms} of CO_2(g) at the same temperature. Calculate the molar mass of the unknown gas.

- The kinetic molecular theory of gases presents another equation to be used for the calculation of the kinetic energy of a specified quantity of the gas.
- If the quantity of the gas is one mole, its kinetic energy is called "**the molar kinetic energy**", with "**KE**" as its symbol:

$$KE = 1.5 \times R \times T$$

- This equation enables us to calculate the average kinetic energy of only one molecules "**ke**" by dividing the equation by Avogadro's number:

$$\text{ke} = \frac{\text{KE}}{\text{N}_\text{A}} = 1.5 \times \frac{\text{R}}{\text{N}_\text{A}} \times T = 1.5 \times \text{k} \times \text{T}$$

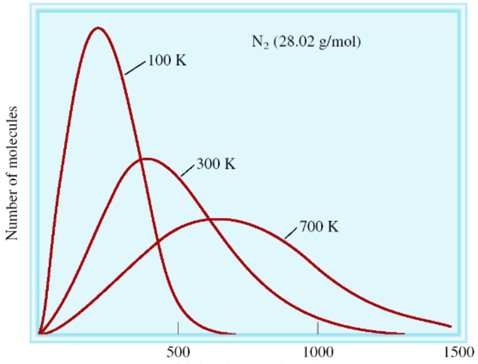
- "k" is Boltzmann constant, Both equations of kinetic energy of one mole or of only one molecule of the gas, indicate that the **kinetic energy of a specified quantity** is the same for all gases if their amounts and temperatures are the same

5.7.2 Application of kinetic theory to the gas laws

- **Boyle's Law**
  - ✓ The P exerted by a gas results from impacts of its molecules collisions on the walls
  - ✓ The number of collisions with the walls per second is proportional to the number of molecules per unit volume
  - ✓ Decreasing the volume of the gas increases the number of molecules per unit volume and hence increases number of collisions
  - ✓ The pressure of a gas is inversely proportional to the volume it occupies.
- **Charles's Law**
  - ✓ The average kinetic energy of molecules is proportional to its absolute temperature
  - ✓ Increasing the temperature increases the speed, the kinetic energy, the number of collisions, and the pressure. so, to keep "P" constant the volume of the gas increases
- **Avogadro's Law**
  - ✓ In Avogadro's law, the pressure of a gas is directly proportional to the amount of the gas at constant temperature and pressure
  - ✓ If we increase the amount of the gas the pressure will remain constant only if the volume increase
- **Dalton's Law of Partial Pressures**
  - ✓ The pressure of one type of molecule is unaffected by the presence of another type
  - ✓ The total pressure is given by the sum of individual gas pressures.

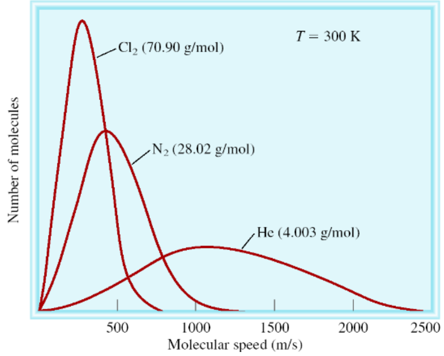
5.7.3 Distribution of molecular speeds

- The average kinetic energy of molecules and the mean square speed remain constant at constant temperature. How many molecules are moving at particular speed? The following figure show *Maxwell speed distribution curves* for nitrogen gas at three different temperatures:



- The peak of any curve represents ***the most probable speed***, that is, the speed of the largest number of molecules at the specified temperature
- The most probable speed increases as temperature increases

- The curve begins to flatten out with increasing temperature, indicating as temperature increases a larger numbers of molecules are moving at greater speed
- The following figure shows the speed distributions of three gases at the same temperature.

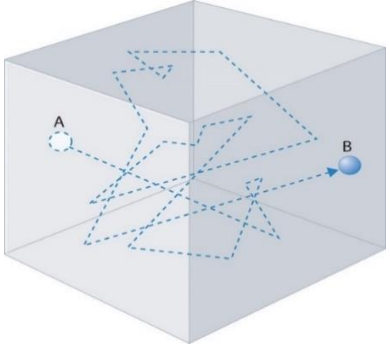


- The difference in the curves is due to molecular masses

5.7.4 Gas diffusion and effusion

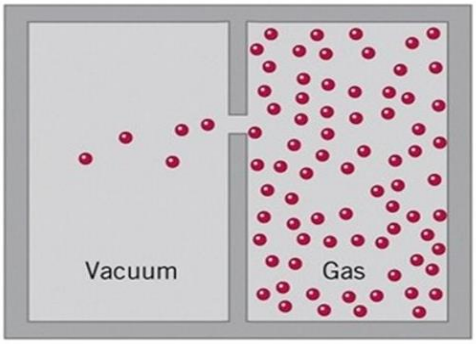
First: Gas diffusion

- Diffusion is the gradual mixing of molecules of a gas with molecules of another due to their kinetic properties
- Even though molecular speeds are very great, the diffusion process takes a long time to complete because diffusion of gases always happens gradually
- For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell. The following figure shows that the reason is that a molecule experiences numerous collisions while moving from one point “A” to another “B”:



Second: Gas effusion

- Gas effusion is the escape which a gas under pressure from one container to another by passing through a small opening:



- Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion
- A He-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores is faster for the lhelium atoms than for the air molecules

Third: Graham's law

In 1832 the Scottish chemist Thomas Graham found that under the same conditions of temperature and pressure, rates of diffusion for gases (r) are inversely proportional to the square roots of their molar masses or densities:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

Example 5.15

A gas made up only of C and H atoms effuses through a porous wall in 1.50 min. Under the same conditions of T and P, it takes an equal volume of Br_2 vapor 4.73 min to effuse through the same wall. Calculate the molar mass of the unknown gas and suggest its molecular formula.

Solution

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$r_1 = \frac{V_1}{\text{Time}_1}$ and $r_2 = \frac{V_2}{\text{Time}_2}$ but $V_1 = V_2$ therefore, $\frac{\frac{V_1}{\text{Time}_1}}{\frac{V_1}{\text{Time}_2}} = \frac{\text{Time}_2}{\text{Time}_1} = \sqrt{\frac{M_2}{M_1}}$

$$\frac{4.73 \text{ min}}{1.50 \text{ min}} = \sqrt{\frac{159.808}{M_1}}$$

$M_1 = 16.07 \frac{g}{mol}$

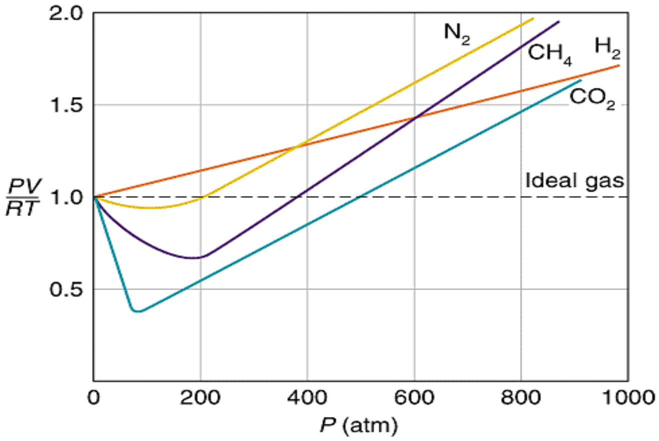
This gas is methane, because its molar mass is 16.04 $\frac{g}{mol}$, and is formed from C and H

Practice exercise 6.15

A gas evolved from the fermentation of glucose effuses through a porous wall in 15.0 min. Under the same T and P, it takes 12.0 min for an equal volume of N_2 to effuse through the same wall. Calculate the molar mass of the gas and suggest what the gas might be.

5.8 Deviation from ideal behavior

- The gas laws and the kinetic molecular theory assume that:
  1) Attractive and repulsive forces between molecules of the gas are **negligible**
  2) The volume occupied by the molecules of the gas is **negligible**
- These two assumptions are in fact not true and cannot be accepted except under strict conditions
- When a gas obeys these conditions, it is honored as the "**perfect gas**" and rewarded with an equation bearing its name "**the perfect gas equation**": P × V = n × R × T
- The question now is: "Under what conditions will not real gases exhibit perfect behavior?"
- The following curves shows "$\frac{PV}{RT}$" plotted against "P" for one mole of each of the four real gases and the ideal gas all at the same temperature
- For the one mole of the ideal gas $\frac{PV}{RT} = 1$ at all pressures, but for one mole of any of the the other gases, $\frac{PV}{RT} = 1$ only at zero or extremely small pressures
- Significant deviations occur as pressure increases. The following is the interpretation to these observations:



- The following is the interpretation to these observations:
  Attractive forces operate among molecules at short distances. therefore, at low pressures the molecules in a gas are far apart and they experience no attractive or repulsive forces. At high pressures, the molecules are much closer to one another and intermolecular forces are enough to affect the motion of the molecules, and the gas will not behave perfectly. This nonerections is much significant at lower temperature because cooling a gas decreases the molecules' average kinetic energy, which makes molecules movement less freely.
- In 1873, the physicist van der Waals studied real gases accurately, he modified the ideal gas equation to consider intermolecular forces and tiny molecular volumes. The following is his logic:
  1) The intermolecular attractions exerted between a molecule and its neighbors softens its collisions against the wall which makes the gas pressure lowers than if it is ideal. To correct thi deviation, resulting from lowering the pressure, a certain correction value must be added to the real pressure. This value is "$\mathbf{a \times \frac{n^2}{V^2}}$". This means that the gas pressure must be corrected to be ($\mathbf{P + a \times \frac{n^2}{V^2}}$). "a" is constant for each gas, and it is related to the strength of the forces between its molecules
  2) Volume in the perfect gas equation, "V", represents the volume of the container as a free space that is occupied by nothing. However, each molecule occupys a finite, although small, volume, so the effective volume of the gas is less than the volume of the container by a certain value equals to "$\mathbf{n \times b}$". This means that the gas volume must be corrected to be ($\mathbf{V - n \times b}$). "b" is constant for each gas, and it is related to the volume occupied by the molecules of the gas.
  3) From the previous two corrections the law of the real gas is written as:
  $$(P + a \times \frac{n^2}{V^2}) \times (V - n \times b) = n \times R \times T$$
  This equation is called the "**van der Waals or real gas equation**"
  4) If the gas is a perfect gas the values of "a" and "b" are zero.

Example 5.16
Given that 3.50 moles of NH_3 occupy 5.20 L at 47° C, calculate the pressure of the gas (in atm) using (A) the ideal gas equation and (B) the van der Waals equation. (a = 4.17 atm L^2/mol^2, b = 0.0371 L/mol)

Solution

A) $P = \frac{n \times R \times T}{V} = \frac{3.5\ \text{mol} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 320\ \text{K}}{5.2\ \text{L}} = 17.7\ \text{atm}$

B) $P = \left(\frac{n \times R \times T}{V - n \times b}\right) - (a \times \frac{n^2}{V^2})$

$$P = \left(\frac{3.5\ \text{mol} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 320\ \text{K}}{5.2\ \text{L} - 3.5\ \text{mol} \times 0.0371\ \frac{\text{L}}{\text{mol}}}\right) - (4.17\ \frac{\text{atm L}^2}{\text{mol}^2} \times \frac{(3.5\ \text{mol})^2}{(5.2\ \text{L})^2}) = 16.2\ \text{atm}$$

Practice exercise 5.16

At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

6. THERMOCHEMISTRY

6.1 The nature of energy and types of energy

Energy is usually defined as the capacity to do work which is “force × distance.

All forms of energy are capable of doing work but not all of them are equally relevant to chemistry. ***Thermochemistry*** is *the study of heat transfer in chemical reactions*.

6.1.1 Types of energy

- Chemists define *work* as *directed energy change resulting from a process.* Kinetic energy, the energy produced by a moving object, is one form of energy that is of interest to chemists. Others include radiant energy, thermal energy, chemical energy, and potential energy
  - ✓ *Radiant energy*, or *solar energy, comes from the sun* and is Earth’s primary energy source. Solar energy heats the atmosphere and Earth’s surface, stimulates the growth of vegetation through photosynthesis, and influences global climate patterns
  - ✓ *Thermal energy* is *the energy associated with the random motion of atoms and molecules.* In general, thermal energy can be calculated from temperature measurements. The more vigorous the motion of the atoms and molecules in a sample of matter, the hotter the sample is and the greater its thermal energy. It is important to understand the distinction between ***thermal energy*** and heat. ***Heat*** is *the transfer of thermal energy between two bodies that are at different temperatures.* Also, we need to distinguish carefully between thermal energy, heat and temperature
  - ✓ *Chemical energy* is *stored within the structural units of chemical substances;* its quantity is determined by the type and arrangement of constituent atoms. When substances participate in chemical reactions, chemical energy is released, stored, or converted to other forms of energy
  - ✓ *Potential energy* is *energy available by virtue of an object’s position.* For instance, because of its altitude, a rock at the top of a cliff has more potential energy and will make a bigger splash if it falls into the water below than a similar rock located partway down the cliff. Chemical energy can be considered a form of potential energy because it is associated with the relative positions and arrangements of atoms within a given substance.
- All forms of energy can be converted from one form to another
  - ✓ We feel warm when we stand in sunlight because radiant energy is converted to thermal energy
  - ✓ When we exercise, chemical energy in our bodies is used to produce kinetic energy
  - ✓ When a ball falls downhill, its potential energy is converted to kinetic energy

6.1.2 The law of conservation of energy

Energy can be neither destroyed nor created. When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is the ***law of conservation of energy: the total quantity of energy in the universe is constant***

6.2 Energy change in chemical reactions

- Combustion reactions involving fuels in daily life aim for heat released more than for their products, which are water and carbon dioxide
- Almost all chemical reactions absorb release energy in the form of heat. We speak of the “heat flow” from a hot object to a cold one. Although the term “heat” by itself

implies the transfer of energy, we customarily talk of “heat absorbed” or “heat released” when describing the energy changes that occur during a process

6.3 The system the surroundings and the universe

- The ***system***, which is *the specific part of the universe that is of interest to us.* For chemists, systems usually include substances involved in chemical and physical changes. For example, in an acid-base neutralization experiment, **the system** may be a beaker containing 50 mL of HCl to which 50 mL of NaOH is added
- The ***surroundings*** which are *the rest of the universe outside the system*
- There are three types of systems:
  - ✓ An ***open system*** *can exchange matter and energy, usually in the form of heat with its surroundings.* For example, an open system may consist of a quantity of water in an open container
  - ✓ A ***closed system*** *can exchange energy with its surroundings but not matter*. For example, a closed system may consist of a quantity of water in a closed container that does not allow any substance to leave or enter but may absorb or release heat
  - ✓ An ***isolated system*** *cannot exchange both matter and energy with its surroundings*. For example, an isolated system may consist of a quantity of water in an isolated container that does not allow any substance or energy to leave or enter
- Chemical reactions either release or absorb energy. examples are:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + \text{energy}$$

$$\text{energy} + 2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

6.4 Introduction to thermodynamics

6.4.1 Work and heat

First work

- Work is many kinds (**mechanical work, electrical wor**k, **surface work**) and others
- Work is a way of transferring energy from a place to another. It is not a property of the system. We can say: the temperature of a substance is 25° C, but we cannot say: the work of the system is 250 J
- We will concentrate only on the work of expansion and compression of gases
- The work done by or on the gas is given by the following equation:

$$w = -P \times (V_{\text{final}} - V_{\text{initial}})$$

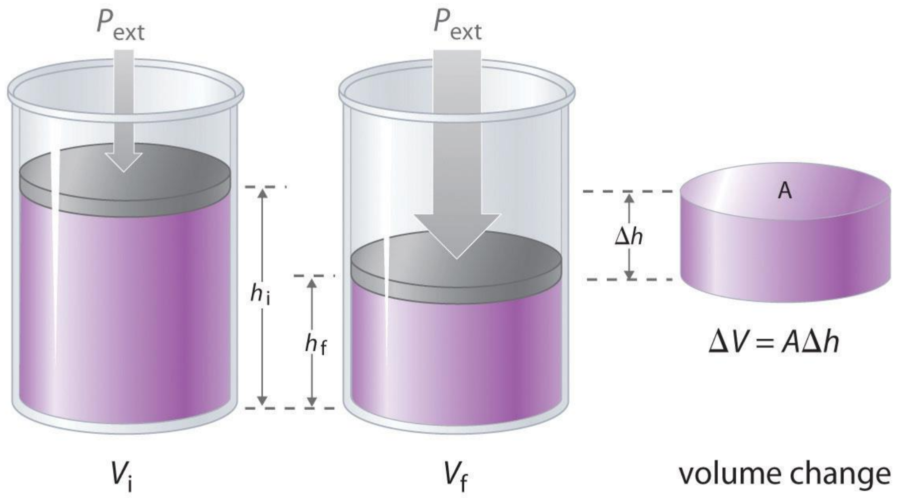
$$w = -P \times \Delta V$$

  - ✓ The negative sign is to make the sign of work negative in cases of expansion and positive in cases of compression
  - ✓ Units of the PV-work:

$$\text{units of } w = \text{Pascal} \times m^3 = kg\ m^{-1}\ s^{-2} \times m^3 = kg\ m^2\ s^{-2} = J$$

$$\text{units of } w = atm \times L = atm\ L$$

  - ✓ 1 atm L = 101.325 J
- The figure below shows a gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume. The gas expanded against a constant opposing external atmospheric pressure.
- The work done by the gas has a negative quantity indicating that its energy is decreased
- The work done on the gas has a negative quantity indicating that its energy is increased



EXAMPLE 6.1

A gas expands from 2.0 L to 6.0 L at constant T. Calculate “w” if the expansion is against:

A) a vacuum B) a constant pressure of 1.2 atm

Solution

A) w = – PΔV = – (0 × ΔV) = 0

B) $w = -P\Delta V = -\{1.2 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}}\} \times \{(6-2) \text{ L} \frac{\text{m}^3}{1000 \text{ L}}\} = -4.86 \times 10^{-2}$ J

Practice Exercise 6.1

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done by the gas if it expands against a constant pressure of 4.00 atm.

Second: Heat

- Heat is a way of transferring energy from a place to another. It is not a property of the system. We can say: the temperature of a substance is 25° C, but we cannot say: the heat of the system is 250 J
- For example, it takes 4184 J of energy to raise the temperature of 100 g of water from 20°C to 30°C. This energy can be gained in different ways such as:
  - ✓ Directly as heat energy from burner, without doing any work
  - ✓ By work as in stirring the water with a magnetic stir bar
  - ✓ By some combination of the procedures described in above
- Heat needed to increase the substance temperature defers from substance to another, for the same substance it depends on its mass, and and for the same mass of the same substance it depends on number of Celsius (or Kelvin) degrees is to be increased
  - ✓ **First: specific heat (s)**
    The specific heat of a substance is the quantity of heat required to raise the temperature of **one gram** of the substance by **one degree Celsius**. Its units are $\frac{\text{J}}{\text{g °C}}$.
    The specific heat of a substances are measured, calculated and listed in tables
  - ✓ **Second: heat capacity (C)**
    The heat capacity of a substance is the quantity of heat required to raise the temperature of **any given mass**, (m), of the substance by **one degree Celsius**. Its units are $\frac{\text{J}}{\text{°C}}$. The relationship between the heat capacity and the specific heat of is:

$$C = m \times s$$

- ✓ **Third: quantity of heat (q)**
  The **quantity of heat** is the amount of heat required to raise the temperature of **any given mass**, (m), of the substance by **any Celsius degrees**. Its unit is J. The equation relating the quantity of heat, heat capacity and the specific heat is:

$$q = C \times \Delta t = m \times s \times \Delta t$$

EXAMPLE 6.2

A sample of water has a mass equals to 466 g is heated from 8.50 °C to 74.60 °C. Calculate the amount of heat absorbed (in kilojoules) by the water. **(s_{H_2O} = 4.184 $\frac{J}{g\,°C}$)**

Solution

$q = m \times s \times \Delta t = 466\ g \times 4.184\ \frac{J}{g\,°C} \times (74.60\ °C – 8.50\ °C) = 129000\ J$

$q = 129000\ J \times \frac{1\ kJ}{1000\ J} = 129\ kJ$

Practice Exercise 6.2

An iron bar (s = 0.45 J/g °C) of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

6.4.2 The first law of thermodynamics

- The **first law of thermodynamics** is based on the law of conservation of energy: “energy can be converted from one form to another but cannot be created or destroyed”
- The change in internal energy, ΔE, is given by the following equation:

$$\Delta E = E_{final} – E_{initial}$$

  where $E_{initial}$ and E_{final} are the initial and the final internal energies of the system
- ΔE may be positive, negative or zero
- The internal energy of a system has two components:
  1) **The kinetic energy component** which consists of various types of molecular motion and the movement of electrons within molecules
  2) **The potential energy component** which is determined by the attractive interactions between electrons and nuclei, the repulsive interactions between electrons and by interaction between molecules
- Internal energy of a system cannot be determined but changes in internal energy can be
- The first law of thermodynamic is:

$$\Delta E = q + w$$

- The sign conventions for "q" and "w" are as follows:
  - ✓ q is positive for an endothermic process but negative for an exothermic process
  - ✓ w is positive for work done on the system by the surroundings but negative if done by the system on the surroundings
- Internal energy is a property of the system and therefore is a state function
- Heat and work are not properties of a system and therefore are not state functions

EXAMPLE 6.3

If the work done on a gas is 462 J and the heat released by the gas is 128 J, calculate the change in the gas internal energy.

Solution

$\Delta E = q + w = (–128\ J) + (+\ 462\ J) = +\ 334\ J$

Practice Exercise 6.3

A gas expands and does P-V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

6.5 Enthalpy of chemical reactions

- The heat absorbed or released by a system, at constant temperature, as result of a change in the state of the system is called **heat of reaction**:
  - ✓ If also the volume is constant, it is named "change in internal energy" (ΔE)
  - ✓ If also the pressure is constant, it is named "change enthalpy" (ΔH)
- Our concern is about changes in enthalpy rather than changes in internal energy
- For any reaction of the type:

$$\text{Reactants} \rightarrow \text{products}$$

- Enthalpy of reaction is:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- There is no way to measure t H_{products} and $H_{\text{reactants}}$ and we do not need to know its value because what we care about only is the increase or decrease in its value, (ΔH)
  - ✓ For an endothermic process, ΔH is positive ($\Delta H > 0$)
  - ✓ For an exothermic process ΔH is negative ($\Delta H < 0$)

6.6 Thermochemical equations

- At 0°C and a pressure of 1 atm, ice melts to form liquid water

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ}$$

That is, 6.01 kJ of heat must be absorbed to covert 1 mole of ice to 1 mole of liquid water at constant temperature and pressure

- Another example is the combustion of methane (CH_4) at constant T and P:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l). \qquad \Delta H = -2890.4 \text{ kJ}$$

That is 2980 kJ of heat must be released to as a result of combusting 1 mole of methane

- ΔH value does not refer to a reactant or a product. But all the following are true for the previous reaction:
  1) $\Delta H = -2890.4$ kJ/ mol CH_4
  2) $\Delta H = -2890.4$ kJ/ 2 mol O_2
  3) $\Delta H = -2890.4$ kJ/ mol CO_2
  4) $\Delta H = -2890.4$ kJ/ 2 mol H_2O
  5) $\Delta H = -2890.4$ kJ
- A ***thermochemical equation*** cannot be called so unless it satisfies the following:
  1) It ***must be*** balanced
  2) The states of all substances ***must be*** specified
  3) The value of ΔH ***must be*** written
- Thermochemical equations can be manipulated with as follows:
  1) Multiplying a thermochemical equation by a number or a fraction gives a correct thermochemical equation only if the value of ΔH is multiplied by the same number
  2) Reversing a thermochemical equation gives a correct thermochemical equation if the sign of ΔH is changed to its opposite
  3) Adding several thermochemical equations together gives a correct thermochemical equation if all values of ΔH are added together (**This is called Hess's law**).

EXAMPLE 6.4

Given the thermochemical equation

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H = -198.2 \text{ kJ}$$

calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

Solution

Given moles of SO_2 = $\frac{87.9\ \text{g}}{64.07\frac{\text{g}}{\text{mol}}}$ = 1.372 mol

	$2SO_2$	+	O_2	→	$2SO_3$	ΔH
Equation moles	2 mol					− 198.2 kJ
Givnen moles	1.372 mol					X

X = $\frac{-\ 198.2\ \text{kJ} \times 1.372\ \text{mol}\ SO_2}{2\ \text{mol}\ SO_2}$ = – 135.97 kJ

Practice Exercise 6.4

Calculate the heat released when 266 g of phosphorus (P_4) burns in air according to the equation

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ ΔH = – 3013 kJ/mol

6.7 Relationship between ΔH and ΔE

- We know that:

$$\boxed{\begin{array}{l}\Delta E = \Delta H - P \times \Delta V \\ \Delta E = \Delta H - R \times T \times \Delta n_g\end{array}}$$

It is very important not to forget that the subscript "g" is to emphasize that when calculating **Δn** only gases count:

$$\Delta n_g = n_{\text{gases produced}} - n_{\text{gases reacted}}$$

✓ Let's consider the reaction between sodium metal and water at 1 atm and 298 K is:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \quad \Delta H = -\ 367.5\ \text{kJ}$$

➢ When 2 moles of solid Na react with 2 moles of liquid water, 367.5 kJ of heat is released

➢ H_2 gas produced needs a space to occupy. Therefore, it pushes the air toward the atmosphere which means that some of heat produced is used to do work, against atmospheric pressure, P

➢ To calculate the change in internal energy, we apply the previous equation:

$$\Delta E = \Delta H + w = \Delta H - R \times T \times \Delta n_g$$

$$\Delta E = (-\ 367.5\ \text{kJ}) - (8.314 \times 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} \times 298\ \text{K} \times 1\ \text{mol}) = -\ 369.98\ \text{kJ}$$

EXAMPLE 6.5

Calculate ΔE for the following reaction at 1 atm and 25°C:

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ΔH = – 566.0 kJ

Solution

$\Delta E = \Delta H - R \times T \times \Delta n_g$

$\Delta n_g = (2\ \text{mol}) - (3\ \text{mol}) = -\ 1\ \text{mol}$

$\Delta E = (-\ 566.0\ \text{kJ}) - (8.314 \times 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} \times 298\ \text{K} \times -\ 1\ \text{mol}) = -\ 563.5\ \text{kJ}$

Practice Exercise 6.5

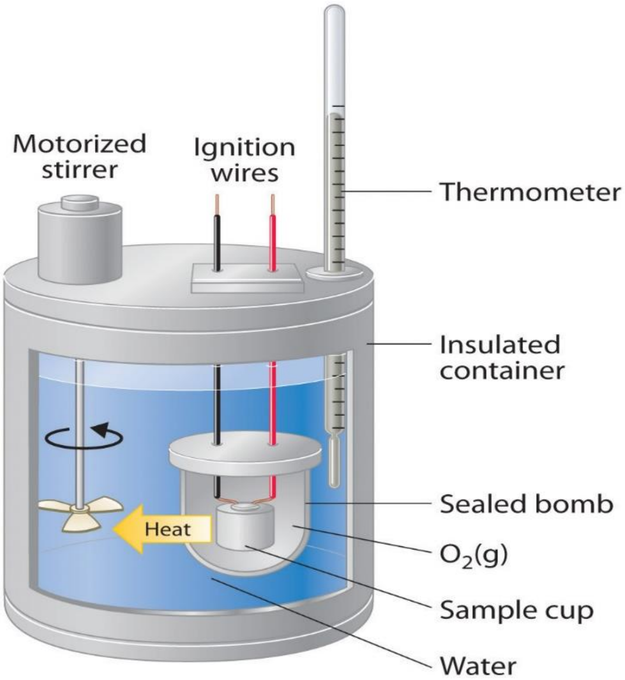
What is ΔE for the formation of 1 mole of CO at 1 atm and 258C?

$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ ΔH = –110.5 kJ

6.8 Calorimetry

calorimetry is *the measurement of heat changes* and a ***calorimeter*** is a closed container designed specifically for determining ΔH

- **Constant-volume calorimetry**
  - ✓ *Constant-volume bomb calorimeter* is an isolated steel container (a bomb) we put inside the substance that we need to determine its enthalpy of combustion, and is filled by oxygen gas



- ✓ The isolated bomb is immersed in a known amount of water, and the sample is ignited electrically
- ✓ The heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water
- ✓ Because the heat is released at constant volume:

$$q_v = \Delta E$$

- ✓ We can calculate ΔH using the equation "$\Delta H = \Delta E + R \times T \times \Delta n_g$"
- ✓ $q_v = -q_{calorimeter} = -C_{calorimeter} \times \Delta T$:
  $C_{calorimeter}$ is the heat capacity of the bomb and the water around and it is given
  ΔT is the rise in temperature which the thermometer reads

EXAMPLE 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$) was burned in a constant-volume bomb calorimeter. The temperature of the water rose from 20.28 °C to 25.95 °C. Calculate the molar heat of combustion of naphthalene.

(Heat capacity of the bomb plus water = 10.17 kJ/°C), (molar mass of naphthalene = 128.2 g/mol)

Solution

$$q_v = C_v \times \Delta T$$

$$q_v = -q_{calorimeter} = -10.17\ \frac{kJ}{°C} \times (25.95\ °C - 20.28\ °C) = -57.66\ \frac{kJ}{1.435\ g}$$

$$q_v = = -57.66\ \frac{kJ}{1.435\ g} \times 128.2\ \frac{g}{mol} = -5151\ \frac{kJ}{mol}$$

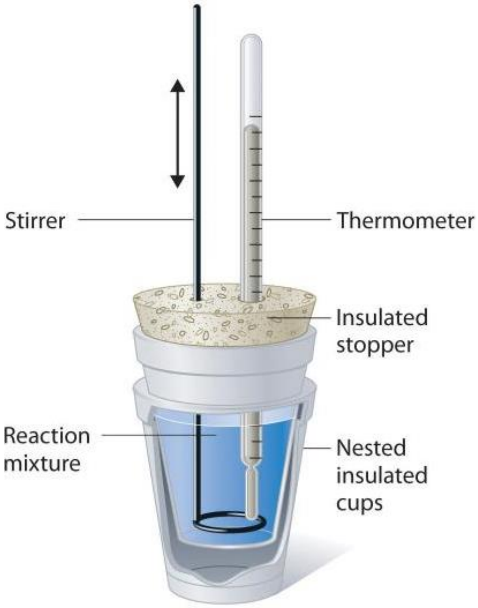
Practice Exercise 6.6

A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. The temperature of the water rose by 4.20 °C. Calculate the molar heat of combustion of methanol.

(Heat capacity of the bomb plus water = 10.4 kJ/°C), (molar mass of methane = 32 g/mol)

- **Constant-pressure calorimetry**
  - ✓ The constant-pressure calorimeter is used to determine the heat changes for noncombustion reactions

- ✓ A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups



- ✓ Because the pressure is constant, the heat change for the process is equal to the enthalpy change (ΔH)
- ✓ The calorimeter as an isolated system and we neglect the small heat capacity of the coffee cups in our calculations. Table 6.3 lists some reactions that have been studied with the constant-pressure calorimeter.

EXAMPLE 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

Solution

$q_{\text{water}} = C_{\text{water}} \times \Delta T = s_{\text{water}} \times m_{\text{water}} \times \Delta T_{\text{water}}$

$q_{\text{water}} = 4.184\ \frac{\text{J}}{\text{g °C}} \times 100\ \text{g} \times (23.17\ °\text{C} - 22.50\ °\text{C}) = 280.3\ \text{J}$

$q_{\text{lead}} = C_{\text{lead}} \times \Delta T = s_{\text{lead}} \times m_{\text{lead}} \times \Delta T_{\text{water}}$

$-280.3\ \text{J} = s_{\text{lead}} \times 26.47\ \text{g} \times (23.17\ °\text{C} - 89.98\ °\text{C}) = 280.3\ \text{J}$

$s_{\text{lead}} = 0.158\ \frac{\text{J}}{\text{g °C}}$

Practice Exercise 6.7

A stainless steel-ball with mass of 30.14 g at 117.82°C was placed in a constant-pressure calorimeter of negligible heat capacity containing = 120.0 mL of water at 18.44°C. If the specific heat of the ball is 0.474 $\frac{\text{J}}{\text{g °C}}$, calculate the final temperature of the water.

EXAMPLE6.8

A 100 mL of 0.5 M HCl was mixed with 100 mL of 0.500 M NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions was the same at 22.50°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis:

$$\text{NaOH}(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H2O}(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g °C, respectively).

Solution

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

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

$\mathrm{q_{reaction}} = -\mathrm{q_{solution}} = -\mathrm{s_{solution}} \times \mathrm{m_{solution}} \times \Delta\mathrm{T_{solution}}$

$\mathrm{q_{reaction}} = -4.184\,\frac{\mathrm{J}}{\mathrm{g\,°C}} \times (100\ \mathrm{g} + 100\ \mathrm{g}) \times (25.86\ °\mathrm{C} - 22.50\ °\mathrm{C}) = -2810\ \mathrm{J}$

Number of mles of HCl = Number of mles of NaOH = $\frac{0.5\ \mathrm{mol} \times 0.1\ \mathrm{L}}{1\ \mathrm{L}} = 0.05\ \mathrm{mol}$

Heat of neutralization = $\frac{-2810\ \mathrm{J}}{0.05\ \mathrm{mol}} = -56200\,\frac{\mathrm{J}}{\mathrm{mol}} = -56.200\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)\Delta\mathrm{H} = -56.200\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

Practice Exercise 6.8

A 400 mL of 0.6 M HNO_3 was mixed with 400 mL of 0.3 M $Ba(OH)_2$ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at 18.46°C. What is the final temperature of the solution? Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g °C, respectively)

6.9 Standard enthalpy of formation and reaction

- A **formation reaction** is the reaction in which **one** substance is produced as a result of the reaction of its **elements in their standard states**
- The quantity of heat released or absorbed at standard pressure (1 atm) because of the formation of one mole of a substance from the reaction between its elements in their standard states is called **standard molar enthalpy of formation (ΔH_f°)**
- This means that if the substance we have is an element in its standard state, it has no formation reaction. Therefore, its standard enthalpy of formation equals **zero**.

When any element is in its standard state its $\Delta H_f^\circ = 0$

- The following reaction equations are examples of formation reactions:
  - ✓ $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -296.84$ kJ
  - ✓ $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(g)$ $\Delta H = -601.6$ kJ

    (Note: both reactions can also be called a combustion reaction)
  - ✓ $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3CH_2OH(l)$ $\Delta H = -277.6$ kJ
  - ✓ $3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$ $\Delta H = -104.7$ kJ
  - ✓ $6C(\text{graphite}) + 6H_2(g) + 3O_2 \rightarrow C_6H_{12}O_6(s)$ $\Delta H = -1271$ kJ
- **Enthalpy of reaction by direct method:** The standard enthalpies of formation are one of the most important tools for determining the standard enthalpy of any physical or chemical change, ΔH_{rxn}°. This can be accomplished simply by the following equation:

$$\boxed{\Delta H_{rxn}^\circ = \Sigma\Delta H_{f,products}^\circ - \Sigma\Delta H_{f,reactants}^\circ}$$

This equation says that the standard enthalpy of any change equals the sum of the standard enthalpies of formation of products minus the sum of the standard enthalpies of formation of reactants

EXAMPLE 6.9

The thermite reaction involves aluminum and iron(III) oxide

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

This reaction is highly exothermic, and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with Fe_2O_3.

$\Delta H^\circ_{f,Al_2O_3(s)} = -\,1669.8\ \frac{kJ}{mol}$, $\Delta H^\circ_{f,Fe(l)} = 12.40\ \frac{kJ}{mol}$, $\Delta H^\circ_{f,Fe_2O_3(s)} = -\,822.2\ \frac{kJ}{mol}$

Solution

$\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{f,products} - \Sigma\Delta H^\circ_{f,reactants}$

$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(Al_2O_3) + 2\Delta H^\circ_f(Fe)] - [2\Delta H^\circ_f(Al) + \Delta H^\circ_f(Fe_2O_3)]$

$\Delta H^\circ_{rxn} = [(-\,1669.8\ kJ/mol) + (2\ mol \times 12.40\ kJ/mol)]$

$-\,[(2\ mol \times 0) + (-\,822.2\ kJ/mol)]$

$\Delta H^\circ_{rxn} = -\,822.8$ kJ/2 mol of Al reacted

Mass of Al reacted = n × M = 2 mol × 26.98 g/mol = 53.96 g

– 822.8 kJ per 53.96 g Al

X kJ per 1 g Al

$$X = \frac{-\,822.8\ kJ \times 1\ g}{53.96\ g} = -\,15.25\ kJ/g$$

Practice Exercise 6.9

Benzene (C_6H_6) burns in air to produce carbon dioxide gas and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. $\Delta H^\circ_{f,CO_2(g)} = -\,393.5\ \frac{kJ}{mol}$, $\Delta H^\circ_{f,H_2O(l)} = -\,285.8\ \frac{kJ}{mol}$, and $\Delta H^\circ_{f,C_6H_6(l)} = 49.04\ \frac{kJ}{mol}$

- The following table gives some.

Compound	ΔH°_f ($\frac{kJ}{mol}$)	Compound	ΔH°_f ($\frac{kJ}{mol}$)	Compound	ΔH°_f ($\frac{kJ}{mol}$)
AgBr(s)	– 99.5	$KClO_3$(s)	– 391.4	HBr(g)	– 36.2
AgCl(s)	– 127.0	KF(s)	– 562.6	HCl(g)	– 92.3
AgI(s)	– 62.4	$MgCl_2$(s)	– 641.8	HI(g)	+ 25.9
Ag_2O(s)	– 30.6	$MgCO_3$(s)	– 1113	HNO_3(l)	– 173.2
Ag_2S(s)	– 31.8	MgO(s)	– 601.8	H_2O(g)	– 241.8
Al_2O_3(s)	– 1669.8	$Mg(OH)_2$(s)	– 924.7	NH_4Cl(s)	– 315.4
$BaCl_2$(s)	– 860.1	$MgSO_4$(s)	– 1278.2	NH_4NO_3(s)	– 365.1
$BaCO_3$(s)	– 1218.8	MnO(s)	– 384.9	NO(g)	+ 90.4
BaO(s)	– 558.1	MnO_2(s)	– 519.7	NO_2(g)	+ 33.9
$BaSO_4$(s)	– 1465.2	NaCl(s)	– 411.0	NiO(s)	– 244.3
$CaCl_2$(s)	– 795.0	NaF(s)	– 569.0	$PbBr_2$(s)	– 277.0
$CaCO_3$	– 1207.0	NaOH(s)	– 426.7	$PbCl_2$(s)	– 359.2
CaO(s)	– 635.5	NH_3(g)	– 46.2	PbO(s)	– 217.9
$Ca(OH)_2$(s)	– 986.6	C_2H_2(g)	+ 226.7	PbO_2(s)	– 276.6
$CaSO_4$(s)	– 1432.7	C_2H_4(g)	+ 52.3	Pb_3O_4(s)	– 734.7
CCl_4(l)	– 139.5	C_2H_6(g)	– 84.7	PCl_3(g)	– 306.4
CH_4(g)	– 74.8	C_3H_8(g)	– 103.8	PCl_5(g)	– 398.9
CH_3OH(l)	– 238.6	n– C_4H_{10}(g)	– 124.7	SiO_2(s)	– 859.4
CO(g)	– 110.5	n– C_5H_{12}(l)	– 173.1	$SnCl_2$(s)	– 349.8
CO_2(g)	– 393.5	C_2H_5OH(l)	– 277.6	$SnCl_4$(l)	– 545.2
H_2O(l)	– 285.8	CoO(s)	– 239.3	SnO(s)	– 286.2
H_2O_2(l)	– 187.6	Cr_2O_3(s)	– 1128.4	SnO_2(s)	– 580.7
H_2S(g)	– 20.1	CuO(s)	– 155.2	SO_2(g)	– 296.1
H_2SO_4(l)	– 811.3	Cu_2O(s)	– 166.7	So_3(g)	– 395.2
HgO(s)	– 90.7	CuS(s)	– 48.5	ZnO(s)	– 348.0
HgS(s)	– 58.2	$CuSO_4$(s)	– 769.9	ZnS(s)	– 202.9
KBr(s)	– 392.2	Fe_2O_3(s)	– 822.2		
KCl(s)	– 435.9	Fe_3O_4(s)	– 1120.9		

- **Enthalpy of reaction by indirect method (Hess's law of heat summation)**
  - ✓ Hess's law says “*When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps*”
  - ✓ The general rule in applying Hess's law is to arrange a series of chemical equations (steps) in such a way that, when added together, all species will cancel except for

the reactants and products that appear in the overall reaction. This means that we want the reactants on the left and the products on the right of the arrow

- ✓ Sometimes, we need to multiply one or more of the given equations by appropriate coefficients, and need to reverse one or more of them
- ✓ From the following equations we can obtain the enthalpy of formation of $CO(g)$:

$$\begin{array}{ll} \text{C(graphite)} + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_{rxn} = -\,393.5 \text{ kJ} \\ CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_{rxn} = -\,283.0 \text{ kJ} \end{array}$$

The second equation should be reversed then added to the first:

$$\begin{array}{ll} \text{C(graphite)} + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_{rxn} = -\,393.5 \text{ kJ} \\ CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) & \Delta H^\circ_{rxn} = +\,283.0 \text{ kJ} \\ \hline \text{C(graphite)} + \frac{1}{2}O_2(g) \rightarrow CO(g) & \Delta H^\circ_{rxn} = -\,110.5 \text{ kJ} \end{array}$$

EXAMPLE 6.10

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

$$2\text{C(graphite)} + H_2(g) \rightarrow C_2H_2(g)$$

The equations for each step and the corresponding enthalpy changes are:

$$\begin{array}{ll} \text{A) C(graphite)} + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_{rxn} = -\,393.5 \text{ kJ/mol} \\ \text{b) } H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H^\circ_{rxn} = -\,285.8 \text{ kJ/mol} \\ \text{C) } 2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) & \Delta H^\circ_{rxn} = -\,2598.8 \text{ kJ/mol} \end{array}$$

Solution

Careful look at the desired equation indicates that the first equation must be multiplied by 2; and the third equation must be revered and multiplied by $\frac{1}{2}$. So we will have

$$\begin{array}{ll} 2\text{C(graphite)} + 2O_2(g) \rightarrow 2CO_2(g) & \Delta H^\circ_{rxn} = -\,787.0 \text{ kJ} \\ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H^\circ_{rxn} = -\,285.8 \text{ kJ} \\ 2CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + 2.5O_2(g) & \Delta H^\circ_{rxn} = +\,1299.4 \text{ kJ} \\ \hline 2\text{C(graphite)} + H_2(g) \rightarrow C_2H_2(g) & \Delta H^\circ_{rxn} = +\,226.6 \text{ kJ} \end{array}$$

Practice Exercise 6.10

From the following reactions, calculate $\Delta H^\circ_{f,CH_4(g)}$:

$$\begin{array}{ll} CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) & \Delta H^\circ_{rxn} = -\,890.34 \text{ kJ} \\ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H^\circ_{rxn} = -\,285.84 \text{ kJ} \\ \text{C(graphite)} + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_{rxn} = -\,393.5 \text{ kJ} \end{array}$$

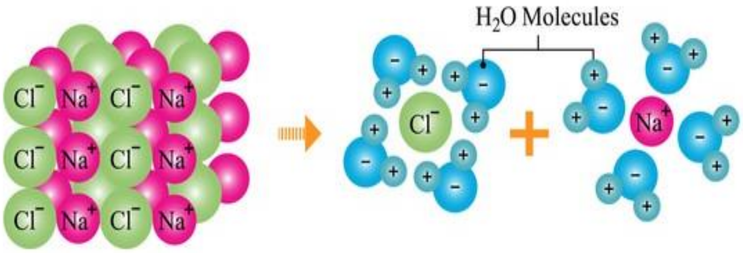
6.10 Heat or enthalpy of solution and dilution

- The **heat (or enthalpy) of solution, ΔH_{soln},** is the heat released (ΔH_{soln} is negative and the process is exothermic) or absorbed (ΔH_{soln} is positive and the process is exothermic)
  - ✓ In solid NaCl, the Na^+ and Cl^- ions are held together by strong electrostatic forces. When a small crystal of NaCl dissolves in water, the three-dimensional network of ions breaks into $Na^+(g)$ and $Cl^-(g)$ ions

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \quad \Delta H = +\,788 \text{ kJ}$$

  - ✓ These ions are stabilized in solution by hydration

$$Na^+(g) + Cl^-(g) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq) \qquad \Delta H = -\,784 \text{ kJ}$$



- ✓ The heat of solution is defined by the following process:

$$\mathrm{NaCl(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} \qquad \Delta H = +\,4\ \mathrm{kJ}$$

- ✓ when 1 mole of NaCl dissolves in water, 4 kJ of heat will be absorbed from the surroundings. We would observe this effect by noting that the beaker containing the solution becomes slightly colder

- The **heat of dilution,** or **enthalpy of dilution, ΔH_{sdil},** is the heat released (ΔH_{soln} is negative and the process is exothermic) or absorbed (ΔH_{soln} is positive and the process is exothermic) as a result of adding more solvent to the prepared solution
  - ✓ Dilution lowers the concentration of the solute
  - ✓ The ***heat of dilution*** is *the heat change associated with the dilution process*
  - ✓ If a certain solution process is endothermic and the solution is subsequently diluted, *more* heat will be absorbed by the same solution from the surroundings
  - ✓ The converse holds true for an exothermic solution process
  - ✓ Diluting concentrated sulfuric acid (H_2SO_4) by adding water to it is very dangerous, because the heat generated could cause the acid solution to boil and splatter. Therefore, we must *never* dilute the concentrated acid by adding water to it but add the concentrated acid slowly to the water (while constantly stirring)

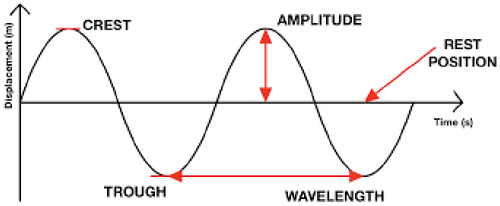
7. QUANTUM THEORY AND THE ELECTRONIC STRUCTURE OF ATOMS

7.1 From classical physics to quantum theory

- The new era in physics started in 1900 with Max Planck's "quantum theory"
- While analyzing the data on radiation emitted by solids heated to various temperatures, Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or ***quanta***
- Physicists had always assumed that energy is continuous and that any amount of energy could be released in a radiation process
- Quantum theory turned physics upside down and altered our concept of nature

First: Properties of waves

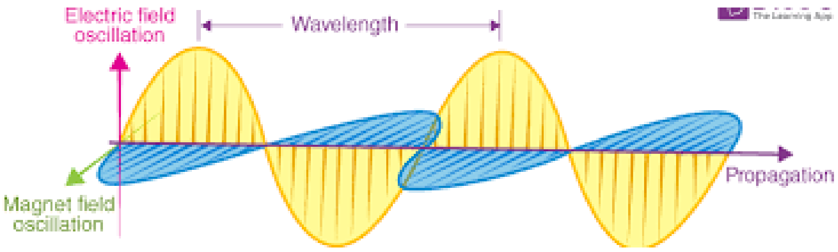
- A **wave** is a vibrating disturbance by which energy is transmitted
- The fundamental properties of a wave are illustrated by the following figure:



- The regular variation of the peaks and troughs enable us to sense the propagation of the waves
- Waves are characterized by their length (λ), amplitude (A), frequency (*v*), wave number (*k*) and speed (*u*)
  - ✓ ***The wave length* (λ)** is *the distance between identical points on successive waves*
  - ✓ ***The wave amplitude* (A)** is *the vertical distance from the midline of a wave to the peak or trough*
  - ✓ ***The wave frequency* (*v*)** is *the number of waves that pass through a certain point in one second*
  - ✓ ***The wave number (k)*** is the number waves in unit length
  - ✓ ***The wave speed (u)*** *is the product of its wavelength and its frequency*

7.2 The electromagnetic radiation

- In 1873 Maxwell proposed that visible light consists of ***electromagnetic waves***
- An ***electromagnetic wave*** *has 2 components: "electric field" and "magnetic field"*
- These two components have the same wavelength, frequency, and speed, but they travel in mutually perpendicular planes



- This provides a mathematical description of the general behavior of light
- This model accurately describes how energy in the form of radiation can be propagated through space as vibrating electric and magnetic fields
- ***Electromagnetic radiation*** is *the emission and transmission of energy in the form of electromagnetic waves*
- In vacuum, electromagnetic waves speed "**c**" is 3.00×10^8 m/s. It differs in other media, but not enough to distort our calculations significantly
- The relation between "***u*** *" or "c*", "**λ**" and "***v***" is:

$$\boldsymbol{u = v \times \lambda} \textbf{ or } \boldsymbol{c = v \times \lambda}$$

- The wavelength of electromagnetic waves is usually given in nanometers (nm)

EXAMPLE 7.1

Calculate the frequency of the green radiation of the traffic signal if its wave length is 522 nm.

Solution

$$\boldsymbol{v} = \frac{\boldsymbol{u}}{\boldsymbol{\lambda}} = \frac{3.00 \times 10^8 \frac{\mathrm{m}}{\mathrm{s}}}{522\ \mathrm{nm} \times \frac{1 \times 10^{-9}\ \mathrm{m}}{1\ \mathrm{nm}}} = 5.75 \times 10^{14}\ \frac{1}{\mathrm{s}} = 5.75 \times 10^{14}\ \mathrm{Hz}$$

Practice Exercise 7.1

Calculate the wavelength (in m) of an electromagnetic wave if its frequency is $3.64 \times 10^7\ Hz$.

- In **a metal**, electrons are held by strong forces that requires high-energy light to remove
- If h $\times\ \nu$ of the beam shot is equal to the energy that binds the electrons in the metal, then the light will have just enough energy "E" to release the electrons:

$$\mathrm{E} = \mathrm{h} \times \nu$$

- If we use a higher frequency light, then not only will the electrons be knocked loose, but they will also acquire a kinetic energy "KE". This is summarized by the equation:

$$\mathrm{E} = \mathrm{h} \times \nu = \mathrm{KE} - \mathrm{W}$$

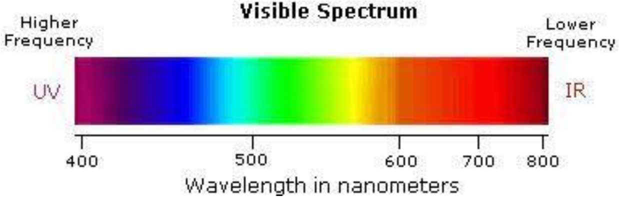
  "W" is the work function which is a measure of how strong the electrons are held in the metal
- The last equation shows that the more energetic the photon the greater the kinetic energy of the ejected electron
- The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal's surface than the weaker beam of light
- Einstein's theory of light posed a dilemma for scientists
  - ✓ First: it explains the photoelectric effect satisfactorily
  - ✓ Second: the particle theory of light is not consistent with its wave behavior
  - ✓ The only way to resolve the dilemma is to accept the idea that light possesses *both* ***particlelike*** and ***wavelike*** properties. This means that light behaves either as a wave or as a stream of particles
  - ✓ This concept, called particle-wave duality, was totally alien to the way physicists had thought about matter and radiation

7.3 Bohr's Theory of the Hydrogen Atom

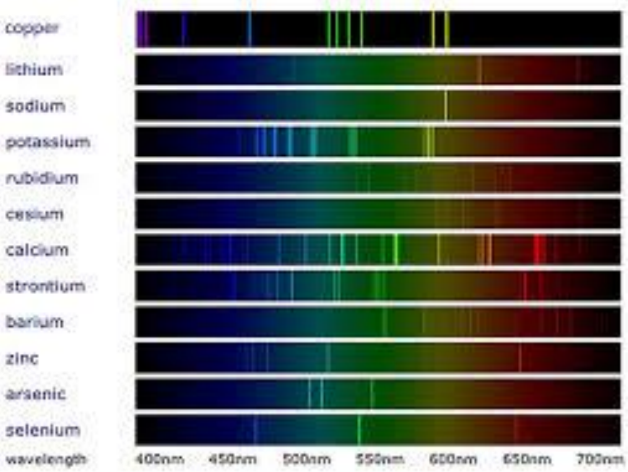
- The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy or with some other form of energy (such as a high-voltage electrical discharge)
- A "red-hot" or "white-hot" iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum

that is sensed by eye. The warmth of the same iron bar represents another portion of its emission spectrum (the infrared region)

- A feature common to the emission spectra of the sun and of a heated solid is that both are continuous, all wavelengths of visible light are there in the spectra



- The emission spectra of atoms in the gas phase do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum
- These ***line spectra*** are *the light emission only at specific wavelengths*
- Every element has a unique emission spectrum. The following figure shows the color emitted by hydrogen atoms in a discharge tube



- The lines in atomic spectra can be used in chemical analysis to identify unknown atoms
- When the lines of the emission spectrum of a known element matches those of an unknown sample, the identity of the unknown sample is established
- Although the utility of this procedure was recognized some time ago, the origin of these lines was unknown until early in the twentieth century

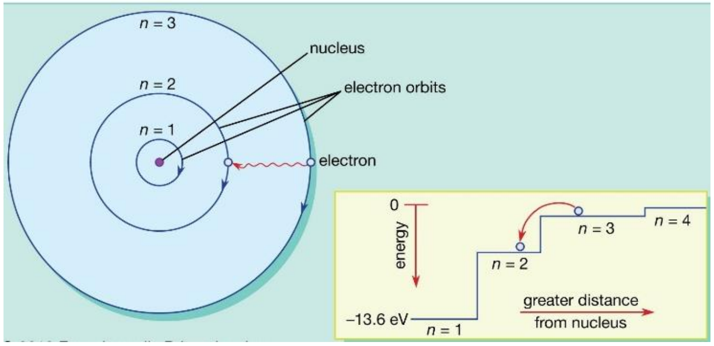
7.4 Emission spectrum of the hydrogen atom

- In 1913, a theoretical explanation of the emission spectrum of the hydrogen atom was presented by the Danish physicist Niels Bohr
- Bohr’s treatment is very complex and is no longer considered to be completely correct. We will concentrate only on his important assumptions and final result
- When Bohr first tackled this problem, physicists already knew that the atom contains electrons and protons, but they thought that electrons whirled around the nucleus in circular orbits at high velocities
- In the hydrogen atom, it was believed that the electrostatic attraction between the positive “solar” proton and the negative “planetary” electron pulls the electron inward and that this force is balanced exactly by the centrifuge force

- According to classical physics, an electron moving in an orbit of a H atom would experience an acceleration toward the nucleus and radiating electromagnetic waves
- Such an electron would quickly spiral into the nucleus and annihilate itself with the proton, but this does not happen, Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies (the energies of the electron are quantized). An electron in any of them will not spiral into the nucleus and will not radiate energy
- Bohr attributed the emission of radiation by an energized H atom to the electron dropping from a higher-energy orbit to a lower one and emitting a quantum of energy
- He showed that the energies that an electron in H atom can occupy are given by

$$E_a = -R_H \times \left(\frac{1}{n^2}\right)$$

  R_H, the Rydberg constant, has for the hydrogen atom the value 2.18×10^{-18} J and "n" is an integer called the principal quantum number; it has the values 1, 2, 3, ...
- The negative sign in the previous equation is an arbitrary convention, signifying that the energy of the electron in the atom is *lower* than the energy of a *free electron*, which is infinitely far from the nucleus; so is assigned arbitrarily a value of zero
- Mathematically, this corresponds to setting "n" equal to infinity. So, $E_\infty = 0$
- As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value, but also more negative
- The most negative value is reached when n = 1, which corresponds to the most stable energy state which is called the ***ground state,*** or the ***ground level*** referring to *the lowest energy state of a system* (which is an atom in our discussion)
- The stability of the electron diminishes for n = 2, 3, 4 ⋯ . Each of these levels is called an ***excited state,*** or ***excited level,*** which is *higher in energy than the ground* state
- A hydrogen electron for which n is greater than 1 is said to be in an excited state
- The radius of each circular orbit in Bohr's model depends on n^2 . Thus, as n increases from 1 to 2 to 3, the orbit radius increases very rapidly
- The higher the excited state, the farther away the electron is from the nucleus (and the less tightly it is held by the nucleus)
- Bohr's theory enables us to explain the line spectrum of the hydrogen atom
- Radiant energy absorbed by the atom causes the electron to move from a lower-energy state (smaller n value) to a higher-energy state (larger n value). Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy state to a lower-energy state
- The **quantized** movement of the electron from one energy state to another is analogous to the movement of a tennis ball either up or down a set of stairs



- The ball can be on any of the steps but never between them

- The journey from a lower step to a higher one is an energy-requiring process, whereas movement from a higher step to a lower step is the opposite
- The quantity of energy involved in either type of change is determined by the distance between the beginning and ending steps
- Similarly, the amount of energy needed to move an electron in the Bohr atom depends on the difference in energy levels between the initial and final states
- To apply that previous equation to the emission process in a hydrogen atom, we suppose that the electron is initially in an excited state characterized by the principal quantum number n_{initial}
- During emission, the electron drops to a lower energy state characterized by the principal quantum number n_{final} (either a less excited state or the ground state)
- The difference between the energies of the initial and final states is

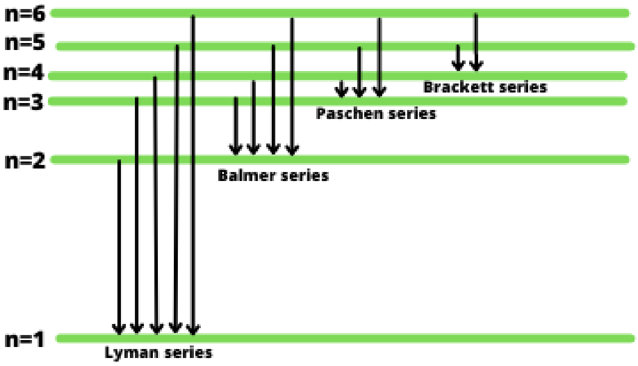
$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$\Delta E = h \times \nu = R_H \times \left(\frac{1}{n_{\text{initial}}^2} - \frac{1}{n_{\text{final}}^2}\right)$$

  - ✓ When a photon is emitted, $n_{\text{initial}} > E_{\text{final}}$ the term in parentheses is negative and ΔE is negative (energy is lost to from the atom)
  - ✓ When photon is absorbed, $n_{\text{final}} > n_{\text{initial}}$, the term in parentheses is positive and ΔE is positive (energy is gained by the atom)
- Each spectral line in the spectrum corresponds to a certain transition in a H atom
- When we study a large number of H atoms, we observe all possible transitions and hence the corresponding spectral lines
- The brightness of a line depends on number of photons having same wavelength
- The emission spectrum of H includes a wide range of wavelengths from the infrared to the ultraviolet.
- The following table lists the series of transitions in the hydrogen spectrum; they are named after their discoverers

series	n_{initial}	n_{final}	Spectral region
Layman	1	2,3...	UV
Balmer	2	3,4...	Visible
Paschen	3	4,5...	IR
Bracket	4	5,6...	IR
Pfund	5	6,7...	IR

The following figure shows the energy levels in the hydrogen atom and the various emission series



- ✓ The Balmer series was particularly easy to study because some of its lines fall in the visible range

EXAMPLE 7.2

Calculate the wavelength of a photon (in nanometers) emitted as a result of transition from the $n_{initial}$ = 5 state to the n_{final} = 2 state in the hydrogen atom.

Solution

$$\Delta E = R_H \times \left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2}\right) = 2.18 \times 10^{-18}\,J \times \left(\frac{1}{25} - \frac{1}{4}\right) = -4.58 \times 10^{-19}\,J$$

$$\lambda = \frac{c}{\nu} = \frac{ch}{\Delta E} = \frac{3 \times 10^{8}\,\frac{m}{s} \times 6.63 \times 10^{-34}\,J\,s}{4.58 \times 10^{-19}\,J} = 4.34 \times 10^{-7}\,m$$

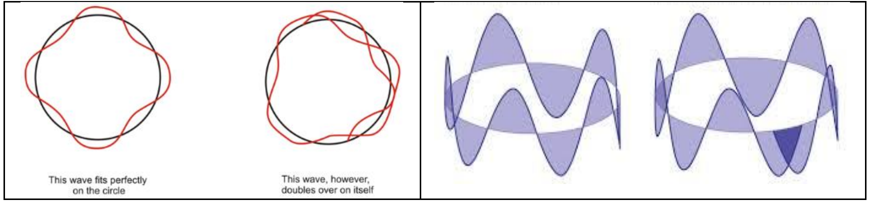
$$\lambda = 4.34 \times 10^{-7}\,m \times \frac{1 \times 10^{9}\,nm}{1\,m} = 434\,nm$$

Practice Exercise 7.2

Calculate the wavelength (in nanometers) of a photon emitted during a transition from $n_{initial}$ = 6 state to the n_{final} = 4 state in the hydrogen atom

7.5 The dual nature of the electron

- Why is the electron in a Bohr atom restricted to orbit the at certain fixed distances?
- De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles (such as electrons) can behave like waves
- According to de Broglie, an electron bound to the nucleus behaves like a *standing wave*
- The greater the frequency the shorter the wavelength of the standing wave
- If an electron behaves like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly. Otherwise the wave would partially cancel itself on each successive orbit and the amplitude of the wave would be reduced to zero, and the wave would not exist. The two following figure show this



- The relation between the circumference of an allowed orbit (2πr) and the wavelength (λ) of the electron is given by

$$2\pi r = n\lambda$$

where r is the radius of the orbit, and n = 1, 2, 3, ...

- Because n is an integer, it follows that r can have only certain values as *n* increases from 1 to 2 to 3 and so on
- Because the energy of the electron depends on the size of the orbit (the value of r), its value must be **<u>quantized</u>**
- De Broglie's reasoning led to the conclusion that waves can behave like particles and particles can behave wave like waves. De Broglie deduced that the particle and wave properties are related by the expression

$$\lambda = \frac{h}{mu} \text{ or } \left(\lambda = \frac{h}{mc}\right)$$

λ, m, and u are the wavelengths associated with a moving particle, its mass (**<u>Note that the left side of the equation involves the wave property "wavelength", whereas the right side involves the particle property "mass"</u>**)

EXAMPLE 7.3

Calculate the wavelength of the "particle" in the following two cases ($\mathbf{h = 6.63 \times 10^{-34}\ J\ s}$):

a) The fastest serve of a tennis ball is about 68 $\frac{m}{s}$. if its mass is 6×10^{-2} kg, calculate the wavelength associated with this serve

b) The speed of an electron is 68 $\frac{\mathrm{m}}{\mathrm{s}}$. if its mass is 9.1049×10^{-31} kg, calculate the wavelength associated with this electron

Solution

a) $\lambda = \frac{\mathrm{h}}{\mathrm{mu}} = \frac{6.63 \times 10^{-34}\ \mathrm{J\ s}}{6 \times 10^{-3}\ \mathrm{kg} \times 68\, \frac{\mathrm{m}}{\mathrm{s}}} = \frac{6.63 \times 10^{-34}\, \frac{\mathrm{kg\ m^2}}{\mathrm{s^2}}\, \mathrm{s}}{6 \times 10^{-2}\ \mathrm{kg} \times 68\, \frac{\mathrm{m}}{\mathrm{s}}} = 1.6 \times 10^{-34}\ \mathrm{m}$

b) $\lambda = \frac{\mathrm{h}}{\mathrm{mu}} = \frac{6.63 \times 10^{-34}\ \mathrm{J\ s}}{9.1049 \times 10^{-31}\ \mathrm{kg} \times 68\, \frac{\mathrm{m}}{\mathrm{s}}} = \frac{6.63 \times 10^{-34}\, \frac{\mathrm{kg\ m^2}}{\mathrm{s^2}}\, \mathrm{s}}{9.1049 \times 10^{-31}\ \mathrm{kg} \times 68\, \frac{\mathrm{m}}{\mathrm{s}}} = 1.1 \times 10^{-5}\ \mathrm{m}$

Practice Exercise 7.3

Calculate the wavelength (in nanometers) of a H atom (mass $= 1.674 \times 10^{-27}$ kg) moving at speed $= 7.00 \times 10^{2}\ \frac{\mathrm{cm}}{\mathrm{s}}$. ($\mathbf{h = 6.63 \times 10^{-34}\ J\ s}$)

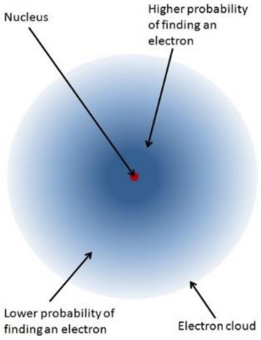
7.6 Quantum mechanics

- Although Bohr's theory was a success it was followed by a series of failure
  - ✓ It did not account for the spectra of atoms containing more than one electron
  - ✓ It did not explain the extra lines in the H spectrum under a magnetic field
  - ✓ It did not explain how can the "position" of a wave be specified when extended in space?
- To describe the problem of trying to locate a subatomic particle that behaves like a wave Heisenberg formulated what is now known as the ***Heisenberg uncertainty principle*** which states that "*it is impossible to know simultaneously both the momentum p* (defined as mass times velocity) *and the position of a particle with certainty*
- Heisenberg uncertainty principle is stated mathematically as:

$$\Delta x \times \Delta p \geq \frac{\mathrm{h}}{4\pi}$$

  - ✓ Δx and Δp are the uncertainties in measuring the position and momentum of the particle, respectively
  - ✓ The ≥ signs have the following meaning: "If the measured uncertainties of position and momentum are large, their product **can be** greater than $\frac{\mathrm{h}}{4\pi}$
  - ✓ The significance of the previous equation is that even in the most favorable conditions for measuring position and momentum, the product of the uncertainties can never be less than $\frac{\mathrm{h}}{4\pi}$. Thus, making measurement of the momentum of a particle *more* precise (Δp is a *small* quantity) means that the position must become *less* precise (Δp will become *larger*)
  - ✓ If the position of the particle is known *more* precisely, its momentum measurement must become less precise
  - ✓ Applying the Heisenberg uncertainty principle to the H atom, shows that its electron does not orbit the nucleus in a well-defined path, as Bohr thought
  - ✓ If it orbits in a well-defined path (violation of the uncertainty principle), we could determine precisely both the position of the electron (from its location on an orbit) and its momentum (from its kinetic energy) at the same time

  - Bohr made a significant contribution to understand atoms, and his suggestion that the energy of an electron in an atom is quantized is unchallenged. But he did not provide a complete description of electronic behavior in atoms
- **Schrödinger formulated an equation called “*Schrödinger equation*”**
  - It describes the behavior and energies of submicroscopic particles
  - It incorporates both particle behavior (***mass***, “m”), and wave behavior (***wave function*** “ψ”), which depends on the location in space of the electron in an atom
  - ψ itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to ψ^2
  - Relating ψ^2 to probability stemmed from the fact that “the intensity of light is proportional to the square of the amplitude of the wave, ψ^2”
  - The most likely place to find a photon is where the intensity is greatest, that is, where the value of ψ^2 is greatest. A similar argument associates ψ^2 with the likelihood of finding an electron in regions surrounding the nucleus
- **The Quantum mechanical description of the hydrogen atom**
  - The Schrödinger equation specifies the possible energy states the electron can occupy in a H atom and identifies the corresponding ψ
  - These energy states and wave functions are characterized by a set of quantum numbers, with which we can construct a model of the H atom
  - Quantum mechanics tells us that we cannot pinpoint an electron in an atom, but it defines the region where it might be at a given time
  - A new called concept “***electron density*** *” gives the probability that an electron will be found in a particular region of an atom*
  - “ψ^2”, defines the distribution of electron density in space around the nucleus
  - Regions of high electron density represent a high probability of locating the electron, whereas the opposite holds for regions of low electron density
  - An ***atomic orbital*** *is the wave function of an electron in an atom*



  - When we say that an electron is in a certain orbital, we mean that its density distribution (the probability of its location in space) is described by the square of the wave function associated with that orbital
  - An atomic orbital, therefore, has a characteristic energy, as well as a characteristic distribution of electron density
  - The Schrödinger equation works nicely for the simple H atom, but it it cannot be solved exactly for any atom with more than one electron!
  - Chemists and physicists have learned to get around this kind of difficulty by approximation. For example, although the behavior of electrons in ***many-***

electron atoms is not the same as in the hydrogen atom, we assume that the difference is probably not too great

- ✓ The energies and wave functions of the hydrogen atom is a good approximations of the behavior of electrons in more complex atoms
- ✓ This approach gives descriptions of electronic behavior in many-electron atoms

7.7 Quantum Numbers

- Solving Schrödinger equation gives three *quantum numbers that* are required to *describe the distribution of electrons in H atom and other atoms*
- They are called: the *principal quantum number,* the *angular momentum quantum number,* and the *magnetic quantum number*
- These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them
- A fourth quantum number (*the spin quantum number)* describes the behavior of a specific electron and completes the description of electrons in atoms

7.7.1 The principal quantum number (n)

- The principal quantum number "n" can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number in the equation "$E_a = -R_H \times (\frac{1}{n^2})$"
- In a H atom, the value of "n" determines the energy of an orbital. (this is not the case for a many-electron atom)
- The larger "n" is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital
- The principal quantum number is called "**the shell**"

7.7.2 The angular momentum quantum number (*l*)

- The angular momentum quantum number "*l*" tells us the "shape" of the orbitals. The values of "*l*" depend on the value of the principal quantum number, "n"
- A given value of "n", has possible integral values from "$l = 0$" to "$l = n - 1$". The values of "*l*" designated by the letters as follows:

l	0	1	2	3
Given letter	s	p	d	f

- These letters are the first letters of the words describing observed spectral lines which are: **s**harp, **p**rincipal, **d**iffused and **f**undamental
- The angular momentum quantum number is called "**the subshell**"

7.7.3 The magnetic quantum number (m_l)

- The magnetic quantum number (m_l) describes the orientation of the orbital in space. the value of m_l depends on the value of *l*
- For a certain value of *l*, there are ($2l + 1$) integral values of m_l as follows:

$$-l, (-l + 1), \cdot\cdot\cdot 0 \cdot\cdot\cdot (+l - 1), +l$$

7.7.4 The spin quantum number, m_s

- m_s <u>describes the direction of an electron spin in its orbital</u>
- Spinning can be either clockwise or anticlockwise with no third option:

$$m_s = +\frac{1}{2} \text{ or } m_s = -\frac{1}{2}$$

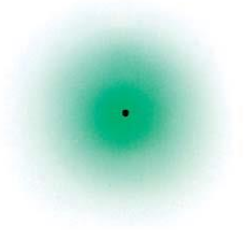
Atomic orbitals

- The "s" subshell has only one orbital
- The "p" subshell has three orbitals that are equal in energy

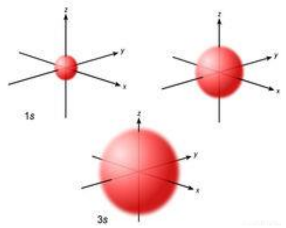
- The “d” subshell has five orbitals that are equal in energy
- The “f” subshell has seven orbitals that are equal in energy

Electron occupies all space it moves within. We know that during most of the time it is as close as possible to the nucleus.

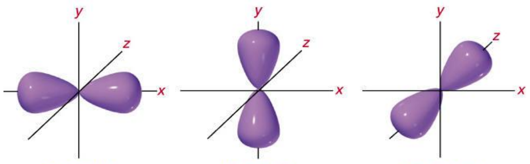
- **Shape of the “s” Orbitals**
  The following figure shows the electron density in the hydrogen 1s orbital. The electron density decreases as the distance from the nucleus increases. There is a 90 percent probability of for the electron to be 100 pm away from the nucleus.



  The following figure shows boundary surface diagrams for the 1s, 2s, and 3s atomic orbitals. All are spherical size increases as the principal quantum number increases.



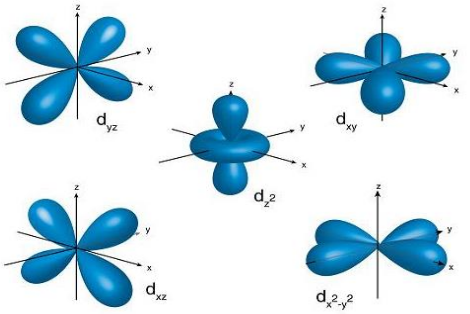
- **Shape of the “p” Orbitals:** The p orbitals start with n = 2. When *l* = 1, its magnetic quantum number have values of − 1, 0 and + 1. Therefore, there are three p orbitals: p_x , p_y and p_z as shown by the following figure.



$2p_x$ orbital $2p_y$ orbital $2p_z$ orbital

  Like s orbitals, p orbitals increase in size from 2p to 3p to 4p orbital and so on.

- **Shape of the “d” Orbitals:** When *l* = 2, there are five d orbitals $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-x^2}$ and $3d_{z^2}$. These orbitals are equal in energy and shown in the following figure.



- **Shape of the “f” Orbitals:** The f orbitals are important in elements with atomic numbers greater than 57. In this general chemistry course, we are not concerned with elements having greater than 57 electrons.

n	***l***	**m_l**	**m_s**	**n**	***l***	**m_l**	**m_s**	**n**	***l***	**m_l**	**m_s**	**n**	***l***	**m_l**	**m_s**
1	0	0	$+\frac{1}{2}$	2	0	0	$+\frac{1}{2}$	3	0	0	$+\frac{1}{2}$	4	0	0	$+\frac{1}{2}$
			$-\frac{1}{2}$				$-\frac{1}{2}$				$-\frac{1}{2}$				$-\frac{1}{2}$
					1	-1	$+\frac{1}{2}$		1	-1	$+\frac{1}{2}$		1	-1	$+\frac{1}{2}$
							$-\frac{1}{2}$				$-\frac{1}{2}$				$-\frac{1}{2}$
						0	$+\frac{1}{2}$			0	$+\frac{1}{2}$			0	$+\frac{1}{2}$
							$-\frac{1}{2}$				$-\frac{1}{2}$				$-\frac{1}{2}$
						$+1$	$+\frac{1}{2}$			$+1$	$+\frac{1}{2}$			$+1$	$+\frac{1}{2}$
							$-\frac{1}{2}$				$-\frac{1}{2}$				$-\frac{1}{2}$
									2	-2	$+\frac{1}{2}$		2	-2	$+\frac{1}{2}$
											$-\frac{1}{2}$				$-\frac{1}{2}$
										-1	$+\frac{1}{2}$			-1	$+\frac{1}{2}$
											$-\frac{1}{2}$				$-\frac{1}{2}$
										0	$+\frac{1}{2}$			0	$+\frac{1}{2}$
											$-\frac{1}{2}$				$-\frac{1}{2}$
										$+1$	$+\frac{1}{2}$			$+1$	$+\frac{1}{2}$
											$-\frac{1}{2}$				$-\frac{1}{2}$
										$+2$	$+\frac{1}{2}$			$+2$	$+\frac{1}{2}$
											$-\frac{1}{2}$				$-\frac{1}{2}$
													3	-3	$+\frac{1}{2}$
															$-\frac{1}{2}$
														-2	$+\frac{1}{2}$
															$-\frac{1}{2}$
														-1	$+\frac{1}{2}$
															$-\frac{1}{2}$
														0	$+\frac{1}{2}$
															$-\frac{1}{2}$
														$+1$	$+\frac{1}{2}$
															$-\frac{1}{2}$
														$+2$	$+\frac{1}{2}$
															$-\frac{1}{2}$
														$+3$	$+\frac{1}{2}$
															$-\frac{1}{2}$

7.8 The rules of electronic distribution

First: The "Aufbau" or the "n + *l*" principle

- This rule states that electrons occupy the lowest-energy subshell before any other higher-energy subshell

- Determining which subshell is lower or higher in energy is achieved by the sum of the values of "n" and "*l*" as shown in the following table

n	***l***	**n + *l***
1	0 (s)	1
2	0 (s)	2
	1 (p)	3
3	0 (s)	3
	1 (p)	4
	2 (d)	5
4	0 (s)	4
	1 (p)	5
	2 (d)	6
	3 (f)	7

- The lowest sum "n + *l*" is the lower energy
- Some higher-energy subshells precede other subshells that are lower in energy. In these cases of subshells having the same value of "n + *l*", the lowest subshell is the one having the lowest value of "n". The above table is rearranged as follows:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p 7d 7f

- We know that any subshell has several orientations in the magnetic field. These orientations do not differ in energy. Therefore, they are shown in the following manner:
  - "s" subshell has only one orientation which is represented as:

s

$m_l = 0$

  - "p" subshell has three orientations which are represented as:

p

$m_l = -1$	$m_l = 0$	$m_l = +1$

  - "d" subshell has five orientations which are represented as:

d

$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$

  - "f" subshell has seven orientations which are represented as:

f

$m_l = -3$	$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$	$m_l = +3$

Second: The Pauli principle

- This second rule states that when an electron occupies an orbital it is impossible for another electron to occupy it unless it spins in an opposite direction of the first electron
- This rule means that, in the same atom, no two electrons can have the same four quantum number (each electron has its own "address")

Third: The Hund's rule

- Number of orientation in the magnetic field (orbital) are **one** in the "s" subshell, **three** in the "p" subshell, **five** in the "d" subshell and **seven** in the "f" subshell
- Hund's rule states that when electrons occupy a subshell which has more than one orientation in the magnetic field (p, d or f) they will not pair in the same orbital as long as other orbitals are empty and the unpaired electrons spins in the same direction

Fourth: The rule of half-filled and fully-filled subshells

- Half-filled and fully-filled subshells add more stability to electrons and atoms

- Starting from the energy level where **n = 4** and higher, the difference in energy between subsequent subshells is so small
- When two consecutive subshells are energetically close to each other, they will seek to be half or fully filled even if this requires an electron to be in the slightly-higher energy subshell rather than the slightly lower energy subshell

The following configurations illustrates how electrons distribute themselves within an atom. It shows this distribution for the first 36 elements in the periodic table of elements.

^{1}H

$1s^1$
↑

^{2}He (Note: its upper shell is full, and its electron configuration is symbolized as [He])

$\mathbf{1s^2}$
↑↓

^{3}Li

	$2s^1$
[He]	↑

^{4}Be

	$2s^2$
[He]	↑↓

^{5}B

	$2s^2$	$2p^1$		
[He]	↑↓	↑		

^{6}C

	$2s^2$	$2p^2$		
[He]	↑↓	↑	↑	

^{7}N

	$2s^2$	$2p^3$		
[He]	↑↓	↑	↑	↑

^{8}O

	$2s^2$	$2p^4$		
[He]	↑↓	↑↓	↑	↑

^{9}F

	$2s^2$	$2p^5$		
[He]	↑↓	↑↓	↑↓	↑

^{10}Ne (Note: its upper shell is full, and its electron configuration is symbolized as [Ne])

	$2s^2$	$2p^5$		
[He]	↑↓	↑↓	↑↓	↑↓

^{11}Na

	$3s^1$
[Ne]	↑

^{12}Mg

	$3s^2$
[Ne]	↑↓

^{13}Al

	$3s^2$	$3p^1$		
[Ne]	↑↓	↑		

^{14}Si

	$3s^2$	$3p^2$		
[Ne]	↑↓	↑	↑	

^{15}P

	$3s^2$	$3p^3$		
[Ne]	↑↓	↑	↑	↑

^{16}S

	$3s^2$	$3p^4$		
[Ne]	↑↓	↑↓	↑	↑

^{17}Cl

	$3s^2$	$3p^5$		
[Ne]	↑↓	↑↓	↑↓	↑

^{18}Ar (Note: its upper shell is full, and its electron configuration is symbolized as [Ar])

	$3s^2$	$3p^6$		
[Ne]	↑↓	↑↓	↑↓	↑↓

^{19}K

	$4s^1$
[Ar]	↑

^{20}Ca

	$4s^2$
[Ar]	↑↓

^{21}Sc

	$4s^2$	$3d^1$				
[Ar]	↑↓	↑				

^{22}Ti

	$4s^2$	$3d^2$				
[Ar]	↑↓	↑	↑			

^{23}V

	$4s^2$	$3d^3$				
[Ar]	↑↓	↑	↑	↑		

^{24}Cr

	$4s^1$	$3d^5$				
[Ar]	↑	↑	↑	↑	↑	↑

^{25}Mn

	$4s^2$	$3d^5$				
[Ar]	↑↓	↑	↑	↑	↑	↑

^{26}Fe

	$4s^2$	$3d^6$				
[Ar]	↑↓	↑↓	↑	↑	↑	↑

^{27}Co

	$4s^2$	$3d^7$				
[Ar]	↑↓	↑↓	↑↓	↑	↑	↑

^{28}Ni

	$4s^2$	$3d^8$				
[Ar]	↑↓	↑↓	↑↓	↑↓	↑	↑

^{29}Cu

	$4s^1$	$3d^{10}$				
[Ar]	↑	↑↓	↑↓	↑↓	↑↓	↑↓

^{30}Zn

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓]

^{31}Ga

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^1$ [↑][ ][ ]

^{32}Ge

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^2$ [↑][↑][ ]

^{33}As

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^3$ [↑][↑][↑]

^{34}Se

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^4$ [↑↓][↑][↑]

^{35}Br

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^5$ [↑↓][↑↓][↑]

^{36}Kr (**Note: its upper shell is full, and its electron configuration is symbolized as [Kr]**)

[Ar] $4s^2$ [↑↓] $3d^{10}$ [↑↓][↑↓][↑↓][↑↓][↑↓] $4p^6$ [↑↓][↑↓][↑↓]

From the above configurations, it appears that noble-gases shells are full of electrons, and any element comes after a noble gas has the configuration of this noble gas as its core electrons plus the extra electrons in the following shell.

Example 7.4

Give the four quantum numbers for the two electrons in a 6s orbital of an atom.

Solution

Quantum number	**n**	***l***	**m_l**	**m_s**
First electron	6	0	0	$+\frac{1}{2}$
Second electron	6	0	0	$-\frac{1}{2}$

Practice exercise 7.4

Give the four quantum numbers for the six electrons in a 3p orbital of an atom

Example 7.5

Why aren't correct the following quantum numbers for the electrons in the "p" subshell of ^{7}N?

Quantum number	**n**	***l***	**m_l**	**m_s**
First electron	2	0	0	$+\frac{1}{2}$
Second electron	2	1	0	$-\frac{1}{2}$
Third electron	2	1	– 1	+ 1

Solution

Electron distribution of nitrogen is as follows:

[He] $2s^2$ [↑↓] $2p^3$ [↑][↑][↑]

- The “n” quantum numbers: they are correct for all the three electrons
- “*l*” quantum numbers: they are correct for the second and the third electrons but wrong for first electron because it is in the second subshell, p, which has *l* = 1
- The “m_l” quantum numbers: according to Hund’s rule, all of the electrons must be unpaired and their quantum numbers must be “– 1”, “0” and “+ 1”
- The “m_s” quantum numbers: according to Pauli’s principle, can be either $+\frac{1}{2}$ or $+\frac{1}{2}$; and according to Hund’s rule, they all must be either $+\frac{1}{2}$ or $-\frac{1}{2}$

Practice exercise 7.5

A person gave the four quantum numbers for the six electrons in the 3p orbitals of an atom. Judge the answer.

Quantum number	**n**	***l***	**m_l**	**m_s**
First electron	3	1	– 1	$+\frac{1}{2}$
Second electron	3	1	– 1	$+\frac{1}{2}$
Third electron	3	0	0	$-\frac{1}{2}$
Fourth electron	3	0	0	$-\frac{1}{2}$
Fifth electron	3	– 1	+ 1	$+\frac{1}{2}$
Sixth electron	4	– 1	+ 1	$+\frac{1}{2}$

7.10 Electron configurations of anions and cations

1) First: Anions

The electrons of anions are distributed using the same rules used for neutral atoms electrons.

H: $1s^1$	**H^-:** $1s^2$ or [He]
F: $1s^2\ 2s^2\ 2p^5$	**F^-:** $1s^2\ 2s^2\ 2p^6$ or [Ne]
O: $1s^2\ 2s^2\ 2p^4$	**O^{2-}:** $1s^2\ 2s^2\ 2p^6$ or [Ne]
N: $1s^2\ 2s^2\ 2p^3$	**N^{3-}:** $1s^2\ 2s^2\ 2p^6$or [Ne]

All these anions have stable noble gas configurations. Notice that F^-, Na^+, and Ne (and F^-, O^{2-}, and N^{3-}) have the same electron configuration. They are said to be **isoelectronic** because they have the same number of electrons, and hence the same electron configuration. Thus, H^- and He are also **isoelectronic**.

2) Second: Cations

Knowing the electron distributions of cations requires writing the distributions of the original atom, then removing electron or electrons as explained below:

- **Cations derived from elements that its upper subshell is “s” or “p”**

  Electrons of cations formed from atoms having “s” or “p” as its upper subshell are removed from the upper subshell and its configuration can be known easily. The electron configurations of some atoms of this kind and their corresponding cations are as follows:

Na: $[Ne]3s^1$	Na^+: [Ne]
Ca: $[Ar]4s^2$	Ca^{2+}: [Ar]
Al: $[Ne]3s^2\ 3p^1$	Al^{3+}: [Ne]

All configuration becomes like the previous noble gas configuration.

- **Cations derived from elements that its upper subshell is "d"**

  In this case electrons are removed from the upper subshell having the bigger principle quantum number as, for example, Ti, Fe, and Zn show below:

$$\text{Ti: [Ar]}4s^2\,3d^2 \rightarrow \text{Ti}^{2+}\text{: [Ar]}3d^2$$
$$\text{Fe: [Ar] }4s^2\,3d^6 \rightarrow \text{Fe}^{3+}\text{: [Ar]}3d^5$$
$$\text{Zn: [Ne]}4s^2\,3d^{10} \rightarrow \text{Zn}^{2+}\text{: [Ne]}3d^{10}$$

Example 7.6

Write the electron configuration of the following:

A) $^{16}S^{2-}$ B) $^{26}Fe^{3+}$

Solution

A) $^{16}S^{2-}$ has 18 electrons, (16 electrons + 2 electrons):

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

B) $^{26}Fe^{3+}$ has 23 electrons, (26 electrons – 3 electrons):

First: we write the electron configuration of the Fe atom:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Second: we find that 4s is the subshell having highest "n" quantum number. Its electrons and a third one from the 3d electrons are removed to form Fe^{3+}. The electron configuration is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Practice exercise 7.6

Write the electron configuration of the following:

A) $^{15}P^{3-}$ B) $^{31}Ga^{3+}$

7.11 The electron configurations and the location of elements in the periodic table

The location of elements in the periodic table depends on its electron configuration:

- **Determining the block:**
  The last subshell (**s, p, d or f**) in its electron configuration is its block
- **Determining the period:**
  The highest principle quantum number (**1, 2, 3, 4, 5, 6 or 7**) in its electron configuration is its period
- **Determining the group of an element in the "s", "p" or "d" block:**
  - If the element is in block "s" the number of electrons in its last "s" subshell is its group number
  - If the element is in block "p" we add 10 to the number of electrons in its last "s" and "p" subshell and the resultant is its group number
  - If the element is in block "d" we add 2 to the number of electrons in its last "d" subshell and the resultant is its group number
- **Determining the group of an element in the "f" block:**
  - If it is in period "6" it is one of the lanthanide group
  - If it is in period "7" it is one of the actinide group

Example 7.7

For each of the four elements having the following atom numbers, determine the block, the period, the group and the group name:

A) 9 B) 10 C) 12 D) 30

Solution

Answering the question requires writing the electron configuration of each:

A) $1s^2\ 2s^2\ 2p^5$

B) $1s^2\ 2s^2\ 2p^6$

C) $1s^2\ 2s^2\ 2p^6\ 3s^2$

D) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

	A	B	C	D
Block	p	p	s	d
Period	2	2	3	4
Group	17	18	2	12
Group name	Halogen	Noble gases	Alkali earth	No group name

Practice exercise 7.7

For each of the four elements having the following atom numbers, determine the block, the period, the group and the group name:

A) 8 B) 17 C) 19 D) 40

8. PHYSICAL PROPERTIES OF SOLUTIONS

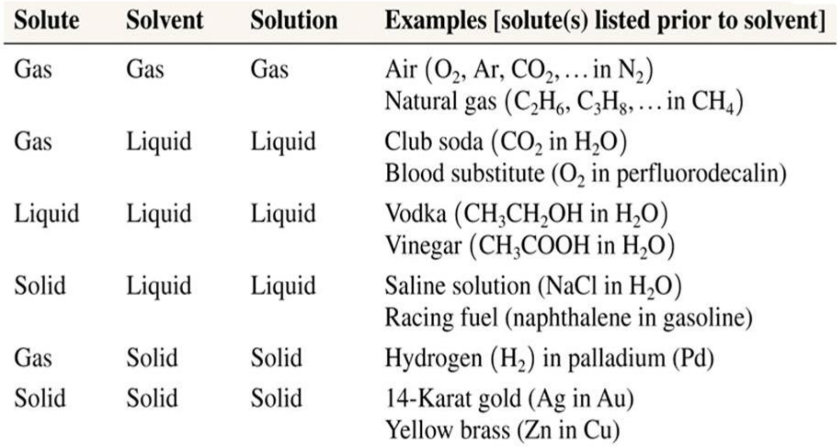
(**NOTE:** ***CHAPTER 12 IN THE TEXTBOOK***)

8.1 Types of solutions

- A solution is a mixture of two or more components. One of the components is called "**solvent**" the other (or the others) is (are) called "**solute**":

Solvent + Solute = Solution

  - The table below gives some common types of solutions.



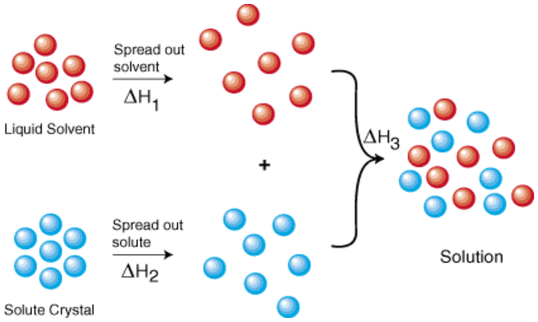
Solute	Solvent	Solution	Examples [solute(s) listed prior to solvent]
Gas	Gas	Gas	Air (O_2, Ar, CO_2, … in N_2) Natural gas (C_2H_6, C_3H_8, … in CH_4)
Gas	Liquid	Liquid	Club soda (CO_2 in H_2O) Blood substitute (O_2 in perfluorodecalin)
Liquid	Liquid	Liquid	Vodka (CH_3CH_2OH in H_2O) Vinegar (CH_3COOH in H_2O)
Solid	Liquid	Liquid	Saline solution (NaCl in H_2O) Racing fuel (naphthalene in gasoline)
Gas	Solid	Solid	Hydrogen (H_2) in palladium (Pd)
Solid	Solid	Solid	14-Karat gold (Ag in Au) Yellow brass (Zn in Cu)

- Our focus will be on liquid solutions:
  - Solutions of gases in liquids
  - Solutions of liquids in liquids
  - Solutions of solids in liquids

8.2 A Molecular view of the solution process

8.2.1 How solution is formed?

- Intermolecular attractions have an important role in the formation of solutions of solids in liquids and of liquids in liquids
- When the liquid or the solid solute dissolves in the liquid solvent particles of the solute disperse throughout the solvent and occupy positions that are originally taken by solvent molecules
- The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:
  1) solvent-solvent interaction
  2) solute-solute interaction
  3) solvent-solute interaction
- We can imagine the solution process in three distinct and simultaneous actions:
  1) the separation of solvent molecules
  2) the separation of solute molecules
  3) the attraction between solvent and solute molecules.



- Because breaking attractive forces requires energy ($\Delta H_1 > 0$ and $\Delta H_2 > 0$) the first and the second actions are endothermic
- Because forming attractive forces releases energy ($\Delta H_3 < 0$) the third action is exothermic
- The enthalpy of solution ΔH_{soln} is given by:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- There are three distinguished cases:

  First case ($\Delta H_{soln} = 0$): If the solute-solvent attractions are **equal to** the solvent-solvent and the solute-solute attractions, the solution process is not endothermic or exothermic and the solution is an **ideal solution.**

  Second case ($\Delta H_{soln} < 0$): If the solute-solvent attractions are **stronger** than the solvent-solvent and the solute-solute attractions, the solution process is exothermic, and the solution is a **non- ideal solution**

  Thitd case ($\Delta H_{soln} > 0$): If the solute-solvent attractions are **weaker** than the solvent-solvent and the solute-solute attractions, the solution process is endothermic, and the solution is a **non- ideal solution**

8.2.2 The "like dissolve like" proverb

- The "**Like** dissolve **like**" means that **"the solute can dissolve in the solvent if the attractive forces between its particles are like those in the solvent particles, but if they are not, the solute cannot dissolve in the solvent**"
- The attractive forces of the solvent are so many
- We will not consider the two famous types
  - The first is called "polar solvents" which dissolve any ionic or polar solute but cannot dissolve any nonionic or nonpolar solute
  - The second is called "nonpolar solvents" in which any nonionic or nonpolar solute can dissolve any nonpolar solute but cannot dissolve any ionic or polar solute
  - The following table gives some of the important polar and nonpolar solvents that are widely used:

POLAR SOLVENTS		NONPOLAR SOLVENTS	
Water	H_2O	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
Formic acid	HCO_2H	Benzene	C_6H_6
Acetic acid	CH_3CO_2H	Toluene	$C_6H_5CH_3$
Methanol	CH_3OH	1,4-dioxene	$(CH_3CH_2O)_2$
Ethanol	CH_3CH_2OH	Chloroform	$CHCl_3$
n-butanol	$CH_3CH_2CH_2CH_2OH$	Diethyl ether	$(CH_3CH_2)_2O$

EXAMPLE 8.1

Knowing that:

A) Molecules of Br_2, C_6H_6, CCl_4, and CS_2 are nonpolar
B) Molecules of H_2O, CH_2O and liquid NH_3 are polar
C) KCl is an ionic compound

Predict the solubility in the following cases:

A) Bromine (Br_2) in benzene (C_6H_6) and in water (H_2O)
B) Potassium chloride (KCl) in (CCl_4) and in liquid ammonia (NH_3)
C) Formaldehyde (CH_2O) in carbon disulfide (CS_2) and in water (H_2O)

Solution

A) Br_2 is soluble C_6H_6 not in H_2O
B) KCl is soluble in NH_3 not in CCl_4
C) CH_2O is soluble in H_2O not in CS_2.

Practice Exercise 8.1

Knowing that I_2 and CS_2 are nonpolar and H_2O is polar, Is iodine (I_2) more soluble in water or in carbon disulfide (CS_2)?

8.3 Concentration units

- The term "concentration" is used to compare the amount of the solute with the amount of the solvent. The greater the amount of solute, the more concentrated the solution is
- Remember that "**Molarity**" was previously explained in chapter 4

8.3.1 Mass percent of solute (Solute%)

- The mass percent of the solute in a solution (**Solute%**) is given by:

$$\textbf{Solute\%} = \frac{\mathbf{m_{solute}}}{\textbf{total mass of solution}} \times \mathbf{100}$$

- Solute% has no unit
- If we have a 25% $C_6H_{12}O_6$ aqueous solution, we conclude that:
  1) Water is the solvent and glucose is the solute
  2) $m_{solution}$ = 100 g, m_{solute} = 25 g and $m_{solvent}$ = 75 g
  3) $n_{solvent}$, n_{solute} and n_{total} can be calculated
  4) $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given

Example 8.2

A solution contains 131.4 g of glucose in 0.5 kg of water. Calculate glucose mass%.

Solution

$$\text{Glucose mass\%} = \frac{m_{glucose}}{\text{total mass of solution}} \times 10^2 = \frac{131.4\text{ g}}{131.4\text{ g} + 0.5\text{ kg} \times 1000\frac{\text{g}}{\text{kg}}} \times 10^2 = 20.81\%$$

Practice Exercise 8.2

A solution contains 8.74 g $NaNO_3$in 75 g of water. Calculate the $NaNO_3$%.

8.3.2 Mole fraction (X)

- Mole fraction of a component of a solution ($\mathbf{X_{component}}$) is given by:

$$\mathbf{X_{component}} = \frac{\mathbf{n_{component}}}{\textbf{total moles of componants}} = \frac{\mathbf{n_{component}}}{\mathbf{n_t}}$$

- Mole fraction has no unit
- If the mole fraction of $C_6H_{12}O_6$ in an aqueous solution is 0.25, we conclude that:
  1) Water is the solvent and glucose is the solute
  2) n_{solute} = 0.25 mol and $n_{solvent}$ = 0.75 mol
  3) m_{solute}, $m_{solvent}$ and $m_{solution}$ can be calculated

4) $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given

Example 8.3

Calculate the mole fraction of 281 g of glucose ($C_6H_{12}O_6$) in 450 mL aqueous solution ($d_{solution} = 0.998\ \frac{g}{mL}$).

solution

Mass of solution = density × volume = $0.998\ \frac{g}{mL} \times 450\ mL = 449.1\ g$

Mass of water = 449.1 g – 281 g = 168.1 g

$n_{glucose} = \frac{m_{glucose}}{M_{glucose}} = \frac{281\ g}{180\frac{g}{mol}} = 1.56\ mol$ **AND** $n_{water} = \frac{m_{water}}{M_{water}} = \frac{168.1\ g}{18\ \frac{g}{mol}} = 9.34\ mol$

$n_t = n_{glucose} + n_{water} = 1.56\ mol + 9.34\ mol = 10.9\ mol$

$X_{glucose} = \frac{n_{glucose}}{n_t} = \frac{1.56}{10.9} = 0.143$

Practice Exercise 8.3

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the mole fraction of sodium nitrate in the solution.

8.3.3 Molality (m)

- Molality (**m**) expresses the concentration of a solution as the number of moles of solute (n_{solute}) in one kilogram of the solvent:

$$\textbf{Molality (m)} = \frac{n_{solute}}{mass_{solvent}\ (kg)}$$

- The molality units are $\frac{mol}{kg}$ which is usually called “molal” and is abbreviated as “m”
- If we have a 0.25 molal $C_6H_{12}O_6$ aqueous solution, we conclude that:
  1) Solvent is water and solute is glucose
  2) $n_{C_6H_{12}O_6} = 0.25$ mol, and m_{solute} can be calculated
  3) $m_{solvent}$ = 1 kg = 1000 g. $n_{solvent}$ and $m_{solution}$ can be calculated
  4) $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

Example 8.4

A solution is made by dissolving 4.35 g glucose ($C_6H_{12}O_6$) in 25.0 mL of water. Calculate the molality of glucose in the solution. Water has a density of 1 g/mL.

Solution

$m_{solvent} = d_{solvent} \times V_{solvent} = 25\ mL \times 1\ \frac{g}{mL} = 25\ g = 0.025\ kg$

$molality = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{\frac{4.35\ g}{180\ \frac{g}{mol}}}{0.025\ kg} = 0.097\ \frac{mol}{kg} = 0.097\ molal = 0.097\ m$

Practice Exercise 8.4

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the molality of sodium nitrate in the solution.

8.3.4 Interconversion between concentration’s units

- The above discussion was an illustration to the main four types of concentration units: solute mass%, mole fraction, molality and molarity
- It was mentioned that knowing any one of them enables us to determine the other three. The following exercises shows how this can be done

Example 8.5

An aqueous solution of hydrochloric acid contains 36% HCl by mass:

A) Calculate the mole fraction of HCl

B) Calculate the molality of HCl

Solution

A) $n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{36\ g}{36.45\ \frac{g}{mol}} = 0.988\ mol$

$m_{solvent} = 100\ g - 36\ g = 64\ g$

$n_{solvent} = \frac{m_{solvent}}{M_{solvent}} = \frac{64\ g}{18\ \frac{g}{mol}} = 3.556\ mol$

$X_{solute} = \frac{n_{solute}}{n_t} = \frac{0.988\ mol}{(0.988\ mol + 3.556\ mol)} = 0.217$

B) $molality = \frac{n_{solute}}{mass_{solv}\ (kg)} = \frac{0.988\ mol}{0.064\ kg} = 15.44\ molal$

Practice Exercise 8.5

Calculate the molality of a sodium nitrate ($NaNO_3$) aqueous solution in which the mass percent of $NaNO_3$ is 43%.

Example 8.6

A solution with a density of 0.876 g/mL contains 5 g of toluene (C_7H_8) dissolved in 225 g of benzene. Calculate the molality and molarity of the toluene solution.

Solution

$n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{5\ g}{92\frac{g}{mol}} = 0.054\ mol$

$m = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{0.054\ mol}{0.225\ kg} = 0.34\ molal$

$V_{soln} = \frac{m_{son}}{d_{soln}} = \frac{5\ g + 225\ g}{0.876\ \frac{g}{mL}} = 262.56\ mL = 0.263\ L$

$Molarity = \frac{n_{solute}}{V_{soln}(L)} = \frac{0.054\ mol}{0.263\ L} = 0.205\ molar$

Practice Exercise 8.6

A solution with a density of 0.998 g/mL contains 281 g of glucose ($C_6H_{12}O_6$) and 168.1 g of water. Calculate the molality and molarity of the glucose solution.

Example 8.7

Calculate the glucose mass% in a 0.73 molal solution of glucose in water.

Solution

$Glucose\% = \frac{m_{glucose}}{\text{total mass of solution}} \times 100$

$n_{glucose} = 0.73\ mol$,, $m_{water} = 1\ kg = 1000\ g$

$m_{glucose} = n_{glucopse} \times M_{glucose} = 0.73 \times 180 = 131.4\ g$

$m_{solution} = m_{glucose} + m_{water} = 131.4 + 1000 = 1131.4\ g$

$Solute\% = \frac{131.4\ g}{1131.4\ g} \times 10^2 = 11.61\%$

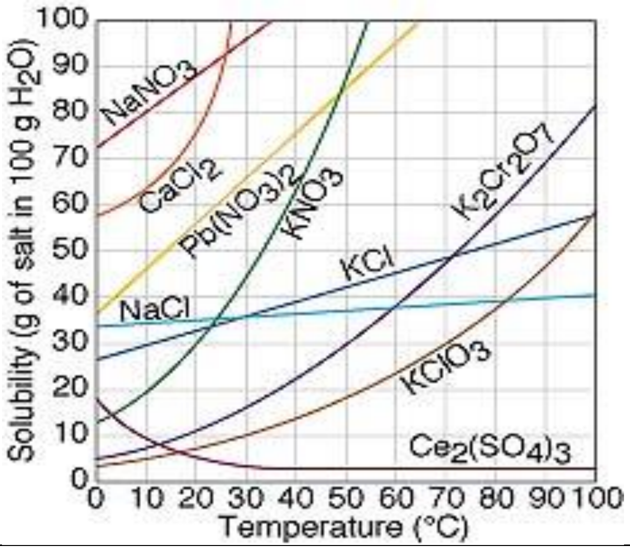
Practice Exercise 8.7

If the molality of a solution of urea (NH_2CONH_2) in water is 0.14 mol/kg, calculate the mass percent of urea in the solution.

8.4 The effect of temperature on solubility

8.4.1 Solid solubility and temperature

The following figure clearly shows that solubility in water increases as temperature increases for most ionic solid salts, decreases for a few ionic solid salts in water increases as temperature decreases and is rarely the same at all temperature



EXAMPLE 8.8

Using the above curves answer the following questions:

1) At 40 °C, which is more soluble KCl or $K_2Cr_2O_7$?
2) At 90 °C, which is more soluble KCl or $K_2Cr_2O_7$?

Solution

1) At 40 °C, KCl is more soluble than $K_2Cr_2O_7$
2) At 90 °C, $K_2Cr_2O_7$ is more soluble than KCl

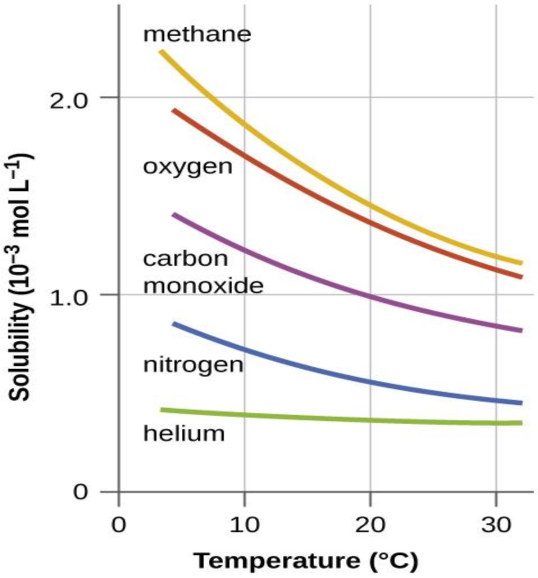
Practice Exercise 8.8

Using the curves of the solubility versus temperature,

1) At what temperature will the solubility of KCl equalizes that of $KClO_3$?
2) At 47 °C, the solubility of KNO_3 is 80 g/100 g of water. At what temperature would the solubility of $NaNO_3$ be the same?

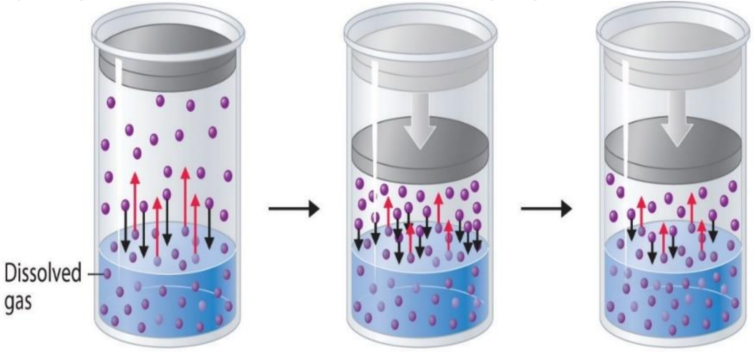
8.4.2 Gas solubility and temperature

The following figure shows n ***all*** cases, the solubility of any gas decreases as temperature increases but differs from a gas to another



8.5 The effect of pressure on the solubility of gases

- Due to the spacing between particles of gases, **pressure has a great effect** on the solubility of gases. Let's look at the following figure:



- The figure shows that as we increase the pressure of the gas above the liquid it is forced to dissolve more of the gas.
- The quantitative relation between gas solubility and its pressure is given by **Henry's law: "the solubility of a gas in a liquid is proportional to its pressure over the solution"**. It is presented by the following equation:

$$\mathbf{c = kP}$$

  "**c**" is the molar concentration (the number of moles of gas in one liter of the solution
  "P" is the pressure (in atm) of the gas over the solution
  "k" is a constant for each gas and is called ***Henry's constant***
- Henry's constant differs from a gas to another and its units are $\frac{\text{mol}}{\text{L} \times \text{atm}}$
- The amount of gas that will dissolve in the liquid depends on how frequently the gas molecules collide with the liquid surface and become trapped. We can understand this matter when we think about a bottle of a refreshment drink:
  1) The bottle is sealed at high pressure of CO_2. This means that amount of CO_2 dissolved in these drinks is many times the amount dissolved under normal atmospheric pressure
  2) When the cap of the bottle is removed the excess dissolved CO_2 comes out of solution, causing the effervescence, and the pressure in the bottle finally falls to atmospheric pressure and the amount of CO_2 remaining in the beverage inside the bottle is then determined only by the normal atmospheric partial pressure of CO_2, 0.0003 atm.

EXAMPLE 8.9

The solubility of $N_2(g)$ in water at 25 °C and 1 atm is 6.8×10^{-4} $\frac{\text{mol}}{\text{L}}$. What is its molarity if dissolved at atmospheric conditions? **(P_{N_2} in the atmosphere = 0.78 atm)**.

Solution

$c = k \times P$ and $6.8 \times 10^{-4}\ \text{mol/L} = k \times 1\ \text{atm}$

$k = \frac{6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}}{1\ \text{atm}} = 6.8 \times 10^{-4}\ \text{mol/L atm}$

$c = 6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L} \times \text{atm}} \times 0.78\ \text{atm} = 5.3 \times 10^{-4}\ \text{mol/L}$

Practice Exercise 8.9

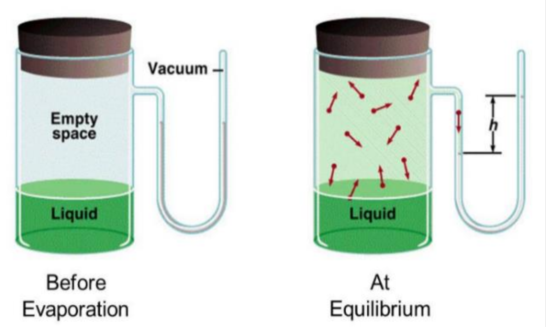
Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's constant for oxygen is 1.3×10^{-3} mol/L atm.

THE PROPERTIES OF A PURE LIQUID CHANGE AFTER IT BECOMES NOT PURE

Vapor pressures, boiling points, and freezing points of pure liquids

First: Vapor pressures of pure liquids

- The liquid molecules that evaporate become gaseous molecules and are called "**vapor**"
- Vapor exert a pressure called "**vapor pressure**"
- Only liquid molecules **that reach the surface of the liquid with the highest energies and speeds** can free themselves from its liquid state and become gaseous (vapor)
- Any liquid molecule that does not have high energy and speed will not vaporize even if it is at the surface of the liquid
- Any liquid molecule that does not satisfy these two conditions will not vaporize
- Let's look carefully to the following figure:



- The above figure shows that before the evaporation process starts, the mercury levels in the U-shaped manometer tube are equal
- As soon as some molecules leave the liquid, a vapor phase is established, and its pressure is called **the vapor pressure**.
- Eventually, the mercury levels stabilize and no further changes in pressure are seen
- As the concentration of molecules in the vapor phase increases, some molecules start to condense from the gas phase to the liquid phase
- Vapor molecules differ in their energies and speeds. The only vapor molecules that can condense back to liquid (trapped by the liquid molecules at the liquid surface) are those colliding the surface of the liquid with the lowest energies and speeds
- Any vapor molecule that does not satisfy these two conditions will not condense
- As condensation rate rises evaporation rate decreases until the two rates become equal
- When the two rates become equal, we say that a state of ***dynamic equilibrium*** is reached
- The vapor pressure measured when this dynamic equilibrium exists between condensation and evaporation is called "**equilibrium vapor pressure**" or simply "**vapor pressure**"
- The equilibrium vapor pressure is the *maximum* vapor pressure of a liquid at a given temperature and it is constant at a constant temperature
- Increasing temperature increases not only the energy and speed of molecules but also increases the number of molecules having high energy and speed
- As temperature increases vapor pressure increases
- Vapor pressure of many liquids at different temperatures are available in tables achieved by physicists and chemists.

Second: Boiling points of pure liquids

- When liquid temperature increases, its vapor pressure increases and equalize the external pressure at a certain temperature
- At this certain temperature the whole liquid molecules become in a situation of transition from the liquid state to the gaseous state, and the surface of the liquid disappears
- This particular situation of evaporation at this particular temperature is called **boiling**
- The temperature at which this happens is called "**the boiling point**" and if the external pressure is the normal pressure (1 atm) it is called "**the normal boiling point**". For example, the boiling point of water is 100 °C only at 1 atm
- If the external pressure is higher than standard pressure the boiling point becomes higher than standard boiling point (for example, at 1.5 atm water will boil at 110.5 °C)
- If the external pressure is lower than standard pressure the boiling point becomes lower than standard boiling point (for example, at 0.4 atm water will boil at 84 °C)
- Off course, the value of this particular temperature differs from liquid to liquid and the liquid which vaporizes easier has the lesser boiling point and vice versa

Third: Freezing points of pure liquids

- Decreasing the temperature of liquid molecules will decrease their energies and speeds and consequently the attractive forces between them increase
- At a ***certain temperature***, the liquid molecules start to be tightly bonded to their neighboring molecules and cannot leave their positions and we say: the liquid ***freezes***
- We call the temperature at which the liquid freezes "**the freezing point**". If the pressure at which liquid freezes is 1 atm this temperature is called "**the normal freezing point**". For example, the standard freezing point of water is 0 °C

8.6 Colligative Properties of Nonelectrolyte Solutions

- **Colligative properties** are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles, regardless of whether they are atoms, ions, or molecules. The colligative properties are vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure
- For our discussion of colligative properties of nonelectrolyte solutions, it is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations ≤ 0.2 $\text{mol/L}_{\text{solution}}$

8.6.1 Vapor pressures lowering

First: the solute is not volatile:

- The pure solvent vapor pressure is $P^{\circ}_{\text{solvent}}$
- The vapor above the solution is the vapor of only the solvent
- We can calculate the molar fractions (X_{solvent} and X_{solute})
- After dissolving solute, its particles become attached to the solute particles
- These attachments hinder the evaporation of the solvent particles which in turn makes the vapor pressure of the liquid lower than $P^{\circ}_{\text{solvent}}$ by an amount of **ΔP** which is called "**vapor pressure lowering**"
- According to Raoult's law:

$$P_{\text{solvent}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$$

- Because the vapor pressure of the solution belongs only to the solvent, P_{solution} is given as follows:

$$P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$$

$$\Delta P = X_{\text{solute}} \times P^{\circ}_{\text{solvent}}$$

EXAMPLE 8.10

Calculate the vapor pressure and the vapor-pressure lowering of a solution made by dissolving 218 g of glucose in 460 mL of water at 30 °C. Assume the density of the solution is 1.00 g/mL. (**M_{glucose} = 180.15 g/mol, $P^{\circ}_{\text{water},30\ °\text{C}} = 31.82$ torr**)

Solution

$n_{\text{water}} = \frac{460\ \text{g}}{18.016\ \frac{\text{g}}{\text{mol}}} = 25.53$ mol	$n_{\text{glucose}} = \frac{218\ \text{g}}{180.15\ \frac{\text{g}}{\text{mol}}} = 1.21$ mol	$X_{\text{water}} = \frac{25.5\ \text{mol}}{25.5\ \text{mol} + 1.21\ \text{mol}} = 0.995$

$P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$

$P_{\text{solution}} = 0.995 \times 31.82$ mmHg = 30.4 mmHg

$\Delta P = P^{\circ}_{\text{solvent}} - P_{\text{solution}} = 31.82$ mmHg – 30.4 mmHg = 1.42 mmHg

Practice Exercise 8.10

Calculate the vapor pressure and the vapor-pressure lowering at 35°C of a solution of 82.4 g of urea in 212 mL of water. (**$P^{\circ}_{\text{water},35\ °\text{C}}$= 42.2 mmHg**)

Second: Vapor pressures of mixed liquids (Raoult's law)

- Here we have **two pure liquid**, liquid "A" and liquid "B" with vapor pressure P°_A and P°_B
- Their number of moles are "n_A and "n_B"
- After they are mixed, their vapor pressure in the mixture are P_A and P_B
- If we mix the n_A mole of A with n_B mole of B, we will get a liquid solution with a known molar fraction of each, X_A and X_B
- Raoul's law for this mixture is:

$$P_{\text{solution}} = P_A + P_B$$

$$(P_A = X_A \times P^{\circ}_A) \qquad \textbf{AND} \qquad (P_B = X_B \times P^{\circ}_B)$$

$$\boxed{\mathbf{P_{solution} = (X_A \times P^{\circ}_A) + (X_B \times P^{\circ}_B)}}$$

- Because $X_A + X_B = 1$, the last equation can be modified to be:

$$P_{\text{solution}} = X_A \times (P^{\circ}_A - P^{\circ}_B) + P^{\circ}_B \qquad \textbf{OR} \qquad P_{\text{solution}} = X_B \times (P^{\circ}_B - P^{\circ}_A) + P^{\circ}_A$$

- All these previous equations are known as **Raoul's law**
- Raoul's law is applicable only if **the forces of attractions between the particles of the mixed liquids are of the same type**
- Any solution obeys Raoul's law is called "**ideal solution**"; if not it is called "**nonideal solution**"

Example 8.11

Calculate the vapor pressure of a solution of 252 g of pentane(*l*) and 1400 g of heptane(*l*) at 20 ºC.

($M_{\text{pentane}} = 72\ \frac{\text{g}}{\text{mol}}$ and $P^{\circ}_{\text{pentane},20\ \text{oC}}$ = 420 mmHg)

($M_{\text{heptane}} = 100\ \frac{\text{g}}{\text{mol}}$ and $P^{\circ}_{\text{heptane},20\ \text{oC}}$ = 36 mmHg)

Solution

$P_{\text{solution}} = (X_{\text{pentane}} \times P^{\circ}_{\text{pentane}}) + (X_{\text{heptane}} \times P^{\circ}_{\text{heptane}})$

$$n_{\text{pentane}} = \frac{m_{\text{pentane}}}{M_{\text{pentane}}} = \frac{252\ \text{g}}{72\ \frac{\text{g}}{\text{mol}}} = 3.5\ \text{mol}$$

$$n_{\text{heptane}} = \frac{m_{\text{heptane}}}{M_{\text{heptane}}} = \frac{1400\ \text{g}}{100\ \frac{\text{g}}{\text{mol}}} = 14\ \text{mol}$$

$$X_{\text{pentane}} = \frac{n_{\text{pentane}}}{n_{\text{pentane}} + n_{\text{heptane}}} = \frac{3.5}{3.5 + 14} = 0.2$$

$X_{\mathrm{heptane}} = 1 - X_{\mathrm{pentane}} = 1 - 0.2 = 0.8$

$P_{\mathrm{solution}} = (0.2 \times 420\ \mathrm{mmHg}) + (0.8 \times 36\ \mathrm{mmHg}) = 112.8\ \mathrm{mmHg}$

Practice Exercise 8.11

Calculate the vapor pressure of a solution of 50 g of methanol and 50 g of ethanol at 20°C.

$\mathbf{(M_{methanol} = 32\ \frac{g}{mol}\ and\ P^{\circ}_{methanol} = 94\ mmHg)\ (M_{ethanol} = 46\ \frac{g}{mol}\ and\ P^{\circ}_{ethanol} = 44\ mmHg)}$

8.6.2 Boiling point elevation

- **Boiling point** (t_b) is the temperature at which the vapor pressure of the liquid equalizes the external pressure
- The **normal boiling point** (t°_b) is the temperature at which the vapor pressure of the liquid equalizes the normal external pressure (1 atm)
- The vapor pressure of the solution became less than that of the pure liquid. So, the vapor pressure of the solution, **at the temperature at which the pure liquid boils**, will be less than that needed for the solution to boil
- The temperature at which the vapor pressure of the solution equalizes the external normal pressure is elevated by a certain value (ΔT_b)
- The value of ΔT_b is proportional to the solution molality (m):

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b\ m$$

- K_b is the **molal boiling-point elevation constant**; its value differs from liquid to another

$$\Delta T_b = \frac{K_b \times n_{\mathrm{solute}}}{m_{\mathrm{solvent}}\ (\mathrm{kg})}$$

$$\Delta T_b\ (^{\circ}\mathrm{C}) = \frac{K_b\ (\frac{\frac{^{\circ}C}{mol}}{kg}) \times \frac{m_{\mathrm{solute}}\ (\mathrm{kg})}{M_{\mathrm{solute}}\ (\frac{kg}{mol})}}{m_{\mathrm{solvent}}\ (\mathrm{kg})} = \frac{K_b\left(\frac{^{\circ}C\ kg}{mol}\right) \times m_{\mathrm{solute}}\ (\mathrm{g}) \times (\frac{1000\ g}{1\ kg})}{M_{\mathrm{solute}}\left(\frac{g}{mol}\right) \times m_{\mathrm{solvent}}\ (\mathrm{g})}$$

$$\boxed{\boldsymbol{\Delta T_b = \frac{K_b \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}}}$$

- The last equation is used to determine "ΔT_b" but with its restriction that the unit of masses is "g"

8.6.3 Freezing point depression

- **Freezing point** is the temperature at which the liquid substance changes its state to solid
- **Normal freezing point** (t°_f) is the temperature at which the liquid substance changes its state to solid at the normal external pressure (1 atm)
- But because the liquid is not pure but contains a solute that is nonvolatile, its molecules cannot freeze at the same temperature when the liquid is pure
- Temperature of the solution must be lowered by a certain value (ΔT_f) to freeze
- The value of ΔT_f is proportional to the solution molality (m):

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f\ m$$

- K_f is the **molal freezing-point depression constant**; its value differs from liquid to another.

$$\Delta T_f = \frac{K_f \times n_{\mathrm{solute}}}{m_{\mathrm{solvent}}\ (\mathrm{kg})}$$

$$\Delta T_f\,(^{o}C) = \frac{K_f\,\left(\frac{\frac{°C}{mol}}{kg}\right) \times \frac{m_{solute}\,(kg)}{M_{solute}\,\left(\frac{kg}{mol}\right)}}{m_{solvent}\,(kg)} = \frac{K_f\left(\frac{°C\,kg}{mol}\right) \times m_{solute}\,(g) \times 1000\,\left(\frac{g}{kg}\right)}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\,(g)}$$

$$\boxed{\mathbf{\Delta T_f = \frac{K_f \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}}}$$

- The last equation is used to determine "ΔT_b" but with its restriction that the unit of masses is "g"

EXAMPLE 8.12

A 7.85-g sample of an unknown compound is dissolved in 301 g of benzene. The freezing point of the solution is 1.05 °C below that of pure benzene. Calculate the molar mass of this compound. (**$K_f = 5.12\ \frac{°C\,kg}{mol}$**)

Solution

$\Delta T_f = 1.05\ °C$

$$\Delta T_f = \frac{K_f\,\frac{°C\,kg}{mol} \times m_{solute}\,(g) \times 1000\frac{g}{kg}}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\,(g)}$$

$$1.05\ °C = \frac{5.12\,\frac{°C\,kg}{mol} \times 7.85\,(g) \times 1000\,\left(\frac{g}{kg}\right)}{M_{solute} \times 301\,(g)}$$

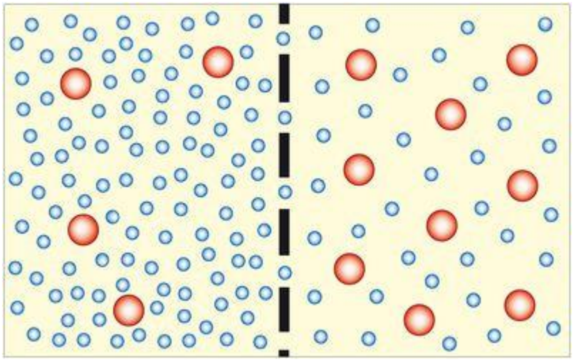
$M_{solute} = 127\ \frac{g}{mol}$

Practice Exercise 8.12

Calculate the boiling and freezing points of a solution containing 478 g of ethylene glycol (Molar mass = 62.01 g/mol) in 3202 g of water. **($M_{ethylene\ glycol}$ = 62.01 g/mol), ($T^{\circ}_{freezing,water}$ = 0 °C), ($T^{\circ}_{boiling,water}$ = 100 °C), ($K_{f,water}$ = 1.86 °C/m, ($K_{b,water}$ = 0.52 °C/m)**

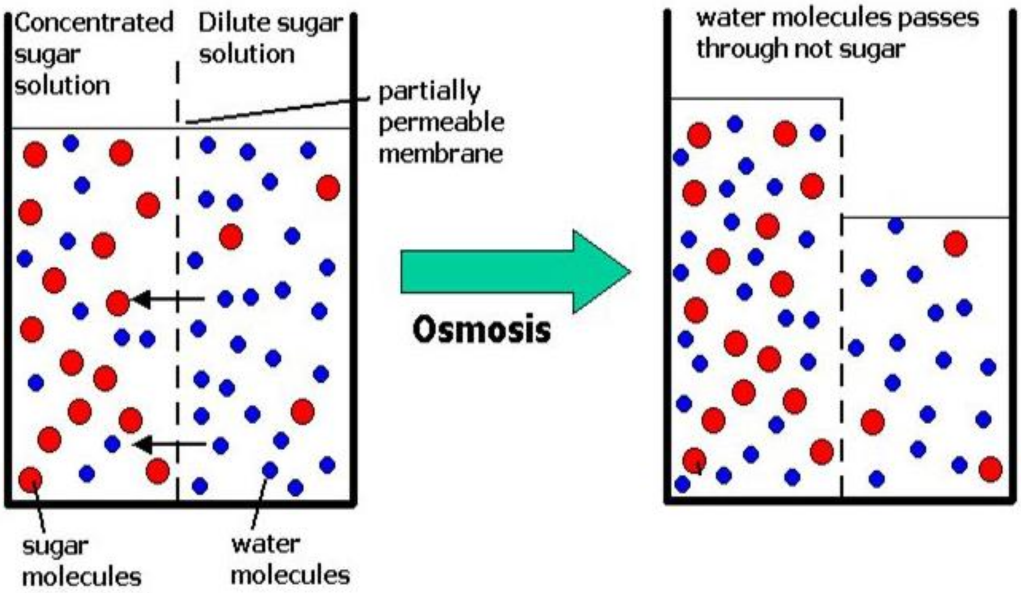
8.6.4 Osmotic pressure

- **What is a semipermeable membrane?**
  - One of the ancient technologies to cool drinking water. is to put it in a pottery pot
  - The walls of the pottery pots permit water inside the to pass through its walls allowing water to be in contact with the colder atmosphere, but does not allow other substances such as ions of other materials to pass through but only allows water
  - Cells' wall of the living creatures depicted below, allow the passage of water from outside to inside and vice versa but not any other materials



  - These walls are named "**semipermeable membranes**" because they allow the passage of solvent molecules and blocks the passage of any solute molecules
- **Osmosis phenomenon**
  - **Osmosis** is the selective passage of **solvent** molecules through a porous membrane or a wall from a dilute solution to a more concentrated one

- First look and inspect the following figure.



- At the middle, there is a **semipermeable membrane**
- Into each compartment a sugar solution is poured
- The volume and temperature of the two sugar solutions are the same but their concentrations are not
- The pressure of water on the right side of the membrane is more than its pressure on the left side
- The amount of water passing through the membrane from right to left will be more than that from left to right
- The surface of the solution in the left side will rise up and that of the right side will falls down
- Eventually, equilibrium is reached, that is when amounts water passing through both sides are the same
- Once this happens the two pressures exerted on both sides of the membrane become equal
- The name of this pressure is **osmotic pressure** and its symbol is "**π**"
- The osmotic pressure (π) of a solution is the pressure required to stop osmosis
- This osmotic pressure of the solution is calculated by the following equation:

$$\pi = M \times R \times T$$

"**M**" is the molarity of the solution and "**T**" is the absolute temperature.

$$\pi = \frac{n}{V} \times R \times T$$

$$\boxed{\pi \times V = n \times R \times T}$$

EXAMPLE 8.13

Calculate the molar concentration of an aqueous solution of an unknown sugar that has an osmotic pressure of 30.0 atm at 25 °C.

Solution

$$M = \frac{\pi}{R \times T} = \frac{30\ \text{atm}}{0.0821\,\frac{\text{atm L}}{\text{mol K}} \times 298\ \text{K}} = 1.23\ \text{mol/L}$$

Practice Exercise 8.13

What is the osmotic pressure (in atm) of a 0.884 M urea solution at 16 °C?

EXAMPLE 8.14

A I L of hemoglobin solution contains 35.0 g of hemoglobin. Calculate the molar mass of hemoglobin if the osmotic pressure is 10.0 mmHg at 25 °C.

Solution

$$M = \frac{\pi}{R \times T} = \frac{10\ \text{mmHg} \times \frac{1\quad \text{atm}}{760\ \text{mmHg}}}{0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 298\ \text{K}} = 5.38 \times 10^{-4}\ \text{mol/L}$$

$$n_{\text{Hb}} = M \times V\ (L) = 5.38 \times 10^{-4}\ \text{mol/L} \times I\ L = 5.38 \times 10^{-4}\ \text{mol}$$

$$M_{\text{Hb}} = \frac{m_{\text{Hb}}}{n_{\text{Hb}}} = \frac{35\ \text{g}}{5.38 \times 10^{-4}\ \text{mol}} = 6.51 \times 10^{4}\ \text{g/mol}$$

Practice Exercise 8.14

A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21 °C. Calculate the molar mass of the polymer.

ANSWERS OF
PRAXTICE EXERCISES

1. CHEMISTRY: THE STUDY OF CHANGE

(Practice Exercise 1.1) 96.5 g
(Practice Exercise 1.2) 341.2 g
(Practice Exercise 1.3) A) 234.22 K and – 37.89 °F, B) 174.44 °C and 447.59 K, C) – 196 °C and – 321.07 °F
(Practice Exercise 1.4) A) 98258.3 Pa and 0.99 bar, B) 466095 Pa and 3469 Torr, C) 135.0 mmHg and 18000 Pa
(Practice Exercise 1.5) A) Two significant figures, B) Four significant figures, C) Three significant figures, D) Two significant figures, E) Three significant figures
(Practice Exercise 1.6) A) 27 L, B) 4.4 g, C) 1.6×10^{7} dm, D) 7.56 × 10–^{2} mL, E) 6.69×10^{4} m,
(Practice Exercise 1.7) 1.07 kg= 2.36 lb
(Practice Exercise 1.8) 1.08×10^{8} dm^{3} = 1.08×10^{5} m^{3}
(Practice Exercise 1.9) $534 \frac{\text{kg}}{\text{m}^3} = 0.534 \frac{\text{g}}{\text{cm}^3}$

2. ATOMS, MOLECULES AND IONS

(Practice Exercise 2.1) number of protons = 29, number of electrons == 29, number of neutrons = 34
(Practice Exercise 2.2) A) Lead(II) oxide, B) Lithium sulfite, C) Manganese(IV) sulfate
(Practice Exercise 2.3) A) $RbSO_4$, B) BaH_2, C) $Al_2(CO_3)_3$
(Practice Exercise 2.4) A) silicon tetrafluoride, B) dichlorine heptoxide
(Practice Exercise 2.5) A) SF_4, B) N_2O_5
(Practice Exercise 2.6) A) hypobromous acid, B) hydrogen sulfate

3. MASS RELATIONSHIPS IN CHEMICAL REACTIONS

(Practice Exercise 3.1) 10.187 amu
(Practice Exercise 3.2) 3.59 mol
(Practice Exercise 3.3) 2569.28 g
(Practice Exercise 3.4) 8.49×10^{21} atoms
(Practice Exercise 3.5) 7.27×10^{23} H atoms
(Practice Exercise 3.6) 1.659 mol
(Practice Exercise 3.7) $32.042 \frac{\text{g}}{\text{mol}}$
(Practice Exercise 3.8) H% = 100 = 2.06%, S% = 32.68%, O% = 65.26%V
(Practice Exercise 3.9) $KMnO_4$
(Practice Exercise 3.10) B_2H_6
(Practice Exercise 3.11) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
(Practice Exercise 3.12) m = 235.02 g H_2O
(Practice Exercise 3.14) m = 0.769 g O_2
(Practice Exercise 3.15) A) moles of actual yield of V = 15.763 mol, B) %yield = 93.09%

4 REACTIONS IN AQUEOUS SOLUTIONS

(Practice Exercise 4.1) A) CuS is insoluble, B) $\mathrm{Ca(OH)_2}$ is insoluble, C) $\mathrm{Zn(NO_3)_2}$ is soluble
(Practice Exercise 4.2) $\mathrm{Al(NO_3)_3(s)} + \mathrm{NaOH(aq)} \rightarrow \mathrm{Al_{aq}^{+3}} + \mathrm{3NO_3}_{\mathrm{aq}}^{+} + \mathrm{Na_{aq}^{+}} + \mathrm{OH_{aq}^{-}}$

(Practice Exercise 4.3) A) $\mathrm{SO_4^{2-}(aq) + 2H^+(aq) \rightarrow H_2SO_4(aq)}$, Because $\mathrm{SO_4^{2-}(aq)}$ accepts protons, it is a Brønsted base, B) $\mathrm{HI(aq) \rightarrow H^+(aq) + I^-(aq)}$, Because$\mathrm{HI(aq)}$ donates protons, it is a Brønsted acid

(Practice Exercise 4.4)

A) $\overset{+3}{\mathrm{P}}\overset{-1}{\mathrm{F}}_3$

$\overset{+7}{\mathrm{Mn}}\overset{-2}{\mathrm{O}}{}_4^-$

(Practice Exercise 4.5) A) Hydrogen displacement, B) Combination reaction, C) Decomposition reaction, D) Metal displacement

(Practice Exercise 4.6) $\mathrm{M = 0.45\ \frac{mol}{L}}$

(Practice Exercise 4.7) $\mathrm{V = 494\ mLv}$

(Practice Exercise 4.8) We take 34.2 mL from the stock solution, then we dilute it with water until its volume reaches 200 mL

(Practice Exercise 4.9) $\mathrm{Br\%\ in\ the\ compound = 92.02\%}$

(Practice Exercise 4.10) $\mathrm{m_{KHB} = 0.382\ g}$

(Practice Exercise 4.11) volume of $\mathrm{H_2SO_4 = 52.4\ mL}$

(Practice Exercise 4.12) $\mathrm{volume_{HI} = 204\ mL}$

5 GASES

(Practice Exercise 5.1) V = 9.29 L

(Practice Exercise 5.2) V = 30.54 L

(Practice Exercise 5.3) P_2 = 4459.7 mmHg

(Practice Exercise 5.4) P_2 = 1.785 atm

(Practice Exercise 5.5) P_2 = 2.62 atm

(Practice Exercise 5.6) d = 13.12 g/Ld = 13.12 g/L

(Practice Exercise 5.7) M = 44.09 g/mol

(Practice Exercise 5.8) B_2H_6

(Practice Exercise 5.9) $V_{\mathrm{NO_2}}$ = 9 L

(Practice Exercise 5.10) V = 37.16 L

(Practice Exercise 5.11) V = 740.150 L

(Practice Exercise 5.12) P_{meth} = 1.286 atm, P_{eth} = 0.066 atm, P_{prop} = 0.018 atm

(Practice Exercise 5.14) M_{uknown} = 19.56 $\frac{\mathrm{g}}{\mathrm{mol}}v$

(Practice Exercise 5.15) This gas is carbon dioxide, because carbon dioxide molar mass is 44 $\frac{\mathrm{g}}{\mathrm{mol}}$, fermentation of glucose produces carbon dioxide

(Practice Exercise 5.16) P = 164.2 atm, Because the real pressure is less than the theoretically calculated pressure, the gas is not an ideal gas.

6 THERMOCHEMISTRY

(Practice Exercise 6.1) w = – 285.55 J

(Practice Exercise 6.2) q = − 34.80 kJ

(Practice Exercise 6.3) ΔE = − 63 J

(Practice Exercise 6.4) Heat evolved = − 6468.91 kJ

(Practice Exercise 6.5) ΔE = − 112.71 kJ

(Practice Exercise 6.6) $q_v = -726.24\ \frac{kJ}{mol}$

(Practice Exercise 6.7) $T_{final} = 21.2\ °C$

(Practice Exercise 6.8) $T_{final} = 22.5\ °C$

(Practice Exercise 6.9) Heat per gram= − 41.83 J/g

(Practice Exercise 6.10) $C(graphite) + 2S(rhombic) \rightarrow CS_2(l)$ $\Delta H^{\circ}_{rxn} = + 86.3\ kJ$

(Practice Exercise 6.11) $C(graphite) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^{\circ}_{f,CH_4(g)} = -74.84\ kJ$

4 QUANTUM THEORY AND THE ELECTRONIC STRUCTURE OF ATOMS

(Practice Exercise 7.1) $\lambda = 1.092 \times 10^2$ m

(Practice Exercise 7.2) $\lambda = 2.63 \times 10^{-1}$ nm

(Practice Exercise 7.3) $\lambda = 5.66 \times 10^{-10}$ m

(Practice Exercise 7.4)

Quantum number	**n**	***l***	**m_l**	**m_s**
First electron	3	1	– 1	$+\frac{1}{2}$
Second electron	3	1	– 1	$-\frac{1}{2}$
Third electron	3	1	0	$+\frac{1}{2}$
Fourth electron	3	1	0	$-\frac{1}{2}$
Fifth electron	3	1	+ 1	$+\frac{1}{2}$
Sixth electron	3	1	+ 1	$-\frac{1}{2}$

(Practice Exercise 7.5)

- The “n” quantum numbers: they are correct for all except the sixth electron because it is in “3p” meaning that “n = 4” is wrong.
- “*l*” quantum numbers: they are correct except the third and the forth electrons. They all must have *l* = 1 because they are in the second subshell, p, which always has *l* = 1.
- The “m_l” quantum numbers: all are correct.
- The “m_s” quantum numbers: all are wrong because Pauli’s principle proved that any two electrons orbiting in the same orbital must have opposite m_s quantum numbers.

(Practice Exercise 7.6) A) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, B) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(Practice Exercise 7.7)

	A	B	C	D
Block	p	p	s	d
Period	2	3	4	5
Group	16	17	1	4
Group name	None	Halogen	Alkali	None

8 SOLUTIONS

(Practice Exercise 8.1) According to the rule “like dissolves like” iodine (I_2) is more soluble in the nonpolar carbon disulfide

(Practice Exercise 8.2) $NaNO_3\% = 10.44\%$

(Practice Exercise 8.3) $X_{NaNO_3} = 0.024$

(Practice Exercise 8.4) molality = 9.29 molal
(Practice Exercise 8.5) molality = 10.76 molal
(Practice Exercise 8.6) molality = 9.29 molal
(Practice Exercise 8.7) Solute% = 0.83%
(Practice Exercise 8.8) A) At 100 ºC, B) At 10 ºC
(Practice Exercise 8.9) $c = 2.86 \times 10^{-4} \frac{\text{mol}}{\text{L atm}}$
(Practice Exercise 8.10) $P_{\text{solution}} = 37.81$ mmHg, $\Delta P = 4.39$ mmHg
(Practice Exercise 8.11) $P_{\text{solution}} = 73.45$ mmHg
(Practice Exercise 8.12) $T_{b,\text{solution}} = 101.25$ °C, $T_{f,\text{solution}} = -4.48$ °C
(Practice Exercise 8.13) $\pi = 20.88$ atm
(Practice Exercise 8.14) $M_{\text{polymer}} = 2.6 \times 10^4$ g/mol

SOLUTIONS OF PRAXTICE EXERCISES

1. CHEMISTRY: THE STUDY OF CHANGW
SOLUTIONS OF PRACICE EXERCISES

Practice exercise 1.1

A piece of platinum with a density of 21.5 $\frac{\mathrm{g}}{\mathrm{cm^3}}$ has a volume of 4.49 $\mathrm{cm^3}$. What is its mass?

Solution

m = d × V = 21.5 $\frac{\mathrm{g}}{\mathrm{cm^3}}$ × 4.49 $\mathrm{cm^3}$ = 95.5 g

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Practice exercise 1.2

The density of sulfuric acid in a certain car battery is 1.41 $\frac{\mathrm{g}}{\mathrm{mL}}$. Calculate the mass of 242 mL of the liquid.

Solution

m = d × V = 1.41 $\frac{\mathrm{g}}{\mathrm{mL}}$ × 242 mL = 341.2 g

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Practice exercise 1.3

A) Convert – 38.83 °C, (the freezing point of mercury) to K and to °F.
B) Convert 346 °F, (the freezing point of nitrogen) to °C and to K.
C) Convert 77 K, (the boiling point of nitrogen) to °C and to °F.

Solution

A) Temperature in K = (Temperature in °C + 273.15 °C) × $\frac{1\ \mathrm{K}}{1\ \mathrm{^\circ C}}$
Temperature in K = (– 38.83 °C + 273.15 °C) × $\frac{1\ \mathrm{K}}{1\ \mathrm{^\circ C}}$ = 234.32 K
Temperature in °F = ($\frac{9\ \mathrm{^\circ F}}{5\ \mathrm{^\circ C}}$ × Temperature in °C) + 32 °F
Temperature in °F = ($\frac{9\ \mathrm{^\circ F}}{5\ \mathrm{^\circ C}}$ × – 38.83 °C) + 32 °F = − 37.89 °F

B) Temperature in °C = (Temperature in °F − 32 °F) × $\left(\frac{5\ \mathrm{^\circ C}}{9\ \mathrm{^\circ F}}\right)$
Temperature in °C = (346 °F − 32 °F) × $\left(\frac{5\ \mathrm{^\circ C}}{9\ \mathrm{^\circ F}}\right)$ = 174.44 °C
Temperature in K = (Temperature in °F + 459.67 °F) × $\frac{5\ \mathrm{K}}{9\ \mathrm{^\circ F}}$
Temperature in K = (346 °F + 459.67 °F) × $\frac{5\ \mathrm{K}}{9\ \mathrm{^\circ F}}$ = 447.59 K

C) Temperature in °C = (Temperature in K − 273.15 K) × $\frac{1\ \mathrm{^\circ C}}{1\ \mathrm{K}}$
Temperature in °C = (77 K − 273.15 K) × $\frac{1\ \mathrm{^\circ C}}{1\ \mathrm{K}}$ = – 196 °C
Temperature in °F = (Temperature in K × $\frac{9\ \mathrm{K}}{5\ \mathrm{^\circ F}}$) – (459.67 K)
Temperature in °F = (77 K × $\frac{9\ \mathrm{K}}{5\ \mathrm{^\circ F}}$) – (459.67 K) = – 321.07 °F

Practice exercise 1.4

A) It is found, in a hot day, that the atmospheric pressure in Riyadh is 737 mmHg. How much is this pressure the SI Units and in “bar” units?
B) If the pressure inside a gaseous cylinder is 4.6 atm, how much is this pressure in the SI Units in Torr.

C) If the pressure outside an airplane at 40000 ft-altitude reads 0.18 bar. What would this pressure be in “mmHg” unit and in the SI Units.

Solution

A) Pressure in Pa = Pressure in mmHg × $\frac{133.322\ \text{Pa}}{1\ \text{mmHg}}$

Pressure in atm = 737 mmHg × $\frac{133.322\ \text{Pa}}{1\ \text{mmHg}}$ = 98258.3 Pa

Pressure in ba = Pressure in mmHg × $\frac{1\ \text{bar}}{750.0617\ \ \text{mmHg}}$ × $\frac{1\ \text{bar}}{100000\ \text{Pa}}$

Pressure in ba = 743 mmHg × $\frac{1\ \text{bar}}{750.0617\ \ \text{mmHg}}$ = 0.99 bar

B) Pressure in Pa = Pressure in atm × $\frac{101325\ \text{Pa}}{1\ \text{atm}}$

Pressure in Pa = 4.6 atm × $\frac{101325\ \text{Pa}}{1\ \text{atm}}$ = 466095 Pa

Pressure in Torr = Pressure in atm × $\frac{760\ \text{Torr}}{1\ \text{atm}}$

Pressure in Torr = 4.6 atm × $\frac{760\ \text{Torr}}{1\ \text{atm}}$ = 3496 Torr

C) Pressure in mmHg = Pressure in bar × $\frac{750.06\ \text{mmHg}}{1\ \text{bar}}$

Pressure in mmHg = 0.18 bar × $\frac{750.06\ \text{mmHg}}{1\ \text{bar}}$ = 135.0 mmHg

Pressure in Pa = Pressure in bar × $\frac{100000\ \ \text{Pa}}{1\ \text{bar}}$

Pressure in Pa = 0.18 bar × $\frac{100000\ \ \text{Pa}}{1\ \text{bar}}$ = 18000 Pa

---

Practice exercise 1.5

Determine the number of significant figures in each of the following measurements:

A) 24 mL B) 3001 g C) 0.0320 m^3

D) 6.4 × 10^4 molecules E) 560 kg

Solution

A) Two, because each digit is a nonzero digit

B) Four, because zeros between nonzero digits are significant

C) Three, because zeros to the left of the first nonzero digit do not count as significant figures

D) Two, because each digit is a nonzero digit

E) This is an ambiguous case. The number of significant figures may be three (5.60×10^2) or two (5.6×10^2)

Practice Exercise 1.6

Carry out the following arithmetic operations and round off the answers to the appropriate number of significant figures and present it in scientific notation:

A) 26.5862 L + 0.17 L B) 9.1 g – 4.682 g C) 7.1 × 10^4 dm × 2.2654 × 10^2 dm

D) 6.54 mL ÷ 85.5542 mL E) 7.55 × 10^4 m – 8.62 × 10^3 m

Solution

A) 25.5862 L + 0.17 L = 2.7 × 10 L

B) 9.1 g – 4.682 g = 4.4 g

C) 7.1 × 10^4 dm × 2.2654 × 10^2 dm = 1.6 × 10^7 dm

D) 6.54 mL ÷ 85.5542 mL = 0.07644 mL = 7.64 × 10^{-2} mL

E) 7.55×10^4 m – 8.62×10^3 m = 5.69×10^4 m

Practice exercise 1.7

An aluminum foil has a mass of 1.07 kg. What is its mass in pounds? $\frac{1\ \text{lb}}{0.4536\ \text{kg}} = 1$

Solution

$1.07\ \text{kg} \times \frac{1\ \text{lb}}{0.4536\ \text{kg}} = 2.36\ \text{lb}$

Practice exercise 1.8

The volume of a room is 1.08×10^8 dm^3. What is the volume in m^3?

$\frac{1\ \text{m}^3}{1000\ \text{dm}^3} = 1$

Solution

$1.08 \times 10^8\ \text{dm}^3 \times \frac{1\ \text{m}^3}{1000\ \text{dm}^3} = 1.08 \times 10^5\ \text{m}^3$

Practice exercise 1.9

The density of the lightest metal, lithium (Li), is 534 $\frac{\text{kg}}{\text{m}^3}$. Convert the density to $\frac{\text{g}}{\text{cm}^3}$. $\frac{1000\ \text{g}}{1\ \text{kg}} = 1$ and $\frac{1\ \text{m}^3}{1000{,}000\ \text{cm}^3} = 1$

Solution

$534\ \frac{\text{kg}}{\text{m}^3} \times (\frac{1000\ \text{g}}{1\ \text{kg}}) \times (\frac{1\ \text{m}^3}{1000{,}000\ \text{cm}^3}) = 0.534\ \frac{\text{g}}{\text{cm}^3}$

2. ATOMS, MOLECULES AND IONS
SOLUTIONS OF PRACICE EXERCISES

Practice exercise 2.1

How many protons, neutrons, and electrons are in the isotope of copper: ${}^{63}_{29}Cu$?

Solution

number of protons = atomic number = 29
number of electrons = number of protons = 29
number of neutrons = mass number – number of protons
number of neutrons = 63 – 29 = 34

Practice exercise 2.2

Name the following compounds:

A) PbO B) Li_2SO_3 C) $Mn(SO_4)_2$

Solution

A) The oxide anion (O^{2-}) has two negative charges, so the lead cation must have two positive charges: the compound **lead(II) oxide**
B) The cation is lithium ion and the anion is sulfite: the compound is **lithium sulfite**
C) The sulfate anion (SO_4^{2-}) has two negative charges, so the manganese cation must have four positive charges: the compound **manganese(IV) sulfate**

Practice exercise 2.3

Write formulas for the following ionic compounds:

A) Rubidium sulfate B) Barium hydride C) Aluminum carbonate

Solution

A) The rubidium ion is Rb^+, and the sulfate anion is SO_4^{2-}: the formula is **Rb_2SO_4**
B) The barium ion is $Ba^{2+,}$, and the hydride ion is H^-: the formula is **BaH_2**
C) The aluminum ion is Al^{3+}, and the carbonate ion is CO_3^{2-}: the formula is **$Al_2(CO_3)_3$**

Practice exercise 2.4

Name the following molecular compounds:

A) SiF_4 B**)** Cl_2O_7

Solution

A) There are one nitrogen atom and three fluorine atoms: the compound is **silicon tetrafluoride**
B) There are two chlorine atoms and seven oxygen atoms: the compound is **dichlorine heptoxide**

Practice exercise 2.5

Write chemical formulas for the following molecular compounds:

A) sulfur tetrafluoride B) dinitrogen pentoxide

Solution

A) There are one sulfur atom and four fluorine atoms: the formula is **SF_4**
B) There are two nitrogen atoms and five oxygen atoms: the formula is **N_2O_5**

Practice exercise 2.6

Name the following oxoacid and oxoanion:

A) HBrO B) HSO_4^-.

Solution

A) The reference acid is Bromic acid ($HBrO_3$). HBrO has two fewer O atoms, it is called **<u>hypobromous acid</u>**

B) The reference acid is H_2SO_4. The anion has one H atom less, HSO_4^-, it is called **<u>hydrogen sulfate</u>**.

3. MASS RELATIONSHIPS IN CHEMICAL REACTIONS
SOLUTIONS OF PRACICE EXERCISES

Practice Exercise 3.1

The abundance of the boron isotope, $^{10}_{5}B$ is 19.78% and of the boron isotope $^{11}_{5}B$ is 80.22%. Calculate the average atomic mass of boron.

Solution

Average atomic mass = $\sum$percent of isotope × atomic mass of isotope

Ave. atomic mass = $\{(\frac{19.78}{100}) \times (10.0129 \text{ amu})\} + \{(\frac{80.22}{100}) \times (11.0093 \text{ amu})\}$

Average atomic mass = 10.187 amu

Practice exercise 3.2

How many moles of magnesium (Mg) are there in 87.3 g of Mg?

Solution

$n = \frac{m}{M} = \frac{87.3 \text{ g}}{24.305 \frac{g}{mol}} = 3.59 \text{ mol}$

Practice exercise 3.3

Calculate the number of grams of lead (Pb) in 12.4 moles of lead.

Solution

$m = n \times M = 12.4 \text{ mole} \times 207.2 \frac{g}{mol} = 2569.28 \text{ g}$

Practice exercise 3.4

Calculate the number of atoms in 0.551 g of potassium (K).

Solution

$$\frac{N}{N_A} = \frac{m}{M}$$

$$\frac{N}{5.022 \times 10^{23} \frac{atoms}{mol}} = \frac{0.551 \text{ g}}{39.098 \frac{g}{mol}}$$

$$N = \frac{0.551 \text{ g} \times 5.022 \times 10^{23} \frac{atoms}{mol}}{39.098 \frac{g}{mol}} = 8.49 \times 10^{21} \text{ atoms}$$

Practice exercise 3.5

How many H atoms are in 72.5 g of isopropanol (rubbing alcohol), C_3H_8O?

Solution

$$\frac{m}{M} = \frac{N}{N_A}$$

$$N = \frac{m \times N_A}{M}$$

$N_{\text{hydrogen atoms}} = 8 \times N_{\text{urea molecules}}$

$$N_{\text{hydrogen atoms}} = 8 \times \frac{m \times N_A}{M} = 8 \times \frac{72.5 \text{ g} \times 5.022 \times 10^{23} \frac{atoms}{mol}}{3 \times 12.01 \frac{g}{mol} + 8 \times 1.008 \frac{g}{mol} + 16 \frac{g}{mol}}$$

$$N_{\text{hydrogen atoms}} = \frac{72.5 \text{ g} \times 5.022 \times 10^{23} \frac{atoms}{mol}}{60.094 \frac{g}{mol}} = 7.27 \times 10^{23} \text{ H atoms}$$

Practice exercise 3.6

Calculate the number of moles of chloroform ($CHCl_3$) in 198 g of $CHCl_3$.

Solution

$$n = \frac{m}{M} = \frac{198\text{ g}}{12.01\,\frac{g}{mol} + 1.008\,\frac{g}{mol} + 3 \times 35.45\,\frac{g}{mol}} = 1.659\text{ mol}$$

Practice Exercise 3.7

Calculate the molar mass (in $\frac{g}{mol}$) of methanol (CH_4O).

Solution

$$M_{CH_4O} = 1 \times 12.01\,\frac{g}{mol} + 4 \times 1.008\,\frac{g}{mol} + 1 \times 16\,\frac{g}{mol} = 32.042\,\frac{g}{mol}$$

Practice exercise 3.8

Calculate the percent composition by mass of each of the elements in sulfuric acid (H_2SO_4).

Solution

$$M_{H_2SO_4} = 2 \times 1.008 + 32.06 + 4 \times 16 = 98.076\,\frac{g}{mol}$$

$$H\% = \frac{2 \times 1.008\,\frac{g}{mol}}{98.076\,\frac{g}{mol}} \times 100 = 2.06\%$$

$$S\% = \frac{1 \times 32.06\,\frac{g}{mol}}{98.076\,\frac{g}{mol}} \times 100 = 32.68\%$$

$$O\% = \frac{4 \times 15.00\,\frac{g}{mol}}{98.076\,\frac{g}{mol}} \times 100 = 65.26\%$$

Practice exercise 3.9

Determine the empirical formula of a compound having the following percent composition by mass: K: 24.75%; Mn: 34.77%; O: 40.51%.

Solution

Each 100 g of ascorbic acid contains 24.75 g of K, 34.77 g of H, and 40.51 g of O. therefore:

$$n_K = \frac{m_K}{M_K} = \frac{24.75\text{ g}}{39.098\,\frac{g}{mol}} = 0.6330\text{ mol}$$

$$n_{Mn} = \frac{m_{Mn}}{M_{Mn}} = \frac{34.77\text{ g}}{54.938\,\frac{g}{mol}} = 0.6329\text{ mol}$$

$$n_O = \frac{m_O}{M_O} = \frac{40.51\text{ g}}{15.00\,\frac{g}{mol}} = 2.532\text{ mol}$$

$$K : Mn : O$$

$$0.6330 : 0.6329 : 2.532$$

$$\frac{0.6330}{0.6329} : \frac{0.6329}{0.63296} : \frac{2.532}{0.6329}$$

$$1 : 1 : 4$$

The simplest (smallest) empirical formula is $KMnO_4$

Practice exercise 3.10

A sample of a compound consisting of boron (B) and hydrogen (H) contains 5.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

Solution

$$n_B = \frac{m_B}{M_B} = \frac{5.444\text{ g}}{10.81\,\frac{g}{mol}} = 0.5961\text{ mol}$$

$n_H = \frac{m_H}{M_H} = \frac{1.803\ g}{1.008\ \frac{g}{mol}} = 1.7887\ mol$

$$\begin{array}{ccc} B & : & H \\ 0.5961 & : & 1.7887 \\ \frac{0.5961}{0.5961} & : & \frac{1.7887}{0.5961} \\ 1 & : & 3 \end{array}$$

The simplest (smallest) empirical formula is BH_3

empirical formula molar mass = 1 × 10.81 + 3 × 1.008 = 13.834 g/mol

$\frac{\text{actual molar mass}}{\text{emperical molar mass}} \quad : \quad \frac{30\ \frac{g}{mol}}{13.834\ \frac{g}{mol}} \approx 2$

The actual molar mass is twice the empirical molar mass. Therefore,

The molecular formula is B_2H_6

Practice exercise 3.11

Balance the equation representing the reaction between iron(III)oxide, Fe_2O_3, and carbon monoxide (CO) to yield iron (Fe) and carbon dioxide (CO_2).

Solution

The unbalanced equation is:

$Fe_2O_3 + CO \rightarrow Fe + CO_2$

There is one C atom on both sides. We leave them as they are. We see two Fe atoms on the left and one Fe atom on the right. Therefore, we multiply Fe on the right by 2:

of $\frac{3}{2}$ in front of O_2 on the reactants side:

$Fe_2O_3 + CO \rightarrow 2Fe + CO_2$

This shows that O element is not balanced. With a careful look we can see that multiplying CO and CO_2 by 3 will balance the equation:

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Practice exercise 3.12

Methanol (CH_3OH) burns in air according to the equation

$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$

If 209 g of methanol are used up in a combustion process, what is the mass of H_2O produced?

Solution

Number of moles of CH_3OH:

$n = \frac{m}{M} = \frac{209\ g}{32.043\ \frac{g}{mol}} = 5.522\ mol$

	$2CH_3OH$	+	$3O_2$	→	$2CO_2$	+	$4H_2O$
Equation moles	2 mole		3 mol		2 mol		4 mol
Question of moles	5.522 mol						X

X = number of moles of $H_2O = \frac{4}{2}$ ×number of moles of $C_6H_{12}O_6$

X = number of moles of H_2O = 2 × 5.522 mol = 13.045 mol

m = n × M = 13.045 mol × 18.016 g/mol = 235.02 g H_2O

Practice exercise 3.13

A key step in photochemical smog formation is the following reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO_2):

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

How many grams of O_2 are consumed to produce 2.21 g of NO_2?

Solution

Number of moles of NO_2 = $\frac{m}{M} = \frac{2.21\ g}{45.007\ \frac{g}{mol}}$ = 0.048 mol NO_2

	$2NO$	+	O_2	→	$2NO_2$
Number of moles	2 mole		1 mol		2 mol
Number of moles given			X		0.048 mol

$X = \frac{1\ mol\ O_2 \times 0.048\ mol\ NO_2}{2\ mol\ NO_2}$ = 0.024 mol O_2

m = n × M = 0.024 mol × 32 g/mol = 0.769 g O_2

Practice exercise 3.14

The reaction between Al and **Fe_2O_3** can generate temperatures approaching 3000 °C and is used in welding metals:

$2Al(g) + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

In one process, 124 g of Al are reacted with 601 g of Fe_2O_3. (A) Calculate the mass (in grams) of Al_2O_3 formed. (B) How much of the excess reagent is left at the end of the reaction?

Solution

Number of moles of Al and Fe_2O_3:

$n_{Al} = \frac{m}{M} = \frac{124\ \ g}{25.982\ \frac{g}{mol}}$ = 4.60 mol Al

$n_{Fe_2O_3} = \frac{m}{M} = \frac{601\ \ g}{159.69\ \frac{g}{mol}}$ = 3.76 mol Fe_2O_3

	$2Al$	+	Fe_2O_3	→	Al_2O_3	+	$2Fe$
Equation moles	2 mol		1 mol		1 mol		
Question moles	4.6 mole		3.76 mol		x		
Number of moles given/coefficient	2.3		3.76				

It is clear from the last row that Al is the limiting reagent.

(A)

	$2Al$	+	Fe_2O_3	→	Al_2O_3	+	$2Fe$
Equation moles	2 mol				1 mol		
Question moles	4.6 mole				X		

$X = \frac{4.6\ mole\ Al \times 1\ mol\ Al_2O_3}{2\ mol\ Al}$ = 2.3 mol Al_2O_3

m = n × M = 2.3 mol × 101.964 g/mol = 234.28 g Al_2O_3

(B)

	$2Al$	+	Fe_2O_3	→	Al_2O_3	+	$2Fe$
Equation moles	2 mol		1 mol		1 mol		
Question moles	4.6 mole		Y		x		

$Y = \frac{4.6\ mole\ Al \times 1\ mol\ Fe_2O_3}{2\ mol\ Al}$ = 2.3 mol Fe_2O_3 reacted

Number of excess moles of Fe_2O_3 = 3.76 mol – 2.3 mol = 1.46 mol

m = n × M = 1.46 mol × 159.69 g/mol = 233.15 g Fe_2O_3

Practice exercise 3.15

Industrially, vanadium metal, which is used in steel alloys, can be obtained by reacting vanadium (V) oxide with calcium at high temperatures:

$5Ca + V_2O_5 \rightarrow 5CaO + 2V$

In one process, 1.54×10^3 g of V_2O_5 react with 1.96×10^3 g of Ca. A) Calculate the theoretical yield of V. B) Calculate the percent yield if 803 g of V are obtained.

Solution

A)

<u>First,</u> we calculate the number of moles of reactants

number of moles of V_2O_5 = $\frac{\mathrm{m}}{\mathrm{M}} = \frac{1.54 \times 10^3\ \mathrm{g}}{181.884\ \frac{\mathrm{g}}{\mathrm{mol}}}$ = 8.467 mol

number of moles of Ca = $\frac{\mathrm{m}}{\mathrm{M}} = \frac{1.96 \times 10^3\ \mathrm{g}}{40.078\ \frac{\mathrm{g}}{\mathrm{mol}}}$ = 48.905 mol

number of moles of actual yield of V of = $\frac{\mathrm{m}}{\mathrm{M}} = \frac{803\ \mathrm{g\ g}}{50.942\ \frac{\mathrm{g}}{\mathrm{mol}}}$ = 15.763 mol

<u>Second,</u> we determine the limiting reactant

	$5Ca$	+	V_2O_5	→	$5CaO$	+	$2V$
Equation moles	5		1				
Question moles	48.905		8.467				
Number of moles given/coefficient	9.781		8.467				

It is clear from the last row that V_2O_5 is the limiting reagent.

<u>Finally</u>, we calculate the theoretical yield of V

	$5Ca$	+	V_2O_5	→	$5CaO$	+	$2V$
Equation moles			1				2
Question moles			8.467				X

Theoretical yield of V = $\frac{8.467\ \mathrm{mol} \times 2\ \mathrm{mol}}{1\ \mathrm{mol}}$ = 15.934 mol

B)

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

%yield = $\frac{15.763\ \mathrm{mol}}{15.934\ \mathrm{mol}} \times 100$ = 93.09%

4. REACTIONS IN AQUEOUS SOLUTIONS
SOLUTIONS OF PRACICE EXERCISES

Practice exercise 4.1

Classify the following ionic compounds as soluble or insoluble:

A) CuS B) $Ca(OH)_2$ C) $Zn(NO_3)_2$

Solution

According to the table given in lecture:

A) CuS is insoluble
B) $Ca(OH)_2$ is insoluble
C) $Ca(OH)_2$ is soluble

Practice exercise 4.2

Write the net ionic equation for the reaction an $Al(NO_3)_3(s)$ solution with a NaOH **Solution**

According to the table given in lecture $Al(NO_3)_3(s) + NaOH(aq) \rightarrow$ is water-soluble:

$Al(NO_3)_3(s) + NaOH(aq) \rightarrow Al^{+3}_{aq} + 3NO_3{}^{+}_{aq} + Na^{+}_{aq} + OH^{-}_{aq}$

Practice exercise 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:

A) SO_4^{2-} B) HI

Write the net ionic equation for the reaction an $Al(NO_3)_3(s)$ solution with a NaOH **Solution**

A) $SO_4^{2-}(aq) + 2H^+(aq) \rightarrow H_2SO_4(aq)$
Because $SO_4^{2-}(aq)$ accepts protons, it is a Brønsted base

B) $HI(aq) \rightarrow H^+(aq) + I^-(aq)$
BecauseHI(aq) donates protons, it is a Brønsted acid

Practice exercise 4.4

Assign oxidation numbers to all the elements in the following compound and ion:

A) PF_3 B) MnO_4^-

Solution

A) $\overset{+3}{P}\overset{-1}{F}_3$

B) $\overset{+7}{Mn}\overset{-2}{O}_4^-$

Practice exercise 4.5

Identify the following redox reactions by type:

E) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
F) $S + 3F_2(aq) \rightarrow Pb + SF_6$
G) $2CuCl \rightarrow Cu + CuCl_2(aq)$
H) $2Ag + PtCl_2 \rightarrow 2AgCl + Pt$

Solution

A) Hydrogen displacement
B) Combination reaction
C) Decomposition reaction

D) Metal displacement

Practice exercise 4.6
Calculate the molarity of an 85.0-mL ethanol (C_2H_5OH) solution containing 1.77 g of ethanol?
Solution

$$M = \frac{n_{solte}}{V_{solution}\ (L)} = \frac{\frac{m_{solte}}{M_{solte}}}{V_{solution}\ (L)} = \frac{\frac{1.77\ g}{46\ \frac{g}{mol}}}{0.085\ L} = 0.45\ \frac{mol}{L}$$

Practice exercise 4.7
Calculate the volume, in mL, of a 0.315 M NaOH solution containing 5.22 g of NaOH?
Solution

$$V = \frac{n_{solte}}{M} = \frac{\frac{m_{solte}}{M_{solte}}}{M} = \frac{\frac{5.22\ g}{40\ \frac{g}{mol}}}{0.315\ \frac{mol}{L}} = 0.494\ L = 494\ mL$$

Practice exercise 4.8
How would you prepare 200 mL of a 0.866 M NaOH solution, starting with a 5.07 M stock solution?
Solution

$M_{initial} \times V_{initial} = M_{final} \times V_{final}$

$5.07\ M \times V_{initial} = 0.866\ M \times 200\ mL$

$V_{initial} = \frac{0.866\ M \times 200\ mL}{5.07\ M} = 34.2\ mL$

We take 34.2 mL from the stock solution, then we dilute it with water until its volume reaches 200 mL

Practice exercise 4.9
A sample of 0.3220 g of an ionic compound containing the bromide ion (Br^-) is dissolved in water and treated with an excess of $AgNO_3$. If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?
Solution

Molar $mass_{Br} = 79.9\ \frac{g}{mol}$ and Molar $mass_{AgBr} = 187.8\ \frac{g}{mol}$

Therefore, the percent by mass of Br in AgBr is given by

$$Br\%\ in\ AgBr = \frac{79.9\ \frac{g}{mol}}{187.8\ \frac{g}{mol}} \times 100 = 42.55\%$$

mass of Br in AgBr $= 0.42552 \times 0.6964\ g = 0.2963\ g$

$$Br\%\ in\ the\ compound = \frac{0.2963\ g}{0.3220\ g} \times 100 = 92.02\%$$

Example 4.10
How many grams of KHP are needed to neutralize 18.64 mL of a 0.1004 M NaOH solution?
Solution

$n_{NaOH} = 0.1004\ \frac{mol}{L} \times 18.64\ mL \times \frac{1\ L}{1000\ mL} = 1.872 \times 10^{-3}\ mol$

Because1 mol NaOH ≡ 1 mol KHP, there must be 1.872×10^{-3} mol of KHB

$m_{KHB} = n_{KHB} \times M_{KHB} = 1.872 \times 10^{-3}\ mol \times 204.2\ \frac{g}{mol} = 0.382\ g$

Practice exercise 4.11

Calculate the volume of a 1.28 M H_2SO_4 solution needed to neutralize 60.2 mL of a 0.427 M KOH solution.

Solution

$n_{KOH} = 0.427\ \frac{mol}{L} \times 60.2\ mL \times \frac{1\ L}{1000\ mL} = 2.57 \times 10^{-2}$ mol

Because 1 mol KOH ≡ 0.5 mol H_2SO_4, there must be 1.285×10^{-2} mol of H_2SO_4

volume of $H_2SO_4 = \frac{1.285 \times 10^{-2}\ mol}{1.28 \frac{mol}{1\ L,solution}} = 0.01\ L = 10\ mL$

Practice exercise 4.12

How many milliliters of a 0.206 M HI solution are needed to reduce 22.5 mL of a 0.374 M $KMnO_4$ solution according to the following equation:

$$10HI + 2KMnO_4 + 3H_2SO_4 \rightarrow 5I_2 + 2K_2SO_4 + 8H_2O$$

Solution

$n_{KMnO_4} = \frac{0.374\ mol \times 22.5\ mL,solution}{1000\ mL,solution} = 8.415 \times 10^{-3}$ mol

Because 10 mol HI ≡ 2 mol MnO_4^-, n_{HI} can be calculated:

$n_{HI} = \frac{8.415 \times 10^{-3}\ mol\ mol\ KMnO_4 \times 10\ mol\ HI}{2\ mol\ KMnO_4} = 4.207 \times 10^{-2}$ mol HI

$volume_{HI} = \frac{4.207 \times 10^{-2}\ mol\ HI}{0.206 \frac{mol\ HI}{1\ L,solution}} = 0.204\ L = 204\ mL$

5. GASES
SOLUTIONS OF PRACICE EXERCISES

Practice exercise 5.1

Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 5.54 atm and 76 °C.

Solution

Because n, P and T are all known, we can use the ideal gas equation to calculate V:

$$V = \frac{n \times R \times T}{P} = \frac{2.12\ \text{mol} \times 0.0821\,\frac{\text{L atm}}{\text{K mol}} \times (76\ ^\circ\text{C} + 273\ ^\circ\text{C}) \times \frac{1\ \text{K}}{1\ ^\circ\text{C}}}{5.54\ \text{L}} = 9.29\ \text{L}$$

Practice exercise 5.2

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

Solution

$$V = \frac{n \times R \times T}{P} = \frac{\frac{49.8\ \text{g}}{35.45\,\frac{\text{g}}{\text{mol}}} \times 0.0821\,\frac{\text{L atm}}{\text{K mol}} \times 273\ \text{K}}{1\ \text{atm}} = 30.54\ \text{L}$$

Practice exercise 5.3

A sample of Cl_2(g) occupies 946 mL at 726 mmHg. Calculate its pressure (in mmHg) if the volume is reduced at constant temperature to 154 mL.

Solution

$P_1 \times V_1 = P_2 \times V_2$

726 mmHg × 946 mL = P_2 × 154 mL

P_2 = 4459.7 mmHg

Practice exercise 5.4

A sample of O_2(g) initially at 0.97 atm is heated from 21 °C to 268 °C at constant volume. What is its final pressure?

Solution

At constant n and V: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{0.97\ \text{atm}}{(21\ ^\circ\text{C} + 273\ ^\circ\text{C}) \times \frac{1\ \text{K}}{1\ ^\circ\text{C}}} = \frac{P_2}{(268\ ^\circ\text{C} + 273\ ^\circ\text{C}) \times \frac{1\ \text{K}}{1\ ^\circ\text{C}}}$$

P_2 = 1.785 atm

Practice exercise 5.5

A gas initially at 4.0 L, 1.2 atm, and 66 °C undergoes a change so that its final volume and temperature are 1.7 L and 42 °C. What is its final pressure? Assume the number of moles remains unchanged.

Solution

At constant n: $\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$

$$\frac{1.2\ \text{atm} \times 4.0\ \text{L}}{(66\ ^\circ\text{C} + 273\ ^\circ\text{C}) \times \frac{1\ \text{K}}{1\ ^\circ\text{C}}} = \frac{P_2 \times 1.7\ \text{L}}{(42\ ^\circ\text{C} + 273\ ^\circ\text{C}) \times \frac{1\ \text{K}}{1\ ^\circ\text{C}}}$$

$$P_2 = \frac{1.2\ \text{atm} \times 4.0\ \text{L} \times 315\ \text{K}}{339\ \text{K} \times 1.7\ \text{L}}$$

P_2 = 2.62 atm

Practice exercise 5.6

What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62 °C?

Solution

$$P \times M = d \times R \times T$$

$$779\ \text{mmHg}\ \frac{1\ \text{atm}}{760\ \text{mmHg}} \times 352.018\ \frac{\text{g}}{\text{mol}} = d \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 335\ \text{K}$$

$$d = 13.12\ \text{g/L}$$

Practice exercise 5.7

The density of a gaseous organic compound is 3.38 g/L at 40 °C and 1.97 atm. What is its molar mass?

Solution

$$P \times M = d \times R \times T$$

$$1.97\ \text{atm} \times M = 3.38\ \text{g/L} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times (40\ °\text{C} + 273\ °\text{C})\ \frac{1\ \text{K}}{1\ °\text{C}}$$

$$M = 44.09\ \text{g/mol}$$

Practice exercise 5.8

A gaseous compound is 78.14 percent boron (B) and 21.86 percent hydrogen (H). At 27 °C, 74.3 mL of the gas exerted a pressure of 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

Solution

<u>First</u>, we find the empirical formula and its molar mass

$$\text{B} \quad : \quad \text{H}$$

$$\frac{78.14\ \text{g}}{10.81\ \frac{\text{g}}{\text{mol}}} \quad : \quad \frac{21.86\ \text{g}}{1.008\ \frac{\text{g}}{\text{mol}}}$$

$$7.228\ \text{mol} : 21.69\ \text{mol}$$

$$\frac{7.228\ \text{mol}}{7.228\ \text{moll}} \quad : \quad \frac{21.69\ \text{mol}}{7.228\ \text{mol}}$$

$$1 \quad : \quad 3$$

The empirical formula is: “BH_3”

Molar mass of the empirical formula = $10.81\ \frac{\text{g}}{\text{mol}} + 3 \times 1.008\ \frac{\text{g}}{\text{mol}}$

Molar mass of the empirical formula = $13.834\ \frac{\text{g}}{\text{mol}}$

<u>Second</u>, we find the actual molar mass

$$P \times M = \frac{m}{V} \times R \times T$$

$$1.12\ \text{atm} \times M = \frac{0.0934\ \text{g}}{74.3\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times (27\ °\text{C} + 273\ °\text{C})\ \frac{1\ \text{K}}{1\ °\text{C}}$$

$$M = 27.64\ \text{g/mol}$$

<u>Third,</u> we divide the molecular molar mass by the empirical molar mass,

$$\frac{m}{V} = \frac{27.64\ \frac{\text{g}}{\text{mol}}}{13.834\ \frac{\text{g}}{\text{mol}}} = 1.999 \approx 2$$

The molecular formula = 2 × the empirical formula = B_2H_6

Practice exercise 5.9

The equation of the reaction between nitric oxide and oxygen is:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

If 9.0 L of NO reacted with excess O_2 at certain T and P, calculate the volume and the number of moles of the NO_2 produced?

Solution

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

2 mol 2 mol

2 L 2 L

9 L V_{NO_2}

$$V_{NO_2} = \frac{9\ \mathrm{L} \times 2\ \mathrm{L}}{2\ \mathrm{L}} = 9\ \mathrm{L}$$

Practice exercise 5.10

Sodium azide (NaN_3), used in some automobile air bags, decomposes as follows:

$2NaN_3(g) \rightarrow 2Na(s) + 3N_2(g)$

The nitrogen gas produced quickly inflates the bag. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3.

Solution

$$n_{NaN_3} = \frac{60\ \mathrm{g}}{65.02\ \frac{\mathrm{g}}{\mathrm{mol}}} = 0.923\ \mathrm{mol}$$

$2NaN_3(g) \rightarrow 2Na(s) + 3N_2(g)$

2 mol 3 mol

0.923 mol X

$$X = \frac{0.923\ \mathrm{mol} \times 3\ \mathrm{mol}}{2\ \mathrm{mol}} = 1.385\ \mathrm{mol}$$

$$V = \frac{n \times R \times T}{P} = \frac{1.3885\ \mathrm{mol} \times 0.0821\ \frac{\mathrm{atm\ L}}{\mathrm{mol\ K}} \times (80 + 273)\ \mathrm{K}}{823\ \mathrm{mmHg} \times \frac{1\ \mathrm{atm}}{760\ \mathrm{mmHg}}} = 37.16\ \mathrm{L}$$

Practice exercise 5.11

The combustion equation of methane is:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

If 15.0 moles of methane are reacted, calculate the volume of CO_2 produced at 23.0 °C and 0.985 atm?

Solution

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

1 mol 1 mol

15 mol X

$$X = \frac{15\ \mathrm{mol} \times\ 1\ \mathrm{mol}}{1\ \mathrm{mol}} = 15\ \mathrm{mol}$$

$$V = \frac{n \times R \times T}{P} = \frac{15\ \mathrm{mol} \times 0.0821\ \frac{\mathrm{atm\ L}}{\mathrm{mol\ K}} \times 296\ \mathrm{K}}{0.985\ \mathrm{atm}} = 370\ \mathrm{L}$$

Practice exercise 5.12

A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Solution

$$X_{\mathrm{methane}} = \frac{8.24\ \mathrm{mol}}{8.24\ \mathrm{mol} + 0.421\ \mathrm{mol} + 0.116\ \mathrm{mol}} = 0.939$$

$X_{\text{ethane}} = \frac{0.421\ \text{mol}}{8.24\ \text{mol}+0.421\ \text{mol} + 0.116\ \text{mol}} = 0.048$

$X_{\text{propane}} = \frac{0.116\ \text{mol}}{8.24\ \text{mol}+0.421\ \text{mol} + 0.116\ \text{mol}} = 0.013$

Pressure of any gas in the mixture = its mole fraction × total pressure

$P_{\text{meth}} = 0.939 \times 1.37\ \text{atm} = 1.286\ \text{atm}$

$P_{\text{eth}} = 0.048 \times 1.37\ \text{atm} = 0.066\ \text{atm}$

$P_{\text{prop}} = 0.013 \times 1.37\ \text{atm} = 0.018\ \text{atm}$

Practice Exercise 5.13

Hydrogen gas generated when calcium metal reacts with water is collected as shown in the previous figure. The volume of gas collected at 30°C and 988 mmHg is 641 mL. What is the mass of the $H_2(g)$ obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

Solution

$P_{\text{Total}} = P_{\text{hydrogen}} + P_{\text{water vapor}}$

$P_{\text{hydrogen}} = 988\ \text{mmHg} - 31.82\ \text{mmHg} = 955.18\ \text{mmHg}$

$$n = \frac{P \times V}{R \times T} = \frac{955.18\ mmHg \times \frac{1\ atm}{760\ mmHg} \times 641\ mL \times \frac{1\ L}{1000\ mL}}{o.0821\ \frac{atm\ L}{mol\ K} \times 303\ \text{K}} = 3.24 \times 10^{-2}\ \text{mol}$$

$$m = 3.24 \times 10^{-2}\ \text{mol} \times 2.016\ \frac{\text{g}}{\text{mol}} = 5.54 \times 10^{-2}\ \text{g}$$

Practice exercise 5.14

It is found that the value of U_{rms} of an unknown gas is 1.5 times the value of U_{rms} of $CO_2(g)$ at the same temperature. Calculate the molar mass of the unknown gas.

Solution

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$U_{\text{rms,uknown}} = \sqrt{\frac{3RT}{M_{\text{uknown}}}}$$

$$U_{\text{rms},CO_2} = \sqrt{\frac{3RT}{M_{CO_2}}}$$

$$\frac{U_{\text{rms,uknown}}}{U_{\text{rms},CO_2}} = \frac{\sqrt{\frac{3RT}{M_{\text{uknown}}}}}{\sqrt{\frac{3RT}{M_{CO_2}}}}$$

$$\frac{1.5 \times U_{\text{rms},CO_2}}{U_{\text{rms},CO_2}} = \sqrt{\frac{M_{CO_2}}{M_{\text{uknown}}}}$$

$$1.5 = \sqrt{\frac{44\ \frac{\text{g}}{\text{mol}}}{M_{\text{uknown}}}}$$

$$M_{\text{uknown}} = 19.56\ \frac{\text{g}}{\text{mol}}$$

Practice exercise 5.15

A gas evolved from the fermentation of glucose effuses through a porous wall in 15.0 min. Under the same T and P, it takes 12.0 min for an equal volume of N_2 to effuse through the same wall. Calculate the molar mass of the gas and suggest what the gas might be.

Solution

$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

$r_1 = \frac{V_1}{Time_1}$ and $r_2 = \frac{V_2}{Time_2}$

$V_1 = V_2$

$r_1 = \frac{V_1}{Time_1}$ and $r_2 = \frac{V_1}{Time_2}$

$\frac{\frac{V_1}{Time_1}}{\frac{V_1}{Time_2}} = \sqrt{\frac{M_2}{M_1}}$

$\frac{Time_2}{Time_1} = \sqrt{\frac{M_2}{M_1}}$

$\frac{15 \text{ min}}{12 \text{ min}} = \sqrt{\frac{M_2}{28.014 \frac{g}{mol}}}$

$(1.25)^2 = \frac{M_2}{28.014 \frac{g}{mol}}$

$M_2 = 43.77 \frac{g}{mol}$

This gas is carbon dioxide, because carbon dioxide molar mass is 44 $\frac{g}{mol}$, fermentation of glucose produces carbon dioxide.

Practice exercise 5.16

At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

Solution

Calculation of the pressure if the gas is ideal:

$P = \frac{n \times R \times T}{V}$

$P = \frac{10 \text{ mol} \times 0.0821 \frac{\text{atm L}}{\text{mol K}} \times 300 \text{ K}}{1.5 \text{ L}} = 164.2 \text{ atm}$

Because the real pressure is less than the theoretically calculated pressure, the gas is not an ideal gas.

6. THERMOCHEMISTRY
SOLUTIONS OF PRACICE EXERCISES

Practice Exercise 6.1

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands against a constant pressure of 4.00 atm

Solution

$w = -P \times \Delta V = -4.0\ \text{atm} \times \frac{101325\ \text{Pa}}{\text{atm}} \times (971 - 264)\ \text{mL} \times \frac{1\ \text{m}^3}{1000000\ \text{mL}}$

$w = -285.55\ \text{J}$

Practice Exercise 6.2

An iron bar (s = 0.45 J/g °C) of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

Solution

$q = m \times s \times \Delta t$

$q = 869\ \text{g} \times 0.45\ \frac{\text{J}}{\text{g °C}} \times (5 - 94)\ \text{°C}$

$q = -34803.45\ \text{J}$

$q = -34803.45\ \text{J} \times \frac{\text{kJ}}{1000\ \text{J}}$

$q = -36.80\ \text{kJ}$

Practice Exercise 6.3

A gas expands and does P - V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

Solution

$\Delta E = q + w$

$\Delta E = (+216\ \text{J}) + (-279\ \text{J})$

$\Delta E = -63\ \text{J}$

Practice Exercise 6.4

Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -3013\ \text{kJ/mol}$

Solution

Given moles of $P_4 = \frac{266\ \text{g}}{4 \times 30.974 \frac{\text{g}}{\text{mol}}} = 2.147\ \text{mol}$

	P_4	+	$5O_2$	→	P_4O_{10}	ΔH
Equation moles	1 mol					– 3013 kJ
Givnen moles	2.147 mol					Heat evolved

Heat evolved $= \frac{-3013\ \text{kJ} \times 2.147\ \text{mol}\ P_4}{1\ \text{mol}\ SO_2} = -6468.91\ \text{kJ}$

Practice Exercise 6.5

What is ΔE for the formation of 1 mole of CO at 1 atm and 258 °C?

C(graphite) + $\frac{1}{2}$$O_2(g) \rightarrow CO(g)$ ΔH = –110.5 kJ

Solution

$\Delta E = \Delta H - R \times T \times \Delta n_g$

$\Delta n_g = (1\text{ mol}) - (\frac{1}{2}\text{ mol}) = \frac{1}{2}\text{ mol}$

$\Delta E = (-110.5\text{ kJ}) - (8.314\,\frac{\text{J}}{\text{mol K}} \times \frac{1\text{ kJ}}{1000\text{ J}} \times 531\text{ K} \times 0.5\text{ mol})$

$\Delta E = -\,112.71\text{ kJ}$

Practice Exercise 6.6

A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. The temperature of the water rose by 6.20 °C. Calculate the molar heat of combustion of methanol. (Heat capacity of the bomb plus water = 10.4 kJ/°C), (molar mass of methane = 32 g/mol

Solution

$q_v = C_v \times \Delta T$

$q_v = -\,q_{\text{calorimeter}} = -\,10.4\,\frac{\text{kJ}}{°\text{C}} \times 6.2\,°\text{C} = -\,43.68\,\frac{\text{kJ}}{1.435\text{ g}}$

$$q_v = -\,43.68\,\frac{\text{kJ}}{1.922\text{ g}} \times 32\,\frac{\text{g}}{\text{mol}} = -\,726.24\,\frac{\text{kJ}}{\text{mol}}$$

Practice Exercise 6.7

A stainless steel-ball with mass of 30.14 g at 116.82°C was placed in a constant-pressure calorimeter of negligible heat capacity containing = 120.0 g of water at 18.44°C. If the specific heat of the ball is 0.474 $\frac{\text{J}}{\text{g °C}}$, calculate the final temperature of the water.

Solution

$q_{\text{water}} = s_{\text{water}} \times m_{\text{water}} \times \Delta T_{\text{water}}$

$q_{\text{water}} = 6.184\,\frac{\text{J}}{\text{g °C}} \times 120\text{ g} \times (T_{\text{final}} - 18.44\,°\text{C}) = 502.8\,\frac{\text{J}}{°\text{C}} \times (T_{\text{final}} - 18.44\,°\text{C})$

$q_{\text{lead}} = s_{\text{lead}} \times m_{\text{lead}} \times \Delta T_{\text{lead}}$

$q_{\text{lead}} = 0.474\,\frac{\text{J}}{\text{g °C}} \times 30.14\text{ g} \times (T_{\text{final}} - 116.82\,°\text{C}) = 16.286\,\frac{\text{J}}{°\text{C}} \times (T_{\text{final}} - 116.82\,°\text{C})$

$q_{\text{water}} = -\,q_{\text{lead}}$

$502.8\,\frac{\text{J}}{°\text{C}} \times (T_{\text{final}} - 18.44\,°\text{C}) = -\,16.286\,\frac{\text{J}}{°\text{C}} \times (T_{\text{final}} - 116.82\,°\text{C})$

$502.8\,\frac{\text{J}}{°\text{C}} \times T_{\text{final}} - 9271.63\text{ J} = -\,16.286\,\frac{\text{J}}{°\text{C}} \times T_{\text{final}} + 1683.18\,J$

$502.8\,\frac{\text{J}}{°\text{C}} \times T_{\text{final}} + 16.286\,\frac{\text{J}}{°\text{C}} \times T_{\text{final}} = 9271.63\text{ J} + 1683.18\text{ J}$

$516.086\,\frac{\text{J}}{°\text{C}} \times T_{\text{final}} = 10956.81\text{ J}$

$T_{\text{final}} = 21.2\,°\text{C}$

Practice Exercise 6.8

A 400 mL of 0.6 M HNO_3 was mixed with 400 mL of 0.3 M $Ba(OH)_2$ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at

18.46°C. What is the final temperature of the solution? Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 6.184 J/g °C, respectively)

Solution

$\mathrm{H^+(aq) + NO_3^-(aq) + \frac{1}{2}Ba^{2+}(aq) \ + \ OH^-(aq) \ \rightarrow \ \frac{1}{2}Ba^{2+}(aq) \ + \ NO_3^-(aq) + \ H_2O(l)}$

$\mathrm{H^+(aq) \ + \ OH^-(aq) \ \rightarrow \ H_2O(l)}$

From exercise 7.8: “$\mathbf{H^+(aq) \ + \ OH^-(aq) \ \rightarrow \ H_2O(l)\Delta H \ = -\ 56.200\frac{kJ}{mol}}$”

$\mathrm{n_{water\ produced} \ = \ n_{HNO_3\ consumed} \ = \ 0.6\ \frac{mol}{L} \ \times \ 0.4\ L \ = \ 0.24\ mol}$

$\mathrm{q_{reaction}}$ = Heat produced = $-$ 55.2 kJ $\times$ $\frac{0.24\ \mathrm{mol}}{1\ \mathrm{mol}}$ = $-$ 13.488 kJ

$\mathrm{q_{solution} \ = \ -\,q_{reaction} \ = \ +\,13.488\ kJ \ = \ 13488\ J}$

$\mathrm{q_{solution} \ = \ s_{solution} \ \times \ m_{solution} \ \times \ \Delta T_{solution}}$

$\mathrm{13488\ J \ = \ 4.184\ \frac{J}{g\ °C} \ \times (400\ g + 400\ g) \times \ (T_{final} \ - \ 18.46\ °C)}$

$\mathrm{T_{final} = \ 22.5\ °C}$

Practice exercise 6.9

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kJ/g of benzene. $\Delta H^{\circ}_{\mathrm{f,carbon\ dioxide}(l)}$ = $-$ 393.5 kJ/mol, $\Delta H^{\circ}_{\mathrm{f,water}(l)}$ = $-$ 285.8 kJ/mol, and $\Delta H^{\circ}_{\mathrm{f,benzene}(l)}$ = 49.04 kJ/mol.

Solution

$C_6H_6(l) + 7.5O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ $\qquad \Delta H = ?$

$\Delta H^{\circ}_{\mathrm{rxn}} = \Sigma\Delta H^{\circ}_{\mathrm{f}}(\text{products}) - \Sigma\Delta H^{\circ}_{\mathrm{f}}(\text{reactants})$

$\Delta H^{\circ}_{\mathrm{rxn}} = [6\Delta H^{\circ}_{\mathrm{f}}(CO_2) + 3\Delta H^{\circ}_{\mathrm{f}}(H_2O)] - [\Delta H^{\circ}_{\mathrm{f}}(C_6H_6) + 7.5\Delta H^{\circ}_{\mathrm{f}}(O_2)]$

$\Delta H^{\circ}_{\mathrm{rxn}}$ = (6 mol × − 393.5 kJ/mol + 3 mol × − 285.8 kJ/mol) – (7.5 mol × 0 + 1 mol × 49.04 kJ/mol) = – 3267.44 kJ/mol of C_6H_6 reacted

Molar mass of C_6H_6= 6 × 12.011 + 6 × 1.008 = 78.114 g/mol

$\Delta H^{\circ}_{\mathrm{rxn}}$ = – 3267.44 kJ/78.114 g

Heat per gram = $\frac{-\ 3267.44\ \mathrm{kJ}}{78.114\ \mathrm{g}}$ = − 41.83 J/g

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Practice exercise 6.10

Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that:

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = -\ 393.5$ kJ

$S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g)$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = -\ 295.4$ kJ

$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = -\ 1073.6$ kJ

Solution

Formation reaction of $Cs_2(l)$ is:

$C(\text{graphite}) + 2S(\text{rhombic}) \rightarrow CS_2(l)$ $\qquad \Delta H^{\circ}_{\mathrm{f}} = ?$

Careful look at the desired equation indicates that the first and the second equations must be kept as they are; the second equations must be multiplied by 2, and third equations must be revered:

$C(\text{graphite}) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)}$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = -\ 393.5$ kJ

$2S(\text{rhombic}) + \cancel{2O_2(g)} \rightarrow \cancel{2SO_2(g)}$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = -\ 592.8$ kJ

$\cancel{CO_2(g)} + \cancel{2SO_2(g)} \rightarrow CS_2(l) + \cancel{3O_2(g)}$ $\qquad \Delta H^{\circ}_{\mathrm{rxn}} = +\ 1073.6$ kJ

$C(graphite) + 2S(rhombic) \rightarrow CS_2(l)$ $\Delta H^\circ_{rxn} = +87.3$ kJ

Practice exercise 6.11

From the following reactions, calculate $\Delta H^\circ_{f,CH_4(g)}$:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ = -890.34$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ = -285.84$ kJ

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ kJ

Solution

The formation reaction of $CH_4(g)$ is:

$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^\circ_{f,CH_4(g)} = ?$

We need to find $\Delta H^\circ_{f,CH_4(g)}$

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$ $\Delta H^\circ = +890.34$ kJ

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H^\circ = -571.68$ kJ

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ kJ

$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^\circ_{f,CH_4(g)} = -74.84$ kJ

7. QUANTUM THEORY AND THE ELECTRONIC STRUCTURE OF ATOMS
SOLUTIONS OF PRACICE EXERCISES

Practice Exercise 7.1

Calculate the wavelength (in m) of an electromagnetic wave if its frequency is 3.64×10^7 Hz

Solution

$\lambda = C\nu = 3.00 \times 10^8 \frac{m}{s} \times 3.64 \times 10^7 \frac{1}{s} = 1.092 \times 10^{16}$ m

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Practice Exercise 7.2

Calculate the wavelength (in nanometers) of a photon emitted during a transition from $n_{initial} = 6$ state to the $n_{final} = 4$ state in the hydrogen atom.

$$\Delta E = R_H \times (\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2}) = 2.18 \times 10^{-18} \text{ J} \times (\frac{1}{36} - \frac{1}{16}) = -7.57 \times 10^{-20} \text{ J}$$

$$\lambda = \frac{c}{\nu} = \frac{c \times h}{\Delta E} = \frac{3 \times 10^8 \frac{m \times \times \frac{1\ nm}{1 \times 10^{-9}\ m}}{s} \times 5.63 \times 10^{-34} \text{ J}}{7.57 \times 10^{-20} \text{ J}} = 2.63 \times 10^3 \text{ m}$$

Practice Exercise 7.3

Calculate the wavelength (in nanometers) of a H atom (mass $= 1.674 \times 10^{-27}$ kg) moving at speed $= 7.00 \frac{m}{s}$.

$$\lambda = \frac{h}{mu} = \frac{6.63 \times 10^{-34} \text{ J s}}{1.674 \times 10^{-27} \text{ kg} \times 7.00 \frac{m \times \frac{1 \times 10^{-9}\ nm}{1\ m}}{s}} = 5.66 \times 10^{-17}\ nm$$

Practice exercise 7.4

Give the four quantum numbers for each of the six electrons in a 3p orbital of an atom.

Solution

Quantum number	**n**	***l***	**m$_l$**	**m$_s$**
First electron	3	1	– 1	$+\frac{1}{2}$
Second electron	3	1	– 1	$-\frac{1}{2}$
Third electron	3	1	0	$+\frac{1}{2}$
Fourth electron	3	1	0	$-\frac{1}{2}$
Fifth electron	3	1	+ 1	$+\frac{1}{2}$
Sixth electron	3	1	+ 1	$-\frac{1}{2}$

Practice exercise 7.5

A person gave the four quantum numbers for each of the six electrons in the 3p orbitals of an atm. Judge the answer.

Quantum number	**n**	***l***	**m$_l$**	**m$_s$**
First electron	3	1	– 1	$+\frac{1}{2}$

Second electron	3	1	– 1	$+\frac{1}{2}$
Third electron	3	0	0	$-\frac{1}{2}$
Fourth electron	3	0	0	$-\frac{1}{2}$
Fifth electron	3	– 1	+ 1	$+\frac{1}{2}$
Sixth electron	4	– 1	+ 1	$+\frac{1}{2}$

Solution

- The "n" quantum numbers: they are correct for all except the sixth electron because it is in "3p" meaning that "n = 4" is wrong.
- "*l*" quantum numbers: they are correct except the third and the forth electrons. They all must have *l* = 1 because they are in the second subshell, p, which always has *l* = 1.
- The "m_l" quantum numbers: all are correct.
- The "m_s" quantum numbers: all are wrong because Pauli's principle proved that any two electrons orbiting in the same orbital must have opposite m_s quantum numbers.

Practice exercise 7.6

Write the electron configuration of the following:

A) $^{15}P^{3-}$ B) $^{31}Ga^{3+}$

Solution

A) $^{15}P^{3-}$ has 18 electrons, (15 electrons + 3 electrons):

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$$

B) $^{31}Ga^{3+}$ has 28 electrons, (31 electrons – 3 electrons):

First: we write the electron configuration of the Ga atom:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^1$$

Second: we find that in addition to the 4p subshell also 4s subshell is in the highest "n" quantum number. The electron of 4p and the two electrons of 4s are removed to form Ge^{3+} cation having the following electron configuration

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$$

Practice exercise 7.7

For each of the four elements having the following atomic numbers, determine the block, the period, the group and the group name:

A) 8 B) 17 C) 19 D) 40

Solution

Answering the question requires writing the electron configuration of each:

A) $1s^2\ 2s^2\ 2p^4$

B) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

C) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

D) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^2$

	A	B	C	D
Block	p	p	s	d
Period	2	3	4	5
Group	16	17	1	4
Group name	None	Halogen	Alkali	None

8. SOLUTIONS
SOLUTIONS OF PRACICE EXERCISES

Practice Exercise 8.1

Knowing that I_2 and CS_2 are nonpolar and H_2O is polar, Is iodine (I_2) more soluble in water or in carbon disulfide (CS_2)?

Solution

According to the rule "like dissolves like" iodine (I_2) is more soluble in the nonpolar carbon disulfide

Practice exercise 8.2

A solution contains 8.74 g $\mathrm{NaNO_3}$in 75 g of water. Calculate the $\mathrm{NaNO_3}$%.

Solution

$$\mathrm{NaNO_3\% = \frac{m_{sod.nitrate}}{total\ mass\ of\ solution} \times 100}$$

$$\mathrm{NaNO_3\% = \frac{8.74\ g}{8.74 + 75.0\ g} \times 100 = 10.44\%}$$

Practice exercise 8.3

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the mole fraction of sodium nitrate in the solution

Solution

$$\mathrm{n_{NaNO_3} = \frac{m_{NaNO_3}}{M_{NaNO_3}} = \frac{8.74\ g}{84.997\ \frac{g}{mol}} = 0.103\ mol}$$

$$\mathrm{n_{water} = \frac{m_{water}}{M_{water}} = \frac{75\ g}{18\ \frac{g}{mol}} = 4.167\ mol}$$

$$\mathrm{n_t = n_{NaNO_3} + n_{water} = 0.103\ mol + 4.167 = 4.27\ mol}$$

$$\mathrm{X_{NaNO_3} = \frac{n_{NaNO_3}}{n_t} = \frac{0.103\ mol}{4.27\ mol} = 0.024}$$

Practice exercise 8.4

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the molality of sodium nitrate in the solution**.**

Solution

$$\mathrm{n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{281\ g}{180\ \frac{g}{mol}} = 1.56\ mol}$$

$$\mathrm{molality = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{1.56\ mol}{168.1\ g \times \frac{1\ kg}{1000\ g}} = 9.29\ molal}$$

Practice exercise 8.5

Calculate the molality of a sodium nitrate ($NaNO_3$) aqueous solution in which the mass percent of $NaNO_3$ is 43%.

Solution

$$\mathrm{n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{43\ g}{84.997\ \frac{g}{mol}} = 0.506\ mol}$$

$$\mathrm{m_{solvent}} = 100 – 43 = 57\ \mathrm{g} = 47\ \mathrm{g} \times \frac{1\ kg}{1000\ g} = 0.047\ \mathrm{kg}$$

molality = $\frac{\mathrm{n_{solute}}}{\mathrm{mass_{solv}(kg)}} = \frac{\mathrm{0.506\ mol}}{\mathrm{0.047\ kg}}$ = 10.76 molal

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Practice exercise 8.6

A solution with a density of 0.998 g/mL contains 281 g of glucose ($C_6H_{12}O_6$) and 168.1 g of water. Calculate the molality and molarity of the glucose solution.

Solution

$\mathrm{n_{solute}} = \frac{\mathrm{m_{solute}}}{\mathrm{M_{solute}}} = \frac{\mathrm{281\ g}}{\mathrm{180\ \frac{g}{mol}}}$ = 1.56 mol

molality = $\frac{\mathrm{n_{solute}}}{\mathrm{mass_{solv}(kg)}} = \frac{\mathrm{1.56\ mol}}{\mathrm{168.1\ g \times \frac{1\ kg}{1000\ g}}}$ = 9.29 molal

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Practice Exercise 8.7

If the molality of a solution of urea (NH_2CONH_2) in water is 0.14 mol/kg, calculate the mass percent of urea in the solution

Solution

Urea% = $\frac{\mathrm{m_{urea}}}{\mathrm{total\ mass\ of\ solution}} \times 100$

$\mathrm{n_{urea}}$ = 0.14 mol ,, $\mathrm{m_{water}}$ = 1 kg = 1000 g

$\mathrm{m_{urea}} = \mathrm{n_{urea}} \times \mathrm{M_{urea}}$ = 0.14 mol × 60 $\frac{\mathrm{g}}{\mathrm{mol}}$ = 8.4 g

$\mathrm{m_{solution}} = \mathrm{m_{urea}} + \mathrm{m_{water}}$ = 8.4 g + 1000 g = 1008.4 g

Solute% = $\frac{\mathrm{8.4\ g}}{\mathrm{1008.34\ g}} \times 10^2$ = 0.83%

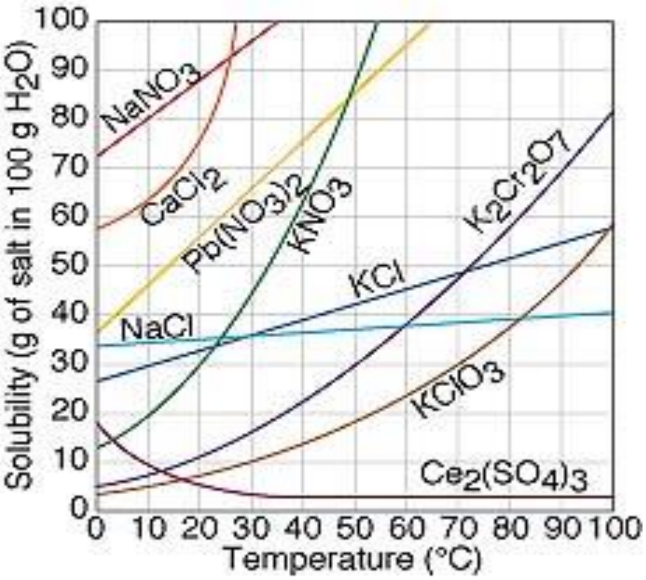
Practice Exercise 8.8

Using the curves of the solubility versus temperature,

A) At what temperature will the solubility of KCl equalizes that of $KClO_3$?

B) At 47 °C, the solubility of KNO_3 is 80 g/100 g of water. At what temperature would the solubility of $NaNO_3$ be the same?

Solution



A) At 100 ºC

B) At 10 ºC

Practice Exercise 8.9

Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's constant for oxygen is 1.3×10^{-3} mol/L atm.

Solution

$c = k \times P = 1.3 \times 10^{-3}\,\frac{\text{mol}}{\text{L atm}} \times 0.22\text{ atm} = 2.86 \times 10^{-4}\,\frac{\text{mol}}{\text{L atm}}$

Practice Exercise 8.10

Calculate the vapor pressure and the vapor-pressure lowering at 35°C of a solution of 82.4 g of urea in 212 mL of water. (**$P^{\circ}_{\text{water},35\ ^{\circ}\text{C}} = 42.2$ mmHg**)

Solution

$n_{\text{water}} = \frac{212\text{ g}}{18.02\,\frac{\text{g}}{\text{mol}}} = 11.767\text{ mol}$	$N_{\text{urea}} = \frac{82.4\text{ g}}{60.06\,\frac{\text{g}}{\text{mol}}} = 1.372\text{ mol}$
$X_{\text{water}} = \frac{11.767\text{ mol}}{11.767\text{ mol} + 1.372\text{ mol}} = 0.896$	

$P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}} = 0.895 \times 42.2\text{ mmHg} = 37.81\text{ mmHg}$

$\Delta P = P^{\circ}_{\text{solvent}} - P_{\text{solution}} = 42.2\text{ mmHg} - 37.81\text{ mmHg} = 4.39\text{ mmHg}$

Practice Exercise 8.11

Calculate the vapor pressure of a solution of 50 g of methanol and 50 g of ethanol at 20$^{\text{o}}$C.

($M_{\text{methanol}} = 32\,\frac{\text{g}}{\text{mol}}$ and $P^{\circ}_{\text{methanol}} = 94$ mmHg) ($M_{\text{ethanol}} = 46\,\frac{\text{g}}{\text{mol}}$ and $P^{\circ}_{\text{ethanol}} = 44$ mmHg)

Solution

$P_{\text{solution}} = (X_{\text{methanol}} \times P^{\circ}_{\text{methanol}}) + (X_{\text{ethanol}} \times P^{\circ}_{\text{ethanol}})$

$n_{\text{methanol}} = \frac{m_{\text{methanol}}}{M_{\text{methanol}}} = \frac{50\text{ g}}{32\,\frac{\text{g}}{\text{mol}}} = 1.56\text{ mol}$ **<u>AND</u>** $n_{\text{ethanol}} = \frac{m_{\text{ethanol}}}{M_{\text{ethanol}}} = \frac{50\text{ g}}{46\,\frac{\text{g}}{\text{mol}}} = 1.087\text{ mol}$

$X_{\text{methanol}} = \frac{n_{\text{methanol}}}{n_{\text{methanol}} + n_{\text{ethanol}}} = \frac{1.56}{1.56 + 1.087} = 0.589$

$X_{\text{ethanol}} = 1 - X_{\text{methanol}} = 1 - 0.589 = 0.411$

$P_{\text{solution}} = (0.589 \times 94\text{ mmHg}) + (0.411 \times 44\text{ mmHg}) = 73.45\text{ mmHg}$

Practice Exercise 8.12

Calculate the boiling and freezing points of a solution containing 478 g of ethylene glycol in 3202 g of water. **($M_{\text{ethylene glycol}} = 62.01$ g/mol), ($T^{\circ}_{\text{freezing,water}} = 0$ °C), ($T^{\circ}_{\text{boiling,water}} = 100$ °C), ($K_{\text{f,water}} = 1.86$ °C/m, ($K_{\text{b,water}} = 0.52$ °C/m)**

Solution

$\text{molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}\,(\text{kg})} = \frac{\frac{m_{\text{solute}}}{M_{\text{solute}}}}{m_{\text{solvent}}\,(\text{kg})} = \frac{\frac{478\text{ g}}{62.01\frac{\text{g}}{\text{mol}}}}{3202\text{ g} \times \frac{1\text{ kg}}{1000\text{ g}}} = 2.41\,\frac{\text{mol}}{\text{kg}} = 2.41\text{ molal}$

$\Delta T_b = K_b\,m = 0.52\,\frac{^{\circ}\text{C}}{\text{molal}} \times 2.41\text{ molal} = 1.25\ ^{\circ}\text{C}$

$\Delta T_b = T_{\text{b,solution}} - T^{\circ}_{\text{b,water}}$

$1.25\ ^{\circ}\text{C} = T_{\text{b,solution}} - 100\ ^{\circ}\text{C}$

$T_{\text{b,solution}} = 101.25\ ^{\circ}\text{C}$

$\Delta T_f = K_f\,m = 1.86\,\frac{^{\circ}\text{C}}{\text{molal}} \times 2.41\text{ molal} = 4.48\ ^{\circ}\text{C}$

$\Delta T_f = T^{\circ}_{\text{f,water}} - T_{\text{f,solution}}$

$4.48\ ^{\circ}\text{C} = 0\ ^{\circ}\text{C} - T_{\text{f,solution}}$

$T_{f,solution} = -\ 4.48\ °C$

Practice Exercise 8.13

What is the osmotic pressure (in atm) of a 0.884 M urea solution at 16 °C?

Solution

$\pi = M \times R \times T$

$\pi = 0.88\ mol/L \times 0.0821\ atm\ L/mol\ K \times 289\ K = 20.88\ atm$

Practice Exercise 8.14

A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21 °C. Calculate the molar mass of the polymer.

Solution

$$M = \frac{\pi}{R \times T} = \frac{8.63\ mmHg \times \frac{1\ \ atm}{760\ mmHg}}{0.0821\frac{atm\ L}{mol\ K} \times 294\ K} = 4.7 \times 10^{-4}\ mol/L$$

$n_{polymer} = M \times V\ (L)$

$n_{polymer} = 4.7 \times 10^{-4}\ mol/L \times 202\ mL \times \frac{1\ L}{1000\ mL} = 9.5 \times 10^{-5}\ mol$

$M_{polymer} = \frac{m_{polymer}}{n_{polymer}} = \frac{2.47\ g}{9.5 \times 10{-}5\ mol} = 2.6 \times 10^{4}\ g/mol$