DIRE-DAWA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

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First year

Semester II

Course: General Chemistry (Chem1012)

WELL COME TO CHEMISTRY CLASS!!!

❖Why should we study chemistry?” Do you have an answer?

- ✓Because it fulfills an academic requirement, but if you consider your daily activities, Most everything you do and encounter during your day involves chemistry.
- ✓Such as, making coffee, cooking eggs, and toasting bread involve chemistry.
- ✓The products you use—like soap and shampoo, the fabrics you wear, the gasoline that propels your car; all of these and more involve chemical substances and processes.
- ✓Whether you are aware or not, chemistry is part of your everyday world.
- ✓ In this course, you will learn many of the essential principles underlying the chemistry of modern-day life.

1.1. Chemistry in Context

- Throughout human history, people have tried to convert matter into more useful forms. *Such as:*
- They chipped pieces of flint into useful tools and carved wood into statues and toys. But they change the shape of a substance without changing the substance itself.
- But as our knowledge increased, humans began to change the composition of the substances as well; clay was converted into *pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread*.

- ✓Humans began to practice chemistry when they learned to *control fire* and use it to cook, make pottery, and smelt metals.
- ✓A variety of drugs such as *aloe, myrrh, and opium* were isolated from plants.
- ✓Dyes, such as *indigo and Tyrian purple*, were extracted from plant and animal matter.
- ✓Metals were combined to form alloys.

  Example, Cu and Sn were mixed together to make bronze and more elaborate smelting techniques produced iron.

- ✓ Alkali were extracted from ashes, and soaps were prepared by combining these alkalis with fats.
- ✓ Alcohol was produced by fermentation and purified by distillation.
- ✓ From alchemy came the historical progressions that led to modern chemistry: *the isolation of drugs from natural sources, metallurgy, and the dye industry.*
- ✓ Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter.

1.1.1. Chemistry as the Central Science

- Chemistry is sometimes referred to as "*the central science*" due to its interconnectedness with other **STEM** disciplines.
- STEM stands for areas of study in the *science, technology, engineering, and math fields*.
- Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure 1.1).

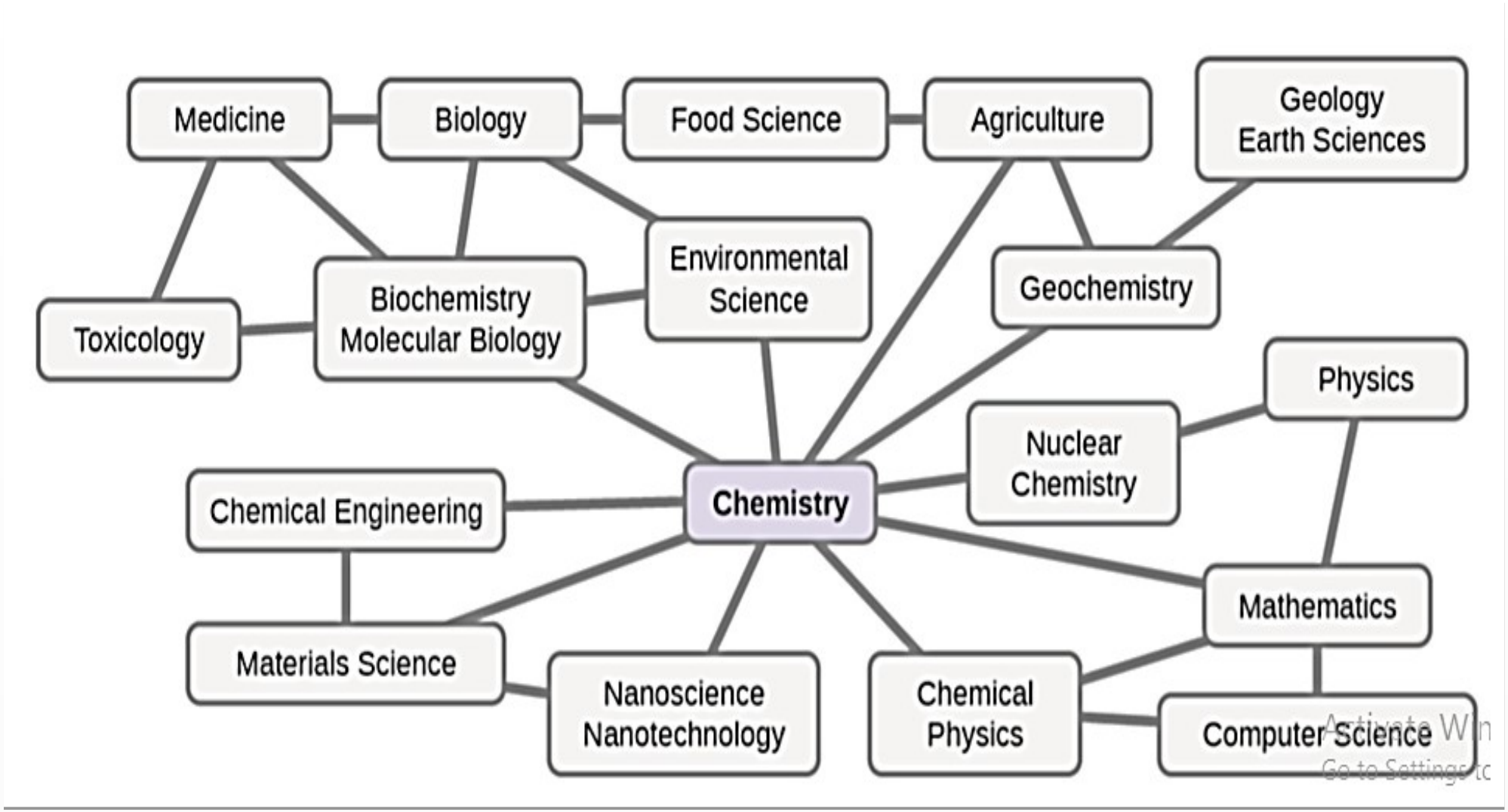


Figure 1.1: The interrelationships between chemistry and other fields.

1.1.2. The Scientific Method

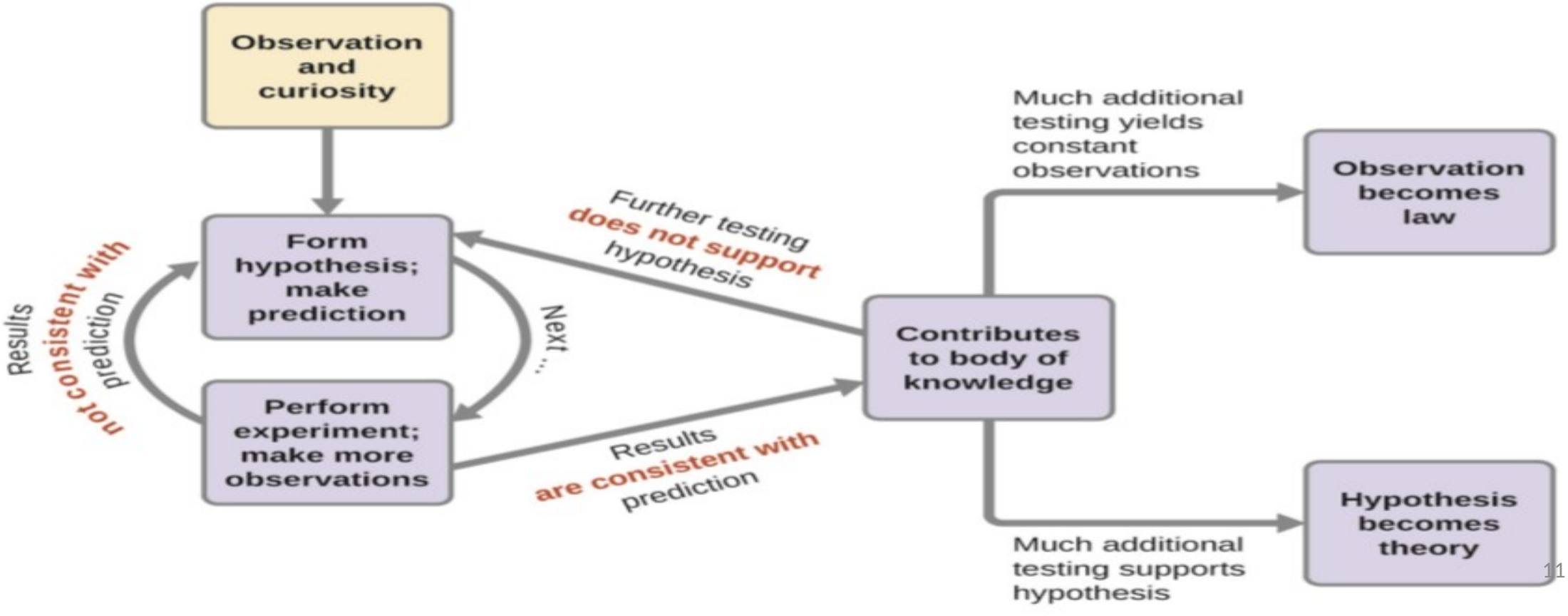
- ***Chemistry*** is a science based on observation and *experimentation.*
- The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory is called the ***scientific method***.

✓ A hypothesis is a tentative explanation of observations that acts as a guide for gathering and checking information.

✓ A hypothesis is tested by *experimentation*, *calculation*, and comparison with the experiments of others and then refined as needed.

- ✓ A ***law*** is *a concise verbal or mathematical statement of a relationship between phenomena that is always the same under the same conditions.*
- ✓ *For example, Sir Isaac Newton's second law of motion, which you may remember from high school science, says that force equals mass times acceleration* ***(F = ma).***
- ✓ 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.

- ✓ Scientific theories are well substantiated, comprehensive, testable explanations of particular aspects of nature.
- ✓ Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available.



1.1.3. The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, *and* symbolic.

- The *macroscopic* domain is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch.

  Example:

  - In daily life, these includes the *food you eat* and the *breeze you feel on your face*,
  - *observing and measuring physical and chemical properties* such as density, solubility, and flammability in chemistry laboratory.

- Some aspects of the microscopic domain are visible through standard optical microscopes, for example, many biological cells.
- ✓ More sophisticated instruments are capable of imaging even smaller entities such as molecules and atoms.
- ✓ Other components of the microscopic include *ions and electrons*, *protons and neutrons*, and *chemical bonds*, each of which is far too small to see.
- *The symbolic domain* contains the specialized language used to represent components of the macroscopic and microscopic domains.

- ✓ *Chemical symbols*, *chemical formulas*, and *chemical equations* are part of the symbolic domain, as are graphs, drawings, and calculations.
- ✓ They help to interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain.
- ✓ One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains,
- ✓ one of the features that make chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

- ✓ H_2O is a liquid at moderate temperatures will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.3) are macroscopic observations.
- ✓ But some properties of water fall into the microscopic domain, what cannot be observed with the naked eye.
- ✓ The description of water as comprising two H atoms and one O atom, and the explanation of freezing and boiling in terms of attractions between these molecule is within the microscopic arena.
- ✓ The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain.

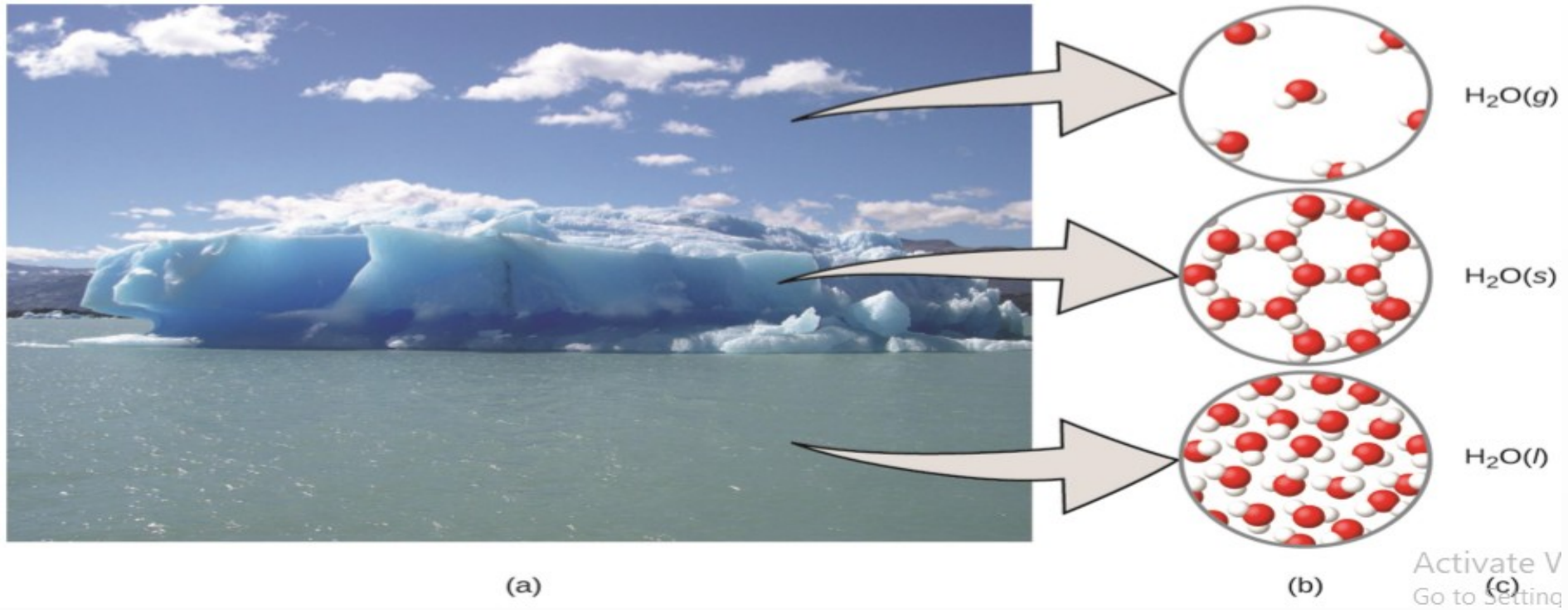


Figure 1.3: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases.

1.2. State and Classification of Matter

- ✓ Matter is defined as anything that occupies space and has mass.
- ✓ Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass.
- ✓ Gases are also matter; if gases did not take up space, a balloon would not inflate (increase its volume) when filled with gas.
- ✓ A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of its container, except that it forms a flat or slightly curved upper surface when acted upon by gravity.

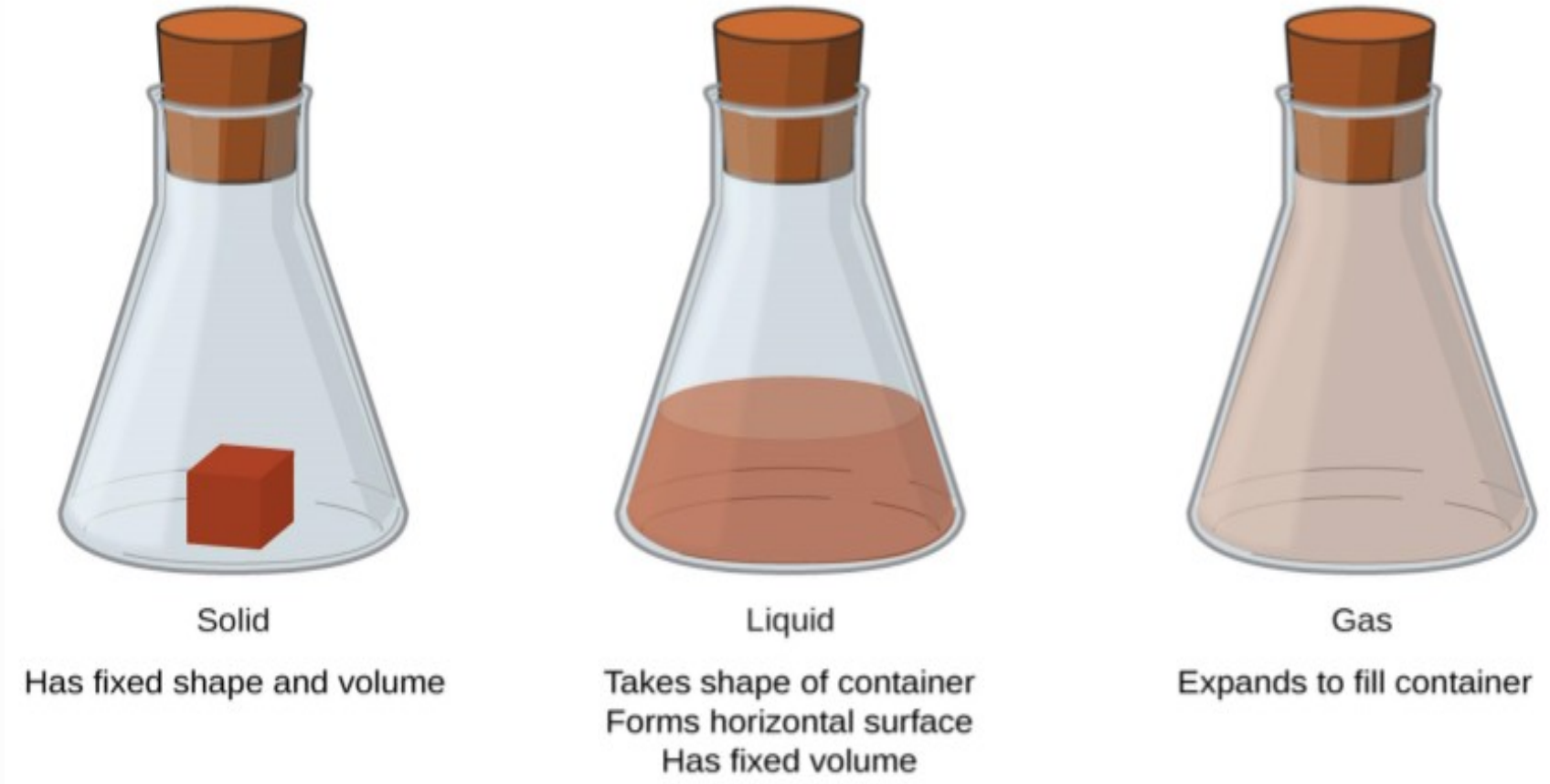


Figure 1.4: The three most common states or phases of matter are solid, liquid, and gas.

- ✓A fourth state of matter, plasma occurs naturally in the interiors of stars.
- ✓Plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.5).
- ✓The presence of these charged particles imparts unique properties to plasma that justify their classification as a state of matter distinct from gases.
- ✓In addition to stars, plasma are found in high-temperature environments, such as lightning strikes, certain TV screens, and specialized analytical instruments used to detect trace amounts of metals.



Figure 1.5: A plasma torch can be used to cut metal.

- ✓ In a tiny cell in a plasma TV, the plasma emits UV light, which in turn causes the display at that location to appear a specific color.
- ✓ The composite of these tiny dots of color makes up the image that you see.

- Matter can also have properties of more than one state when it is a mixture, such as with clouds.
- Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).
- The **mass** of an object is a measure of the amount of matter in it.
- One way to measure an object's mass is to measure the force it takes to accelerate the object.
- A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.
- Although weight is related to mass, it is not the same thing.

❖**Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object.

❖The weight of an object changes as the force of gravity changes, but its mass does not.

✓ An astronaut's mass does not change just because she/he goes to the moon. But her/his weight on the moon is only one-sixth her/his earth-bound weight because the moon's gravity is only one-sixth that of the earth's.

✓*She/he may feel "weightless" during her/his trip when she/he experiences negligible external forces (gravitational or any other), although she/he is, of course, never "massless."*

- The ***law of conservation of matter*** summarizes many scientific observations about matter:

"*It states that there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change*)".

- Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 1.6).

- During the brewing of beer, the ingredients (*water, yeast, grains, malt, hops, and sugar*) are converted into beer (*water, alcohol, carbonation, and flavoring substances*) with no actual loss of substance.

- When glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change.
- In a lead-acid car battery: The original substances (*lead, lead oxide, and sulfuric acid*), which are capable of producing electricity, are changed into other substances (*lead sulfate and water*) that do not produce electricity, with no change in the actual amount of matter.



Classification of Matter

❖Matter can be classified into mixtures and pure substances.

❖A pure substance has a constant composition.

❖All specimens of a pure substance have exactly the same makeup and properties.

❖Any sample of sucrose consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass.

❖Any sample of sucrose also has the same physical properties, such as *melting point, color, and sweetness,* regardless of the source from which it is isolated.

❖Pure substances may be divided into two classes: elements and compounds.

❖ Pure substances that cannot be broken down into simpler substances by chemical changes are called elements.

- ✓ Fe, Ag, Au, Al, S, O, and Cu are examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.
- ✓ Pure substances that can be broken down by chemical changes are called compounds.
  - Mercury (II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen.
  - When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water.
  - Silver (I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light.

- A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation.
- A mixture with a composition that varies from point to point is called a *heterogeneous mixture*.

  Examples:

  - ✓ chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and
  - ✓ granite (quartz, mica, feldspar, and more).

- A **homogeneous mixture**, also called a solution, exhibits a uniform composition and appears visually the same throughout.

  Example:

  - ✓ a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure 1.7).
  - ✓ air, maple syrup, gasoline, and a solution of salt in water.

- Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components.

- Note that the composition of a sports drink can vary. It could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink.



Figure 1.7: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout.

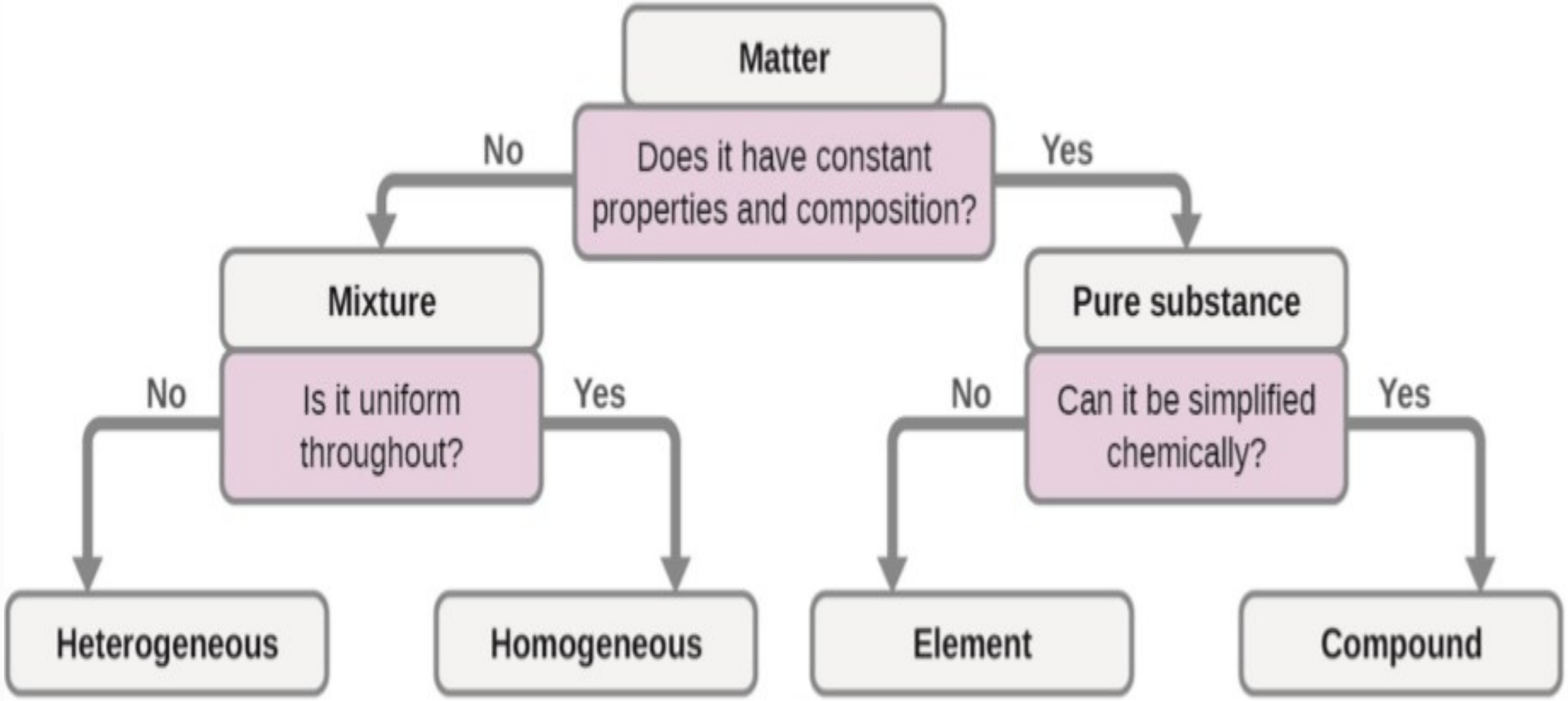


Figure 1.8: Depending on its properties, a given substance classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Table1.1: Elemental Composition of Earth

Element	Symbol	% Mass		Element	Symbol	Percent Mass
Oxygen	O	49.20		Chlorine	Cl	0.19
Silicon	Si	25.67		Phosphorus	P	0.11
Aluminum	Al	7.50		Manganese	Mn	0.09
Iron	Fe	4.71		Carbon	C	0.08
Calcium	Ca	3.39		Sulfur	S	0.06
Sodium	Na	2.63		Barium	Ba	0.04
Potassium	K	2.40		Nitrogen	N	0.03
Magnesium	Mg	1.93		Fluorine	F	0.03
Hydrogen	H	0.87		Strontium	Sr	0.02
Titanium	Ti	0.58		All Others	-	0.47

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1.3. Physical and Chemical Properties

✓ The characteristics that distinguish one substance from another are called properties.

✓ *A physical property* is a characteristic of matter that is not associated with a change in its chemical composition.

Examples: density, color, hardness, melting and boiling points, and electrical conductivity.

- density and color, may be observed without changing the physical state of the matter.
- the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change.

- ✓ *A physical change* is a change in the state or properties of matter without any accompanying change in the chemical identities of the substances contained in the matter.
- ✓ Examples of physical changes include:
- ➢ magnetizing and demagnetizing metals and
- ➢ grinding solids into powder.
- ➢ It observed when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure 1.9).

✓In each of these examples, there is a change in the physical state. but no change in its chemical composition.

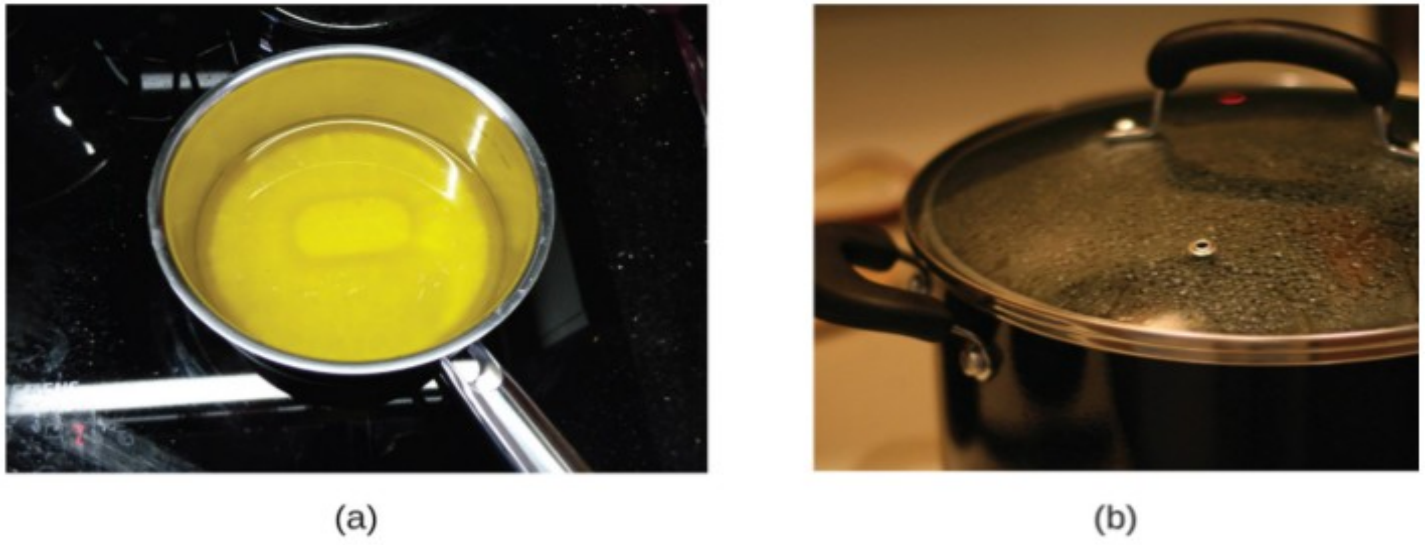


Figure 1.9: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water.

- ✓ The change of one type of matter into another type (or the inability to change) is a *chemical property*.
- ✓ A chemical change always produces one or more types of matter that differ from the matter present before the change.

  Examples:

  - flammability, toxicity, acidity, and many other types of reactivity.
  - Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure 1.10).
  - Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



Figure 1.10: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not.

Figure (a), is a metal machinery that is now mostly covered with reddish orange rust. *Figure (b)*, shows the silver colored chrome parts of a motorcycle. One of the parts is so shiny that you can see a reflection of the surrounding street and buildings.

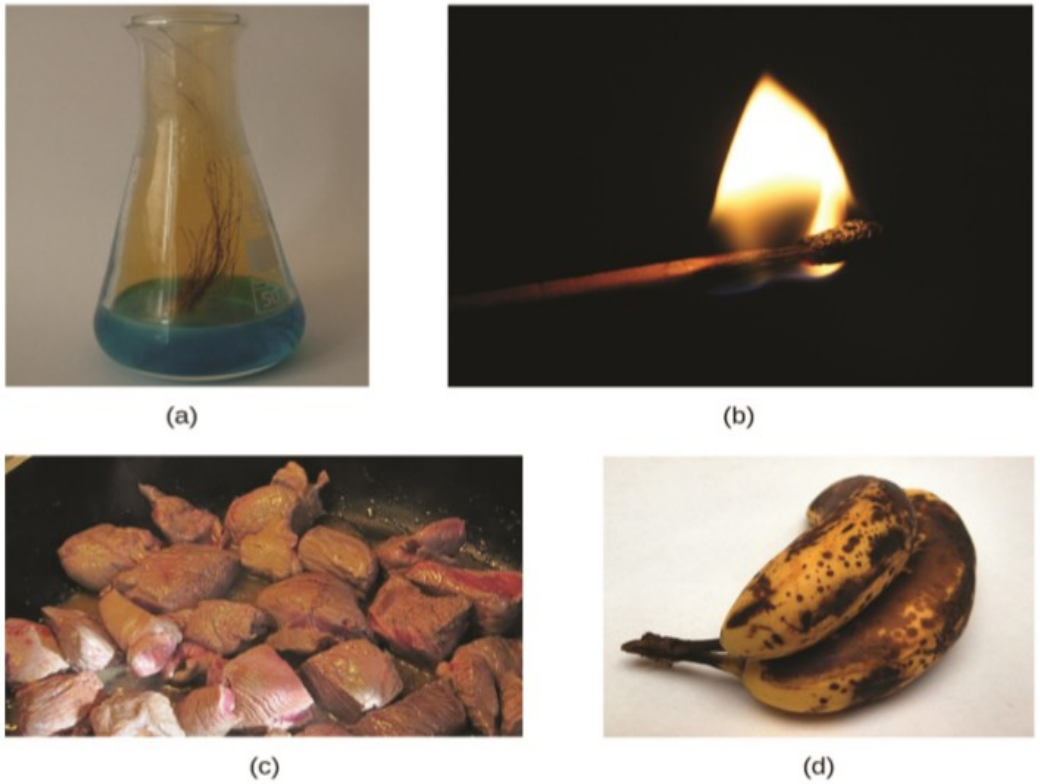


Figure 1.11: **(a)** Copper and nitric acids undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. **(b)** During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. **(c)** Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. **(d)** A banana turning brown is a chemical change as new, darker substances form.

1.4. Extensive and intensive property

Extensive Property	Intensive Property
✓ *depends on the amount of matter present* ✓ Examples: mass and volume of a substance. o for instance, a gallon of milk has a larger mass than a cup of milk.	✓ *does not depend on the amount of matter present* ✓ Temperature is intensive ppty. o If the gallon and cup of milk are each at 20°C, when they are combined, temperature remains at 20°C.

✓A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns.

✓Both the drop and the pot of oil are at the same temperature (intensive), but the pot clearly contains much more heat (extensive property).

1.5. Measurements and Units

✓*Measurements* provide much of the information that informs the *hypotheses, theories, and laws describing the behavior of matter* and *energy in both the macroscopic and microscopic* domains of chemistry.

✓Every measurement provides three kinds of information:

- the size or magnitude of the measurement (a number);
- a standard of comparison for the measurement (a unit); and
- an indication of the uncertainty of the measurement.

➢The number in the measurement can be represented in different ways, including *decimal form and scientific notation*. Scientific notation is also known as exponential notation.

Example: the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg.

- Units, such as liters, gram, and centimeters, are standards of comparison for measurements.
- The standards for these units are fixed by international agreement, and they are called *the International System of Units or SI Units*:
- Units for other properties may be derived from these seven base units.

Table 1.2: Base Units of the SI System

Property Measured	Name of Unit	Symbol of Unit
Length	Meter	m
Mass	Kilogram	kg
Time	Second	s
Temperature	Kelvin	K
electric current	Ampere	A
amount of substance	Mole	mol
luminous intensity	Candela	cd

- ✓ Measurement units are often defined as fractions or multiples of other units.
  - Liquid glycerin is commonly packaged in containers of 20ml of bottle (0.0053 gallon).
- ✓ Fractional or multiple SI units are named using a prefix and the name of the base unit.
- ✓ For example, a length of 1000 meters is also called a kilometer because the prefix kilo means “one thousand,” which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m).
- ✓ The prefixes used and the powers to which 10 are raised are listed in Table 1.3.

Table 1.3: Common Unit Prefixes

Prefix	Symbol	Factor	Example
Femto	F	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
Pico	P	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
Nano	N	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
Micro	μ	10^{-6}	1 microliter (μL) = 1×10^{-6} L (0.000001 L)
Milli	M	10^{-3}	2 millimoles (mmol) = 2×10^{-3} mol (0.002 mol)
Centi	C	10^{-2}	7 centimeters (cm) = 7×10^{-2} m (0.07 m)
Deci	D	10^{-1}	1 deciliter (dL) = 1×10^{-1} L (0.1 L)
Kilo	K	10^{3}	1 kilometer (km) = 1×10^{3} m (1000 m)
Mega	M	10^{6}	3 megahertz (MHz) = 3×10^{6} Hz (3,000,000 Hz)
Giga	G	10^{9}	8 gigayears (Gyr) = 8×10^{9} yr (8,000,000,000 yr)
Tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

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1.5.1. SI Base Units

➢ Length

✓The SI unit of length is the meter (m).

✓A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator.

1 km = 1000 m = 10^{3}m), (1 cm = 0.01 m = 10^{-2}m), (1 mm = 0.001 m = 10^{-3}m).

➢Mass

✓The standard unit of mass in the SI system is the kilogram (kg). The kg was previously defined by the IUPAC as the mass of a specific reference object.

One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).

Temperature

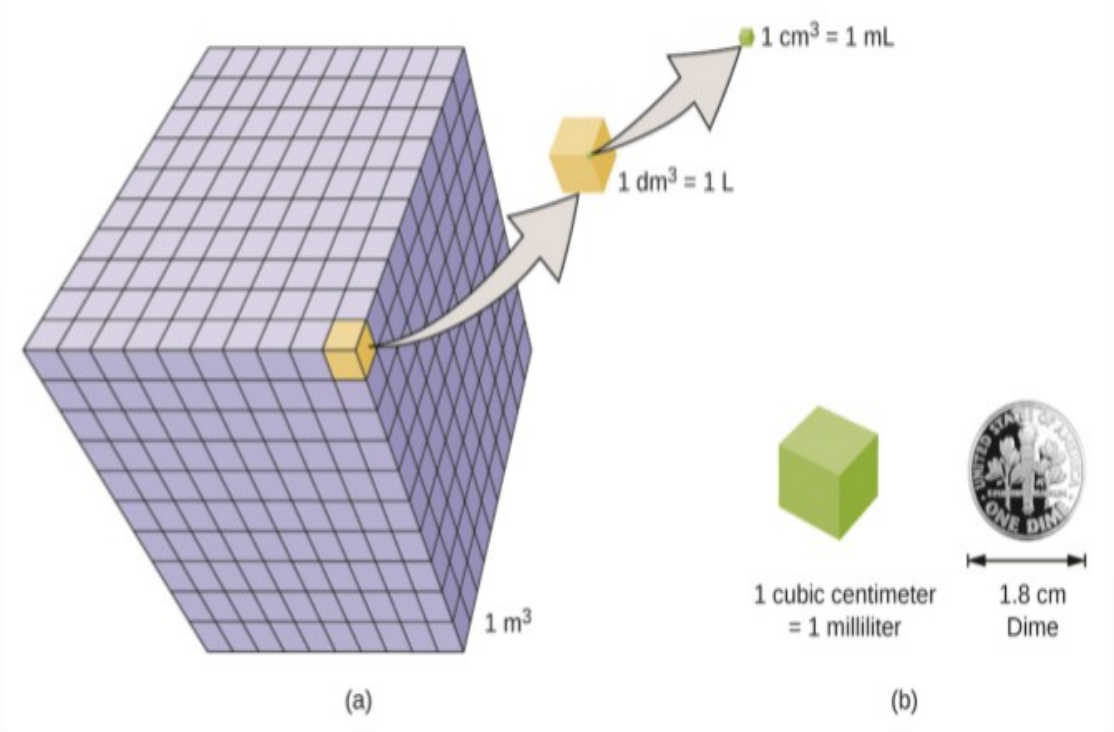
- ✓It is an intensive property. The SI unit of temperature is the kelvin (K).
- ✓The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°).
- ✓The degree Celsius (°C) is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements.
- ✓Water freezes at 273.15 K (0°C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37°C).

Time

- ✓ The SI base unit of time is the second (s).
- ✓ Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 mega seconds = 5,000,000 s = 5 $\times10^{6}$ s. alternatively, hours, days, and years can be used.

1.5.2. Derived SI Units

- ✓We can derive many units from the seven SI base units.
- ✓For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.
- ✓The standard volume is a cubic meter (m3), a cube with an edge length of exactly one meter.
- ✓To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.



Volume

✓Volume is the measure of the amount of space occupied by an object.

✓The standard SI unit of volume is defined by the base unit of length (Figure 1.14).

Figure 1.14: (a) The relative volumes are shown for cubes of 1m³, 1 dm³ (1 L), and 1 cm³ (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1cm³ (1mL) cube.

Density

- ✓The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3).
- ✓For many situations, however, we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases.
- ✓Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 ($density = \frac{mass}{volume}$) to 19 g/cm^3

Table1.4: Densities of Common Substances

Solids	**Liquids**	**Gases (at 25 °C and 1 atm.)**
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
iron 7.9 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
copper 9.0 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
lead 11.3 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
silver 10.5 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
gold 19.3 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
Zinc 7.140g/ cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

Example 1.1: Calculation of Density Gold-in bricks, bars, and coins-has been a form of currency for centuries. In order to fraud people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length. Volume of lead cube = 2.00 cm×2.00 cm × 2.00 cm=8.00cm^3

$$density = \frac{mass}{volume} = \frac{90.7g}{8cm^3} = 11.3g/cm^3$$

1.6. Measurement Uncertainty

- Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway.

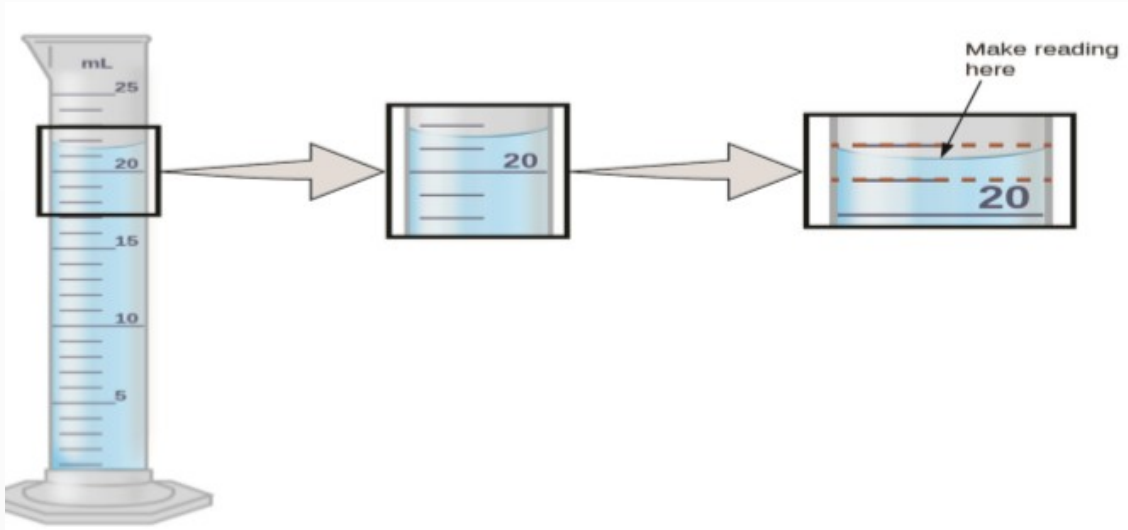
  Example: By counting the eggs in a carton, one can determine exactly how many eggs the carton contains.

- The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram.

- Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

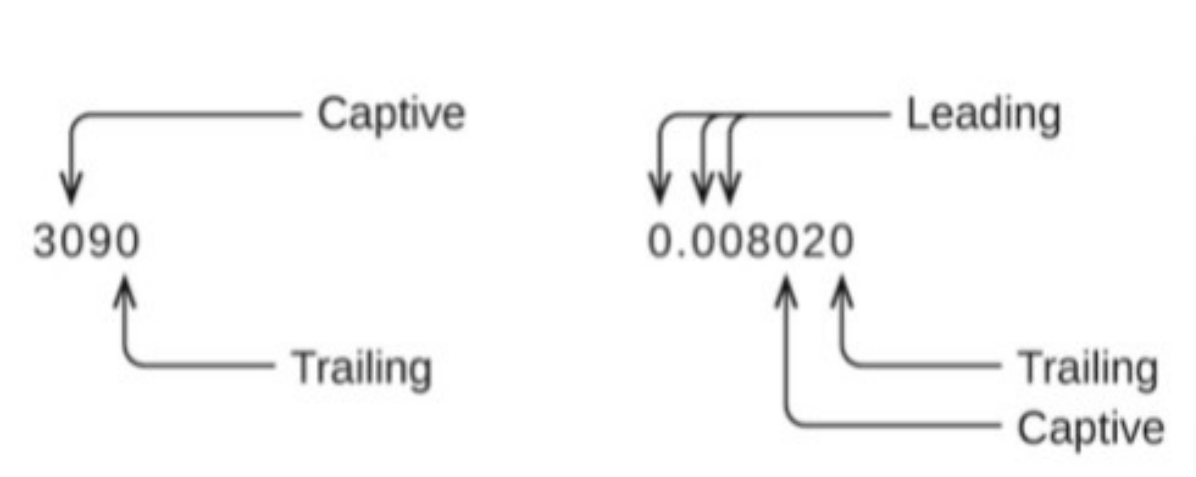
1.6.1. Significant Figures in Measurement

- ✓The numbers of measured quantities, unlike defined or directly counted quantities, are not exact.
- ✓To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.



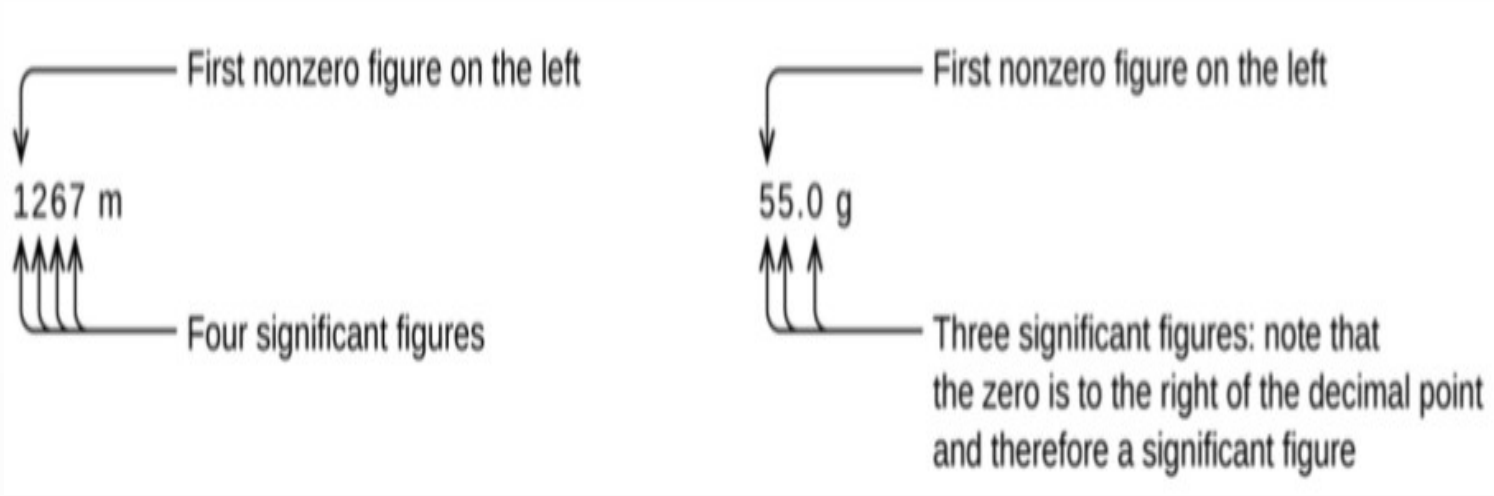
- ✓If the coin is weighed on a more sensitive balance, the mass might be 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram.
- ✓Every measurement has some uncertainty, which depends on the device used (and the user's ability).
- ✓All of the digits in a measurement, including the uncertain last digit, are called *significant figures or significant digits.*
- ✓Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest killogram and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

- ✓ A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement.
- ✓ We will use the terms "*leading," "trailing," and "captive*" for the zeros and will consider how to deal with them.



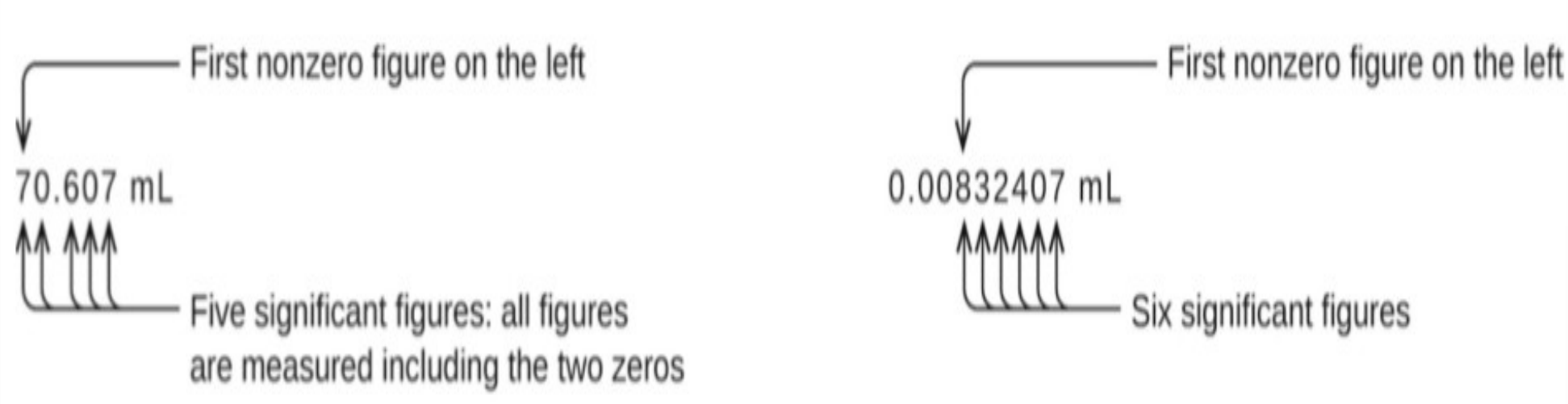
Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right.

✓This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.



✓Captive zeros result from measurement and are therefore always significant.

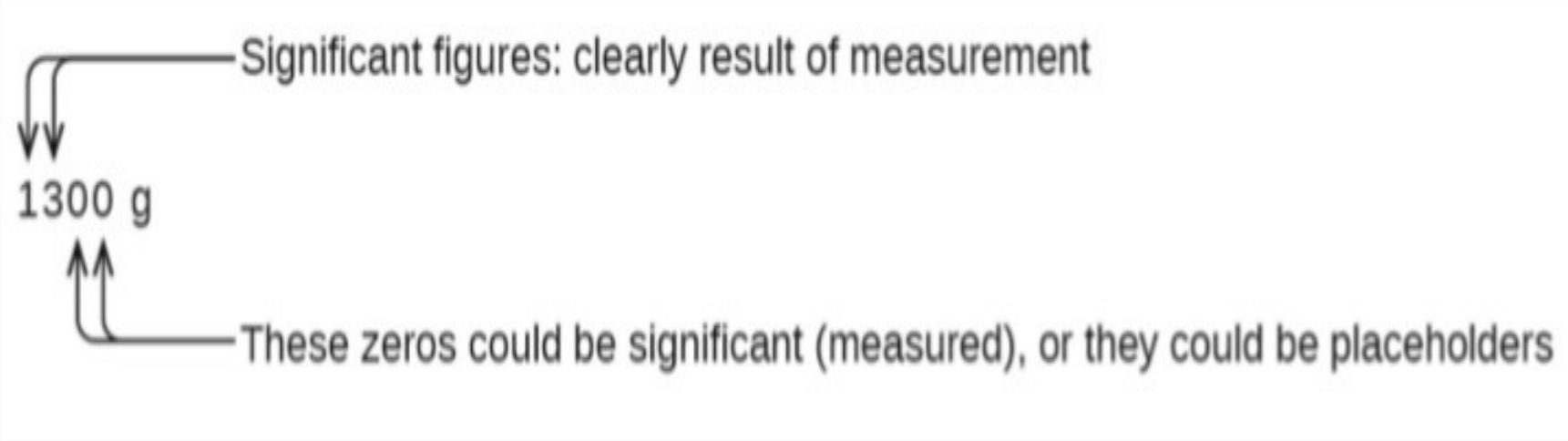
✓Leading zeros, however, are never significant. they merely tell us where the decimal point is located.



The leading zeros in this example are not significant. We could use exponential notation and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location.

- ✓ The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located.
- ✓ The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured).



1.6.2. Significant Figures in Calculations

To report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

1. *When adding or subtracting numbers, round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction).*

2. *When multiplying or dividing numbers, round the result to the same number of digits as the number with the least number of significant figures (the least certain value in terms of multiplication and division).*

3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, “round down” and leave the retained digit unchanged;

- if it is more than 5, “round up” and increase the retained digit by 1;
- if the dropped digit is 5, round up or down, whichever yields an even value for the retained digit.
- (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)

- The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:
- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

Example 1.2: Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)

b. 8.1649 (to three significant figures)

c. c. 0.051065 (to four significant figures)

d. d. 0.90275 (to four significant figures)

Example 1.3 Addition and Subtraction with Significant Figures Rule:

- When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain value in terms of addition and subtraction).

a) Add 1.0023 g and 4.383 g.

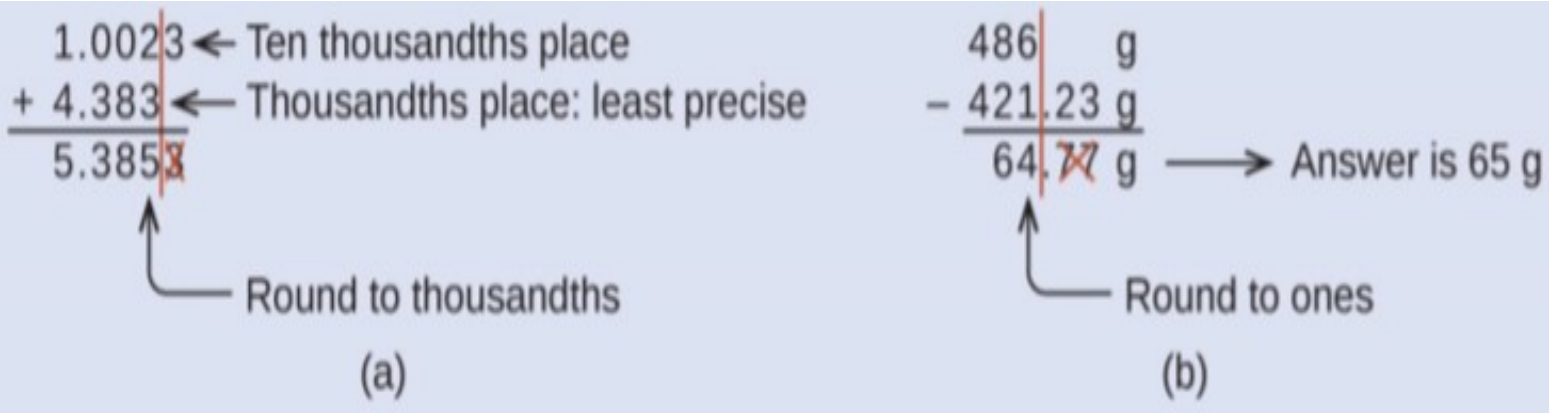
b) Subtract 421.23 g from 486 g.

Solution a) 1.0023 g + 4.383 g = 5.3853 g

Answer is 5.385 g (round to the thousandths place; three decimal places)

b) 486 g − 421.23 g = 64.77 g

Answer is 65 g (round to the ones place; no decimal places)



Example 1.4 Multiplication and Division with Significant Figures Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain value in terms of multiplication and division). (a) Multiply 0.6238 cm by 6.6 cm. (b) Divide 421.23 g by 486 mL.

Solution

a) $0.6238\ \text{cm} \times 6.6\text{cm} = 4.11708\text{cm}^2 \longrightarrow$ result is 4.1cm^2 (round to two significant figures)

four significant figures × two significant figures ⟶ two significant figures

b) $\frac{421.23g}{486mL} = 0.86728g/mL \longrightarrow$ result is 0.867 g/mL (round to three significant figures)

$\frac{\text{five significant figures}}{\text{three significant figures}} \longrightarrow$ three significant figures answer

1.6.3. Accuracy and Precision

- Scientists typically make repeated measurements of a quantity to *ensure the quality of their findings* and to *evaluate both the precision and the accuracy* of their results.
- Measurements are said to be precise if they yield very similar results when repeated in the same manner.
- A measurement is considered accurate if it yields a result that is very close to the true or accepted value.
- Precise values agree with each other; accurate values agree with a true value.

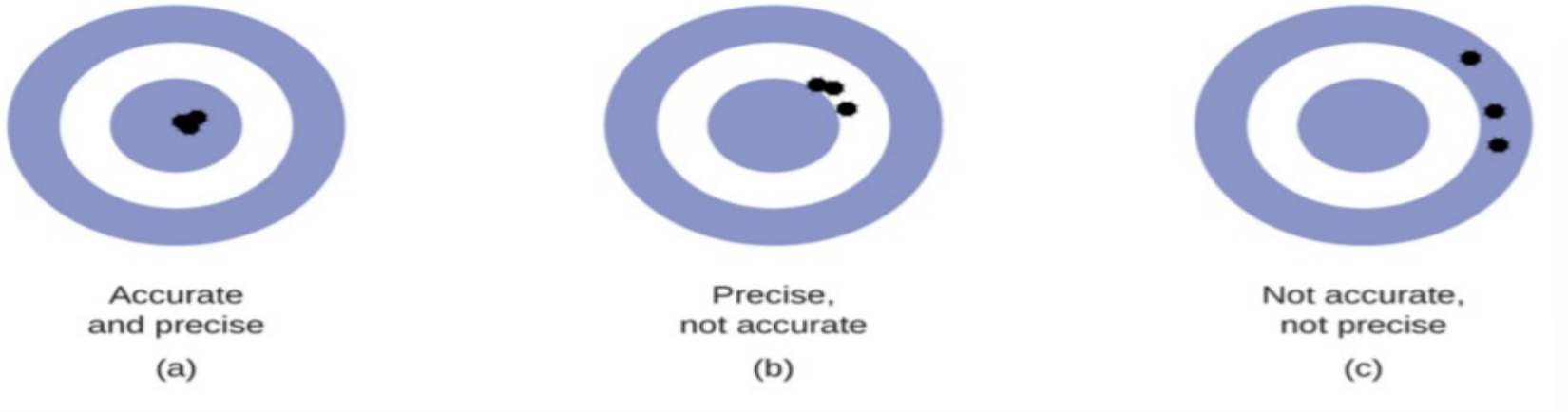


Figure 1.17:

(a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise.

(b) These arrows are close to one another but not on target, so they are precise but not accurate.

(c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

- *Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 283.5g (296 mL) of cough syrup into storage bottles.*

- Table 1.5: Volume (mL) of Cough Medicine Delivered by 283.5g (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

- she/he will report that dispenser **#1** is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low).
- Results for dispenser **#2** represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL).
- she/he can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

1.7. Conversion Factors and Dimensional Analysis

✓A ratio of two equivalent quantities expressed with different measurement units can be used as a unit conversion factor. For example, the lengths of 2.54 cm and 1 in. are equivalent. $\frac{2.54\ cm}{1\ in.}\ (2.54\ cm = 1\ in.)\ or\ 2.54 cm/in.$

Length	Volume	Mass
1 in. = 2.54 cm (exact)	1 liter (l) = 1000cm^3 = 3.78544gl=1.057 quart (qt) = 61.02 in^3 = 0.03532 ft^3	1 kg = 2.2046 lb
1cm=0.01m	1 cubic meter (m^3) = 1000 l = 35.32 ft^3	1 lb = 453.59 g
1mm=0.001m	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g

- When a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted to an equivalent value with different units (such as distance in centimeters).

For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

$$34\ \cancel{in} \times \frac{2.54\ cm}{1\ \cancel{in}} = 86\ cm$$

Exercise: What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since $density = \frac{mass}{volume} d$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in Table 1.6: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

$$9.26 \cancel{lb} \times \frac{453.59\ g}{1 \cancel{lb}} = 4.20 \times 10^3 g$$

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Volume may be converted from quarts to millimeters via two steps:

1. Step 1. *Convert quarts to liters.*

$$4.00 \cancel{qt} \times \frac{1\ L}{1.0567 \cancel{qt}} = 3.78\ L$$

Step 2.*Convert liters to milliliters.*

$$3.78 L \times \frac{1000\ mL}{1 L} = 3.78 \times 10^3 mL$$

$$density = \frac{4.20 \times 10^3 g}{3.78 \times 10^3 mL} = 1.11\ g/mL$$

Conversion of Temperature Units

- ✓We use the word temperature to refer to the hotness or coldness of a substance.
- ✓One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases.
- ✓Temperature scales are defined relative to selected reference temperatures:
- ✓Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure.
- ✓On the Celsius scale, 0°C is defined as the freezing temperature of water and 100°C as the boiling temperature of water.

- ✓On the Fahrenheit scale, the freezing point of water is defined as 32°F and the boiling temperature as 212°F.
- ✓The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).
- ✓Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

$$length\ in\ feet = \left(\frac{1\ ft}{12\ in.}\right) \times length\ in\ inches$$

Where y = length in feet, x = length in inches, and the proportionality constant, m, is the conversion factor.

- The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one (y = mx + b).

Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as x and the Fahrenheit temperature as y, the slope, m, is computed to be:

$$m = \frac{\Delta y}{\Delta x} = \frac{212\ °F - 32\ °F}{100\ °C - 0\ °C} = \frac{180\ °F}{100\ °C} = \frac{9\ °F}{5\ °C}$$

The y-intercept of the equation, b, is then calculated using either of the equivalent temperature pairs, (100°C, 212°F) or (0°C, 32°F), as:

$$\boldsymbol{b = y - mx = 32\ °F - \frac{9\ °F}{5\ °C} \times 0\ °C = 32\ °F}$$

The equation relating the temperature (T) scales is then:

$$\boldsymbol{T°F = (\frac{9\ °F}{5\ °C} \times T°C) + 32\ °C}$$

An abbreviated form of this equation that omits the measurement units is:

$$T\,°F = \left(\frac{9}{5} \times T°C\right) + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T°C = TK - 273.15$$

$$T\,°C = \frac{5}{9}(T°F - 32)$$

Following the same approach, the equations for converting between the Kelvin and Celsius temperature scales are derived to be:

$$TK = T°C + 273.15$$

$$T°C = TK - 273.15$$

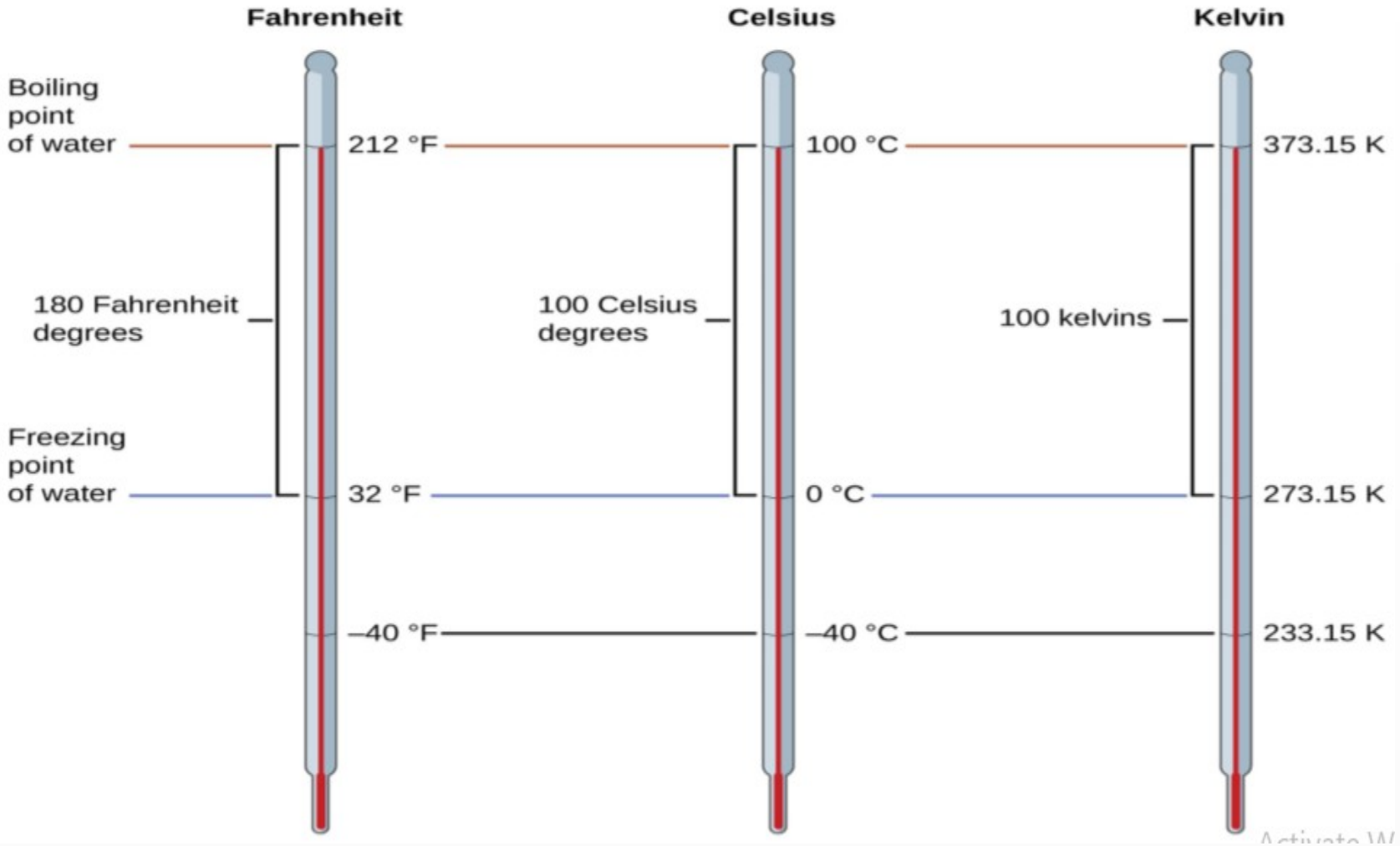


Figure 1.18: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

- Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for non-science contexts in almost all areas of the world.

Example 1.9

Conversion from Celsius

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the Kelvin scale and on the Fahrenheit scale?

Solution

$$K = °C + 273.15 = 37.0 + 273.2 = 310.2\ K$$

$$°F = \frac{9}{5}°C + 32.0 = \left(\left(\frac{9}{5} \times 37.0\right)\right) + 32.0 = 66.6 + 32.0 = 98.6\ °F$$

CHAPTER TWO

Atoms, Molecules and Ions

2.1. Atomic structure and symbolism

- The development of modern atomic theory revealed much about the inner structure of **atoms**.
- It was learned that an atom contains a very small nucleus composed of positively charged **protons** and uncharged **neutrons**, surrounded by a much larger volume of space containing negatively charged **electrons**.
- The **nucleus** contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume.

Cont…

- The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m, about 100,000 times smaller.

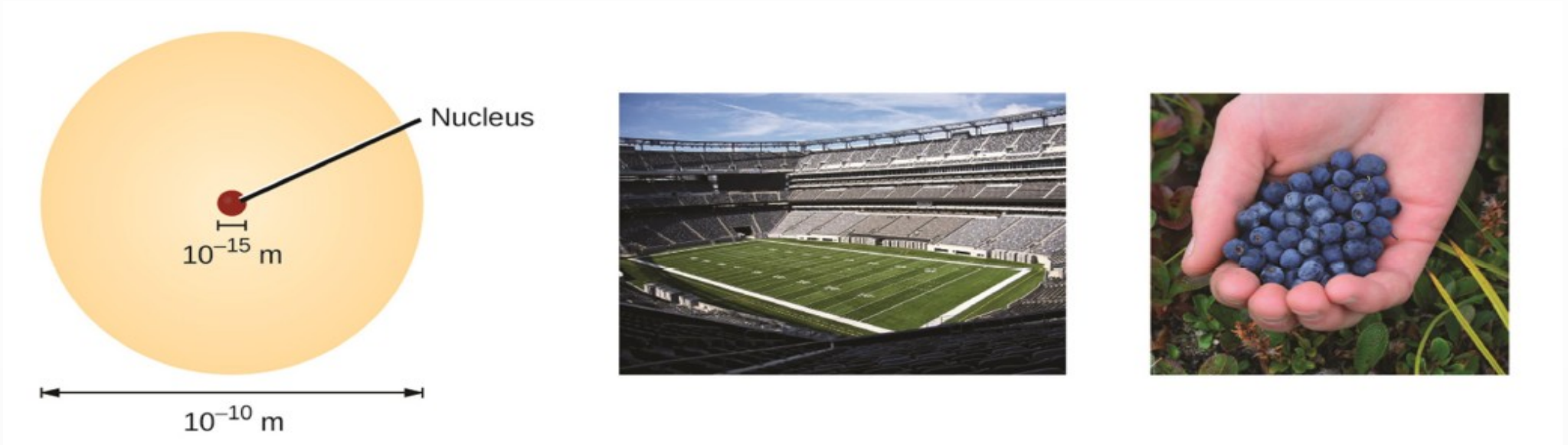


Figure 2.1: If an **atom** could be expanded to the size of a football stadium, the **nucleus** would be the size of a single blueberry.

Cont…

- Atoms and the protons, neutrons, and electrons that compose them are extremely small.
- For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb).
- When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the:

  # **atomic mass unit (amu)** and

  # the **fundamental unit of charge (e).**

Cont…

- The **amu** was originally defined based on hydrogen, the lightest element, then later in terms of oxygen.
- Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly **12 amu**.
- (This isotope is known as "**carbon-12**")
- Thus, one amu is exactly 1/12 of the mass of one carbon-12 atom:

$$1 \text{ amu} = 1.6605 \times 10{-}24 \text{ g}.$$

Cont…

- (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.)
- The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with, $e = 1.602 \times 10^{-19}$ C.

- A **proton** has a mass of 1.0073 amu and a charge of 1+.
- A **neutron** is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral.
- The **electron** has a charge of 1- and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton).

Cont…

- An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass:

- ✓ The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu.

- ✓ This "missing" mass is known as the mass defect.

- The properties of these fundamental particles are summarized in Table 2.1.

Cont…

Table2.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
Electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
Proton	Nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
Neutron	Nucleus	0	0	1.00866	1.67493×10^{-24}

- The number of protons in the nucleus of an atom is its **atomic number (Z).**
- ✓ **For example**, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have.

Cont…

- A **neutral atom** must contain the same number of positive and negative charges, so the number of protons equals the number of electrons.

✓ Therefore, the atomic number also indicates the number of electrons in an atom.

- The total number of protons and neutrons in an atom is called its **mass number (A).**

- The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

Cont…

Atomic number (Z) = number of proton

Mass number (A) = number of proton + number of neutron

A - Z = number of neutron

- Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons.
- When the numbers of these subatomic particles are not equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

✓ Atomic charge = number of proton – number of neutron

Cont…

- An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**.
- Positively charged atoms called **cations** are formed when an atom loses one or more electrons.
  - For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 – 10 = 1+).
  - A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2- charge (8 – 10 = 2-).

Example: The iodine atoms are added as anions, and each has a 1– charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution. The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 – 53 = 74). Since the iodine is added as a 1– anion, the number of electrons is 54 [53 – (1–) = 54].

2.1.1. Chemical Symbols and Isotopes

Chemical Symbols

- A **chemical symbol** is an abbreviation that we use to indicate an element or an atom of an element.
  - ✓ **For example**, the symbol for mercury is Hg. We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).
- Some symbols are derived from the common name of the element; others are abbreviations of the name in another language.
- Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112.

Cont…

- To avoid confusion with other notations, only the first letter of a symbol is capitalized. **For example**, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O).

Element	Symbol	Element	Symbol
Aluminum	Al	iron	Fe (from *ferrum*)
Bromine	Br	lead	Pb (from *plumbum*)
Calcium	Ca	magnesium	Mg
Carbon	C	mercury	Hg (from *hydrargyrum*)
Chlorine	Cl	nitrogen	N
Chromium	Cr	oxygen	O
Cobalt	Co	potassium	K (from *kalium*)
Copper	Cu (from *cuprum*)	silicon	Si
Fluorine	F	silver	Ag (from *argentum*)
Gold	Au (from *aurum*)	sodium	Na (from *natrium*)
Helium	He	sulfur	S
Hydrogen	H	tin	Sn (from *stannum*)
Iodine	I	zinc	Zn

Cont…

Isotopes

- Is element that have the same atomic number/number of proton, but different mass number/number of neutron.
- The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.3)

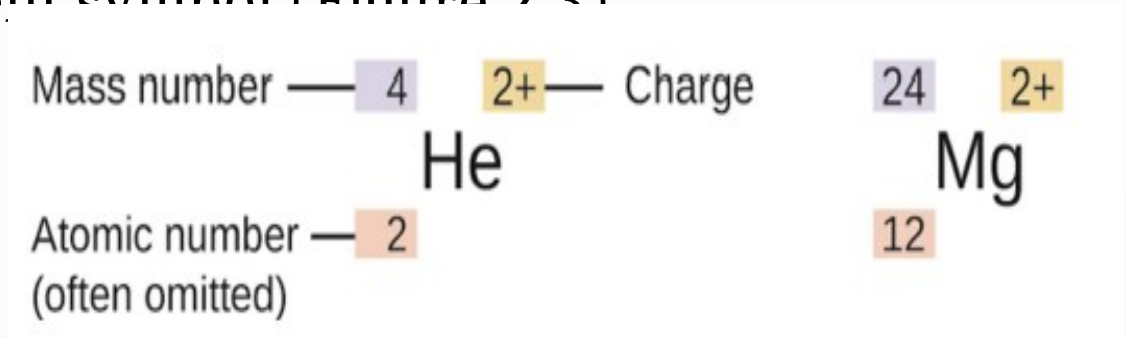


Figure 2.3: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Cont…

- For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg
- These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading.
- For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg- 24." All magnesium atoms have 12 protons in their nucleus. They differ only because a 24Mg atom has 12 neutrons in its nucleus, a 25Mg atom has 13 neutrons, and a 26Mg has 14 neutrons.

Cont…

- Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given below.

Element	Symbol	Atomic No.	No of Protons	No of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}H$(protium)	1	1	0	1.0078	99.989
	$^{2}_{1}H$(deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}H$(tritium)	1	1	2	3.01605	— (trace)
Helium	$^{3}_{2}He$	2	2	1	3.01603	0.00013
	$^{4}_{2}He$	2	2	2	4.0026	100

Cont…

Element	Symbol	Atomic No.	No of Protons	No of Neutrons	Mass (amu)	% Natural Abundance
Lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
Berylliu m	$^{9}_{4}Be$	4	4	5	9.0122	100
Boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1

Cont…

Carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)
Nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
Oxygen	$^{16}_{8}O$	8	8	8	15.9949	99.757
	$^{17}_{8}O$	8	8	9	16.9991	0.038
	$^{18}_{8}O$	8	8	10	17.9992	0.205
Fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
Neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

2.1.2. Atomic mass unit and average atomic mass

- Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number).
- However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

Cont…

- The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element.
- This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

Cont...

- For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu.
- The average atomic mass for boron is calculated to be:

$$boron\ average\ mass = (0.199 \times 10.0129\ amu) + (0.801 \times 11.0093\ amu)$$
$$= 1.99\ amu + 8.82\ amu = 10.81\ amu$$

- It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Exercise 2.1

- Calculation of Average Atomic Mass A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Exercise 2.2

- Calculation of Percent Abundance Naturally occurring chlorine consists of 35Cl (mass 34.96885 amu) and 37Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

2.2. Chemical Formulas

- A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.)
- Molecular formulas are also used as abbreviations for the names of compounds.
- The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule.

Cont...

- For Example, the structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule below.

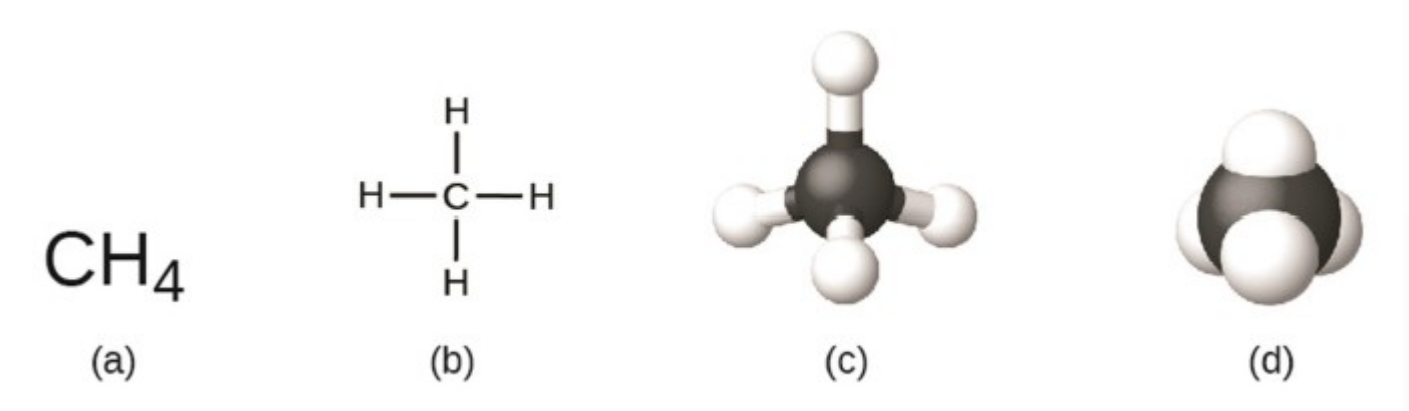


Figure 2.4: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Cont…

- The lines represent bonds that hold the atoms together.
- **A chemical bond** is an attraction between atoms or ions that holds them together in a molecule or a crystal.
- A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.
- Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together.

Cont...

- **For example**, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively.
- Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).
- The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 2.5).

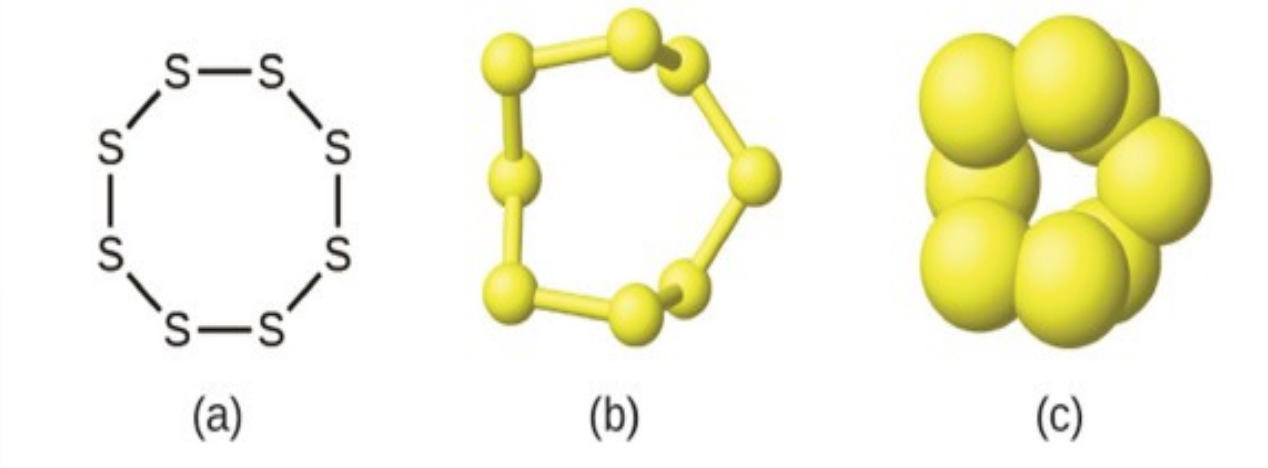
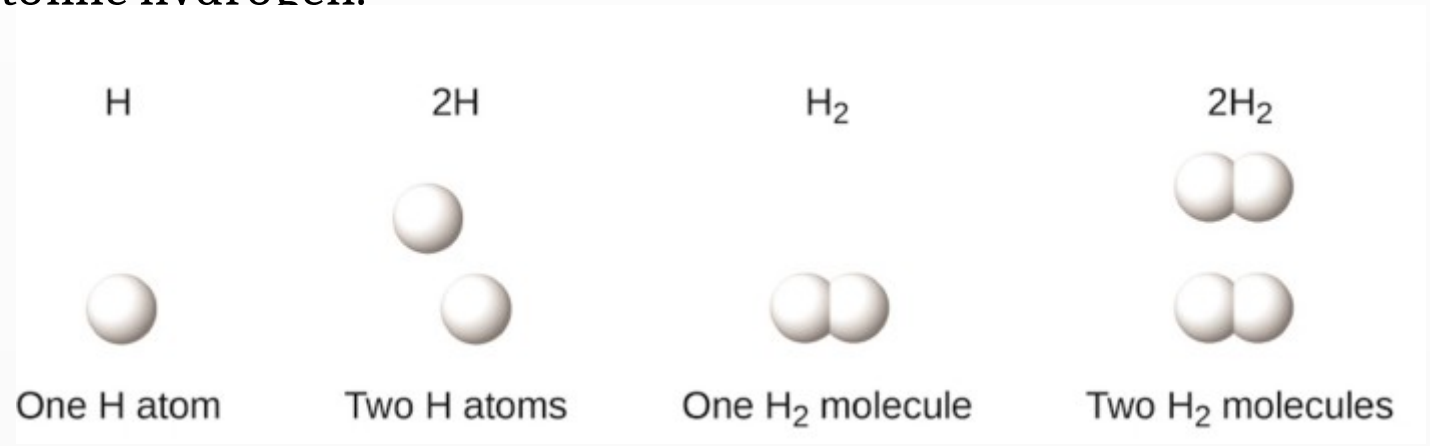


Figure 2.5: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model.

- Sulfur atoms are represented by yellow spheres.

Cont…

- It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen.



Cont…

- **Compounds** are formed when two or more elements chemically combine, resulting in the formation of bonds.

- For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt.

- We sometimes describe the composition of these compounds with **an empirical formula**, which indicates the types of atoms present and the simplest whole number ratio of the number of atoms (or ions) in the compound.

- For example, titanium dioxide has an empirical formula of TiO_2.

Cont...

- This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 2.7).

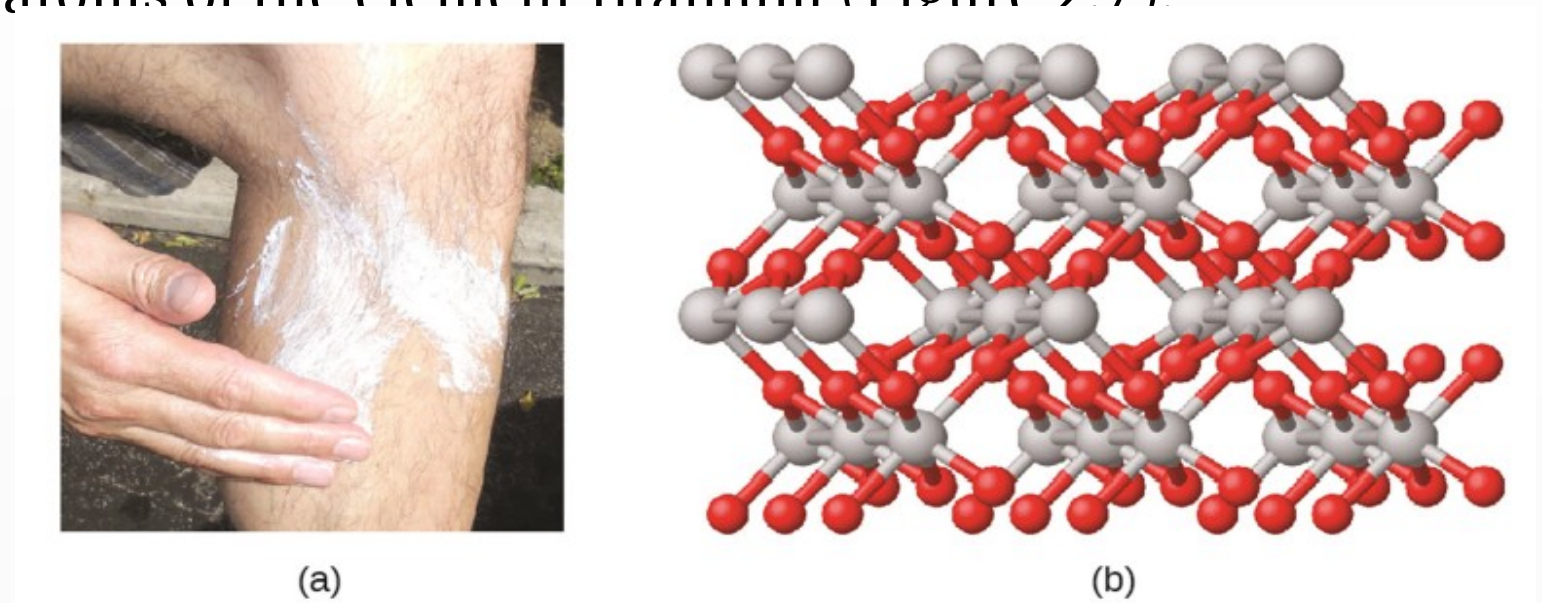


Figure 2.7: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red.

Cont...

- In many cases, the **molecular formula** of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule).

- **For example**, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom.

- Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6.

Cont…

- If we know a compound's formula, we can easily determine the empirical formula.
- **For example**, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$.
- This formula indicates that a molecule of acetic acid contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2.
- Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole number multiple of an empirical formula.

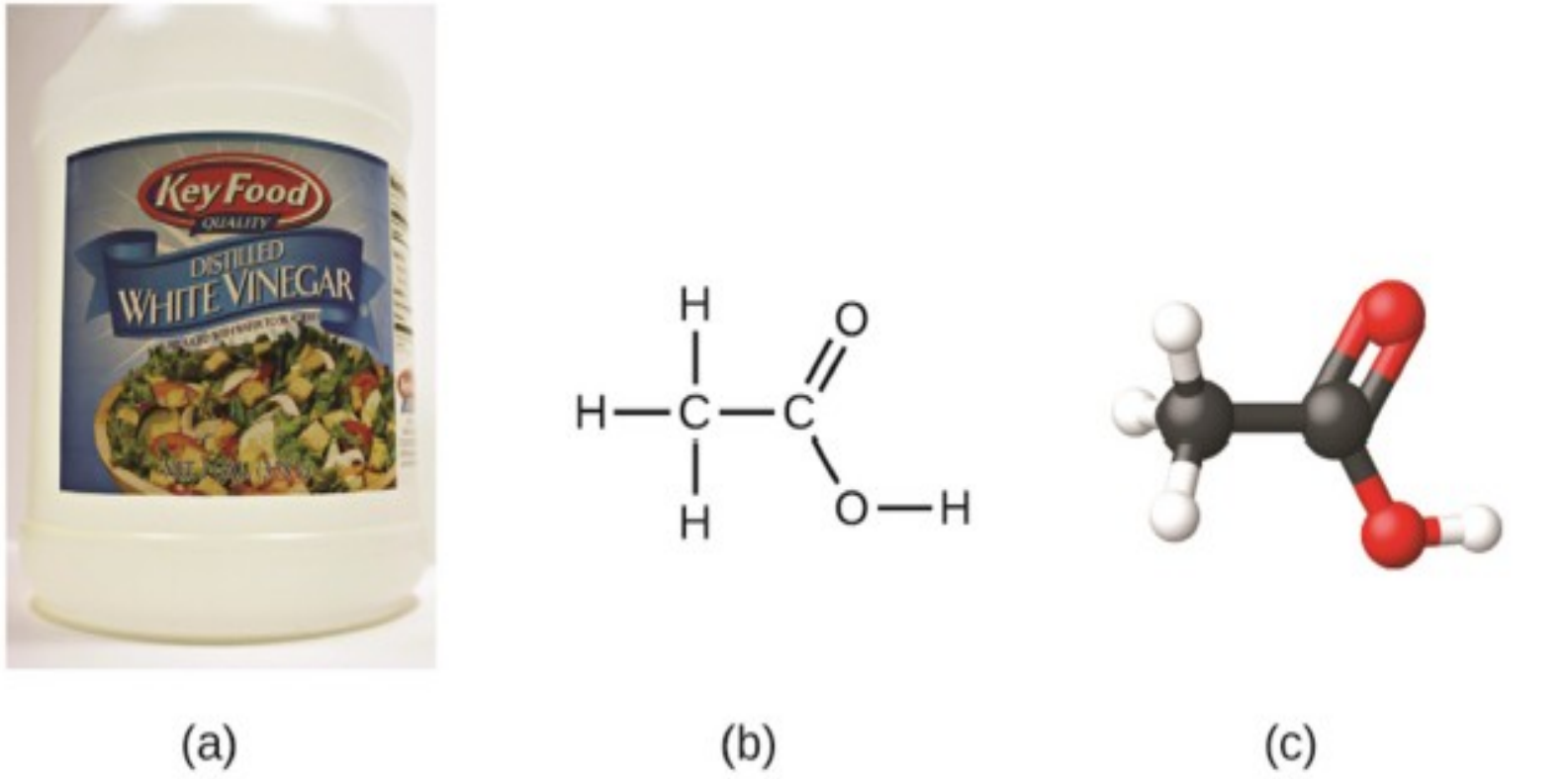


Figure 2.9: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model.

Example

Empirical and Molecular Formulas

Q_1. Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

- The molecular formula is C6H12O6 because one molecule actually contains 6C, 12H, and 6O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH2O.

2.3. The Periodic Table

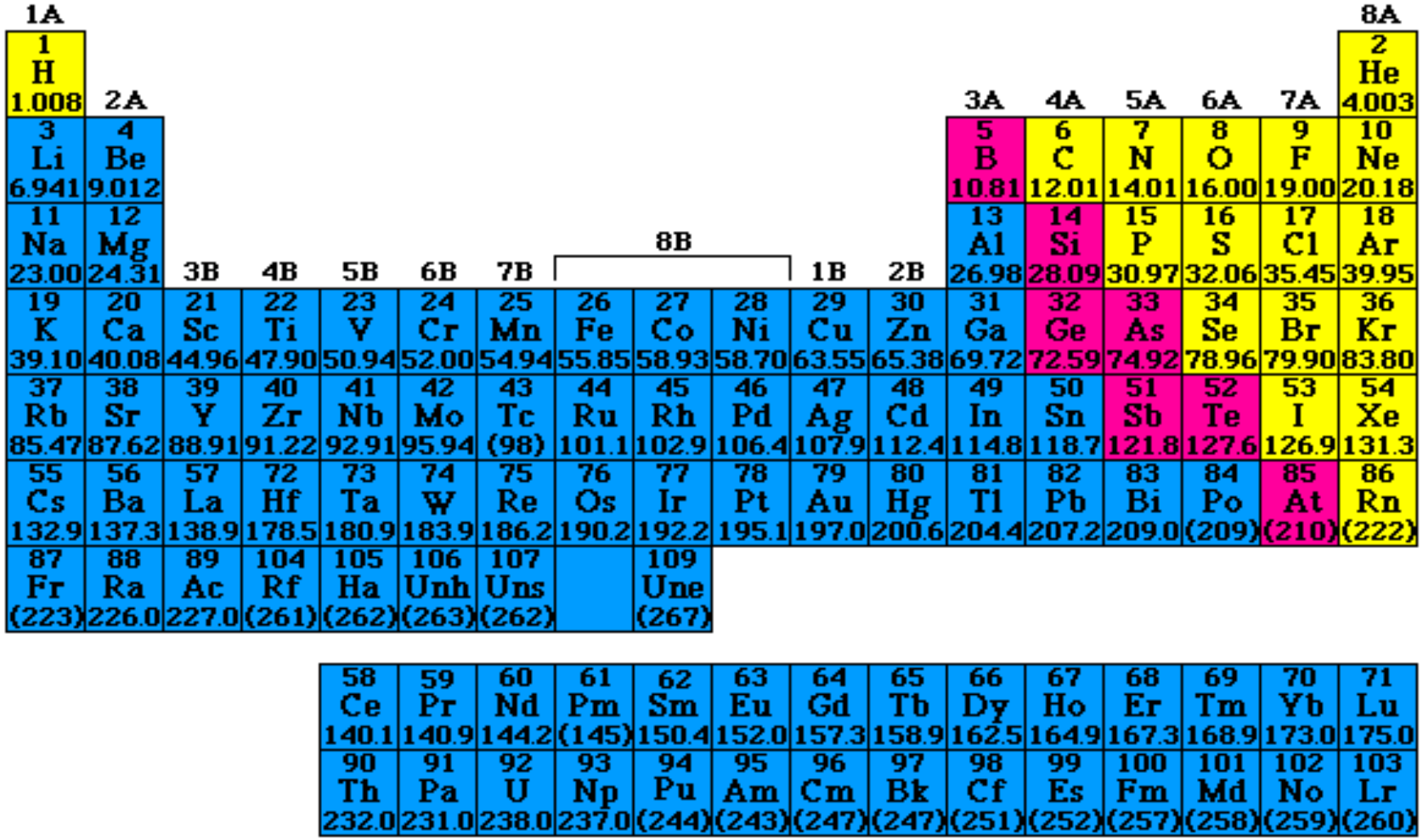
2.3.1. Historical development of the periodic table

- As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors.
- Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time.
- By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses.
- The modern statement of this relationship, the periodic law, is as follows: the properties of the elements are periodic functions of their atomic numbers.

Cont…

- A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column.
- Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name.
- The elements are arranged in seven horizontal rows, called **periods** or series, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column.

Cont...


1A
1 H 1.008
2A
4 Be 9.012
3 Li 6.941
11 Na 23.00
12 Mg 24.31
3B
4B
5B
6B
7B
8B
1B
2B
3A
4A
5A
6A
7A
8A
2 He 4.003
5 B 10.81
6 C 12.01
7 N 14.01
8 O 16.00
9 F 19.00
10 Ne 20.18
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.06
17 Cl 35.45
18 Ar 39.95
19 K 39.10
20 Ca 40.08
21 Sc 44.96
22 Ti 47.90
23 V 50.94
24 Cr 52.00
25 Mn 54.94
26 Fe 55.85
27 Co 58.93
28 Ni 58.70
29 Cu 63.55
30 Zn 65.38
31 Ga 69.72
32 Ge 72.59
33 As 74.92
34 Se 78.96
35 Br 79.90
36 Kr 83.80
37 Rb 85.47
38 Sr 87.62
39 Y 88.91
40 Zr 91.22
41 Nb 92.91
42 Mo 95.94
43 Tc (98)
44 Ru 101.1
45 Rh 102.9
46 Pd 106.4
47 Ag 107.9
48 Cd 112.4
49 In 114.8
50 Sn 118.7
51 Sb 121.8
52 Te 127.6
53 I 126.9
54 Xe 131.3
55 Cs 132.9
56 Ba 137.3
57 La 138.9
72 Hf 178.5
73 Ta 180.9
74 W 183.9
75 Re 186.2
76 Os 190.2
77 Ir 192.2
78 Pt 195.1
79 Au 197.0
80 Hg 200.6
81 Tl 204.4
82 Pb 207.2
83 Bi 209.0
84 Po (209)
85 At (210)
86 Rn (222)
87 Fr (223)
88 Ra 226.0
89 Ac 227.0
104 Rf (261)
105 Ha (262)
106 Unh (263)
107 Uns (262)
109 Une (267)
58 Ce 140.1
59 Pr 140.9
60 Nd 144.2
61 Pm (145)
62 Sm 150.4
63 Eu 152.0
64 Gd 157.3
65 Tb 158.9
66 Dy 162.5
67 Ho 164.9
68 Er 167.3
69 Tm 168.9
70 Yb 173.0
71 Lu 175.0
90 Th 232.0
91 Pa 231.0
92 U 238.0
93 Np 237.0
94 Pu (244)
95 Am (243)
96 Cm (247)
97 Bk (247)
98 Cf (251)
99 Es (252)
100 Fm (257)
101 Md (258)
102 No (259)
103 Lr (260)

2.3.2. Classification of elements in the periodic table

- Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors.

- **For example**, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well.

- Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity.

Cont…

- We can sort the elements into large classes with common properties:

- **Metals** (elements that are shiny, malleable, good conductors of heat and electricity);

- **Nonmetals** (elements that appear dull, poor conductors of heat and electricity); and

- **Metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals).

Cont…

- The elements can also be classified into the **main-group elements** (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.12).

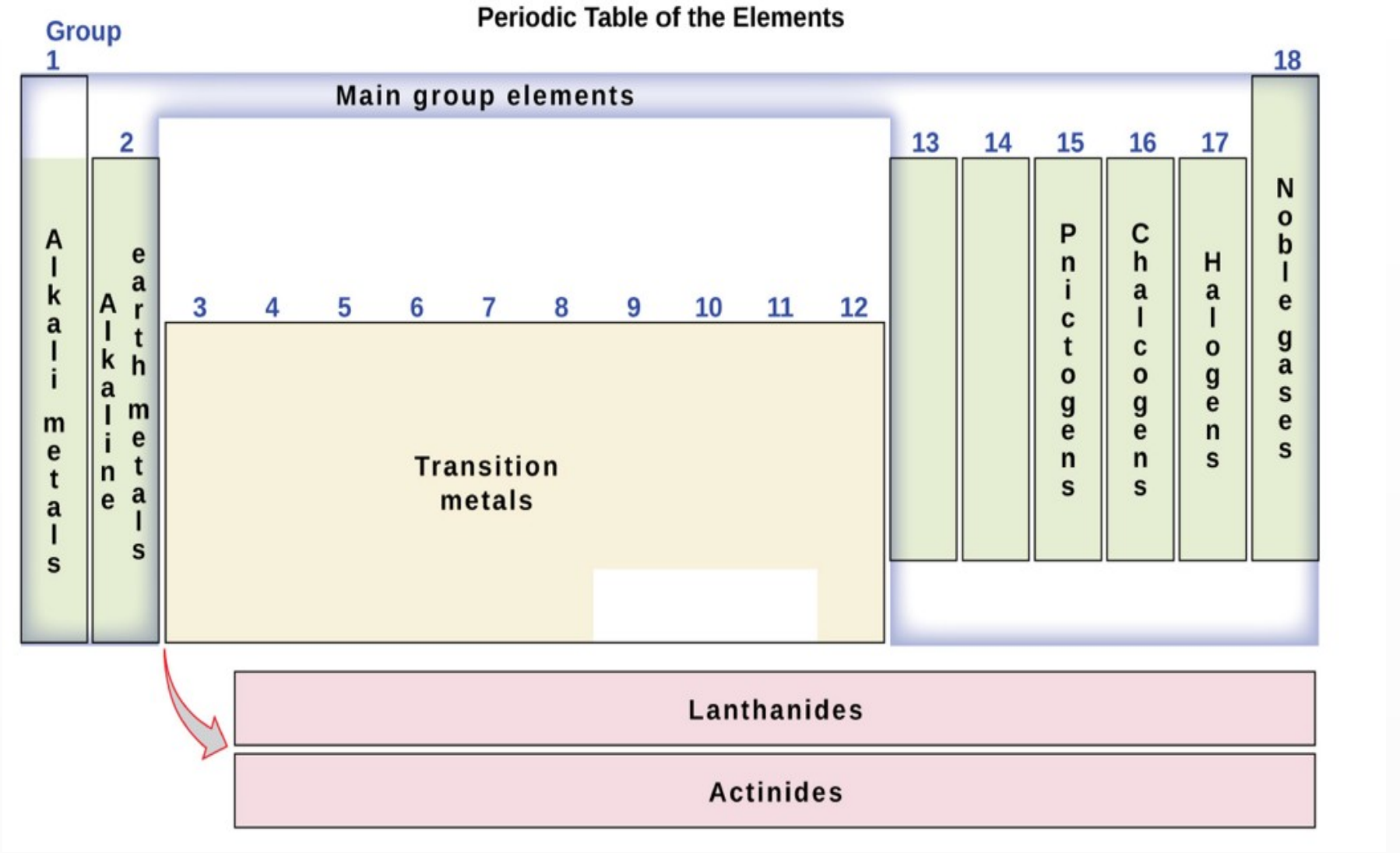


Figure 2.12: The periodic table organizes elements with similar properties into groups.

Cont…

- The elements can be subdivided further by more specific properties, such as the composition of the compounds they form.

- **For example**, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties.

- The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group.

Cont…

- Other groups with specific names are the pnictogens (**group 15**), chalcogens (**group 16**), halogens (**group 17**), and the noble gases (**group 18**, also known as inert gases).
- The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family.
- **Hydrogen** is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

2.4. Ionic and Molecular Compounds

- In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged.
- **Electrons**, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms.
- The **transfer** and **sharing** of electrons among atoms govern the chemistry of the elements.
- During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called **ions** (Figure 2.13).

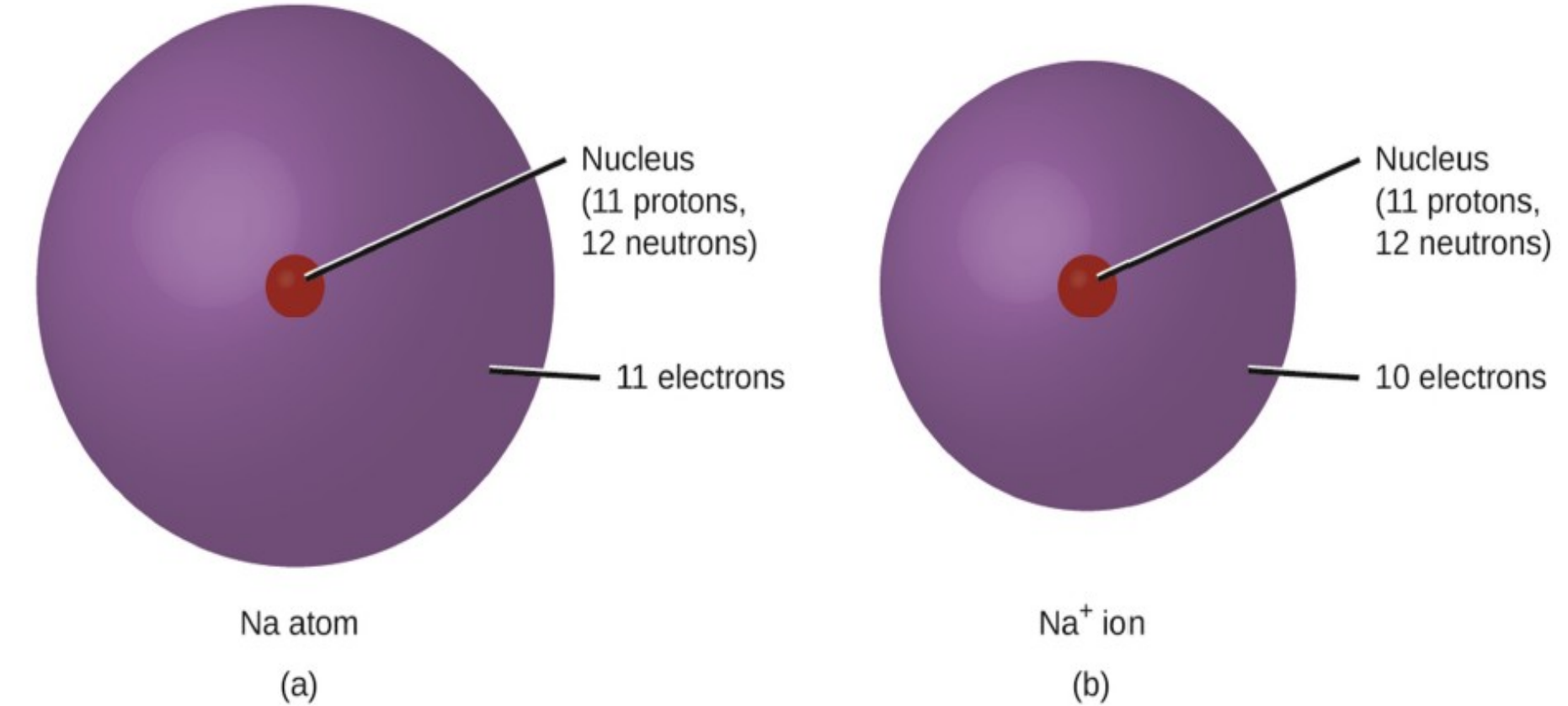


Figure 2.13: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

Cont…

- Atoms in the periodic table can loses or gains one or more electrons to attain noble gas configuration. An atom of an **alkali metal (group 1)** loses one electron and forms a cation with a 1+ charge; An **alkaline earth metal (group 2**) loses two electrons and forms a cation with a 2+ charge, and so on.

- **For example**, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

Cont…

- When atoms of non-metal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table.
- Atoms of group 17 gain one electron and form anions with a 1- charge; atoms of group 16 gain two electrons and form ions with a 2- charge, and so on.

- **For example**, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1- charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-.

Cont…

- Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number.
- That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on.
- Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases.
  - For example, group 17 elements (one group left of the noble gases) form 1– ions; group 16 elements (two groups left) form 2– ions, and so on.

Cont…

- This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table.
- In fact, **transition metals** and some other metals often exhibit variable charges that are not predictable by their location in the table.

- **For example**, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

Example 2.7: Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

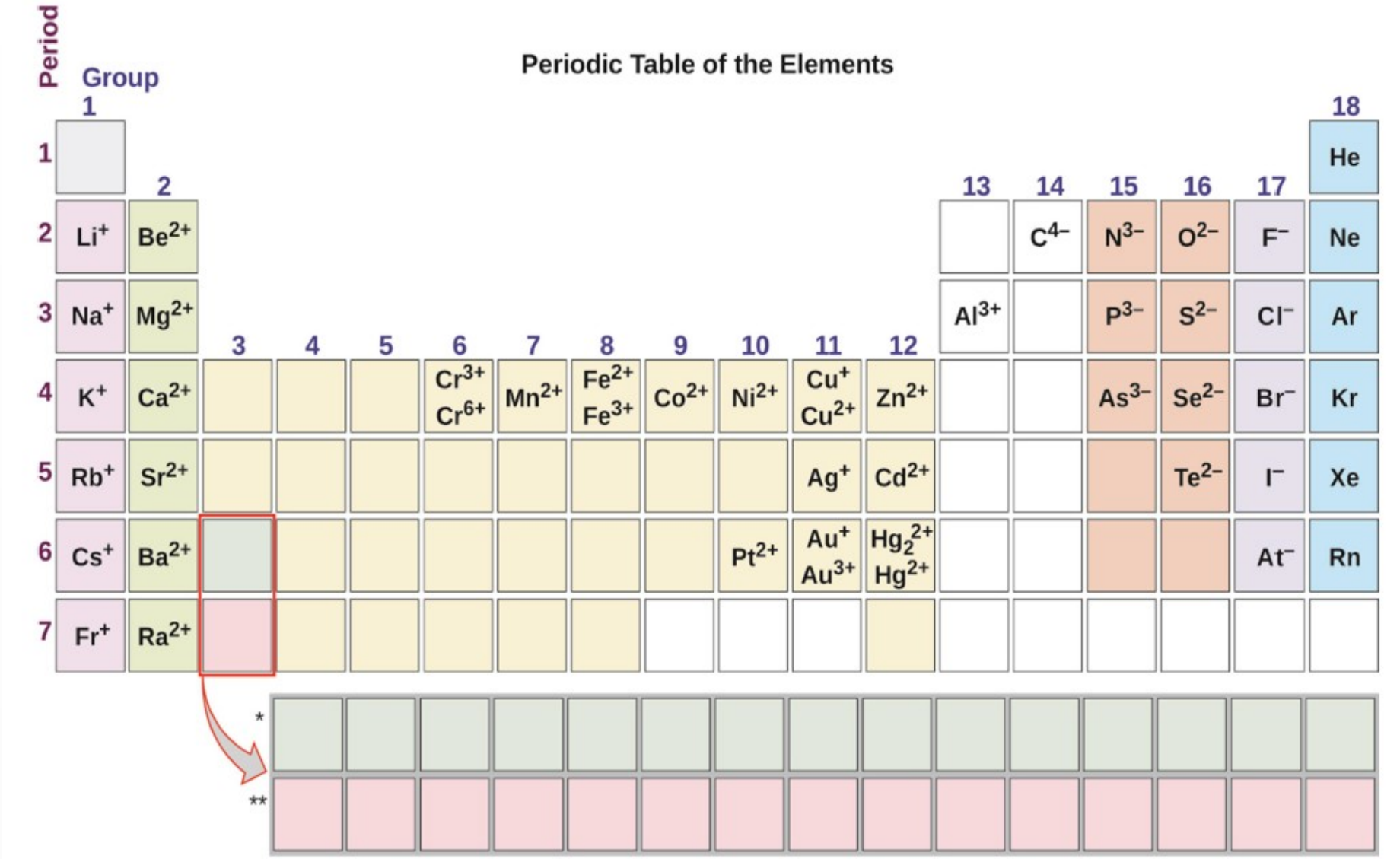


Figure 2.14: Some elements exhibit a regular pattern of ionic charge when they form ions.

Cont…

- The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many **polyatomic ions**.
- These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.4.
- **Oxyanions** are polyatomic ions that contain one or more oxygen atoms.
- At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions.

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
Ammonium	NH_4^+		
Hydronium	H_3O^+		
Peroxide	O_2^{2-}		
Hydroxide	OH^-		
Acetate	CH_3COO^-	acetic acid	CH_3COOH
Cyanide	CN^-	hydrocyanic acid	HCN
Azide	N_3^-	hydrazoic acid	HN_3
Carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
Bicarbonate	HCO_3^-		
Nitrate	NO_3^-	nitric acid	HNO_3
Nitrite	NO_2^-	nitrous acid	HNO_2
Sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
Hydrogen sulfate	HSO_4^-		
Sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
Hydrogen sulfite	HSO_3^-		
Phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
Hydrogen phosphate	HPO_4^{2-}		
Dihydrogen phosphate	$H_2PO_4^-$		
Perchlorate	ClO_4^-	perchloric acid	$HClO_4$
Chlorate	ClO_3^-	chloric acid	$HClO_3$
Chlorite	ClO_2^-	chlorous acid	$HClO_2$
Hypochlorite	ClO^-	hypochlorous acid	HClO
Chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
Dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
Permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Cont…

- Note that there is a system for naming some polyatomic ions; **-ate** and **-ite** are suffixes designating polyatomic ions containing more or fewer oxygen atoms.
- Per- (short for “hyper”) and hypo- (meaning “under”) are prefixes meaning more oxygen atoms than -ate and fewer oxygen atoms than -ite, respectively.

- **For example**, perchlorate is ClO^{4-}, chlorate is ClO^{3-}, chlorite is $ClO^{2-}$and hypochlorite is ClO^{-}. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^{-}while sulfate is SO_4^{2-}.

Cont…

- The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying **chemical bonding.**
- When electrons are **transferred and ions form, ionic bonds result.**
- **Ionic bonds** are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions).
- When electrons are "**shared**" and molecules form, **covalent bonds result**. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms.

2.4.1. Formation of Ionic Compounds

- When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions.
- The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound.

- **For example**, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl.

Cont…

- A compound that contains ions and is held together by ionic bonds is called an **ionic compound**.
- When a metal is combined with one or more nonmetals, the compound is usually ionic.
- This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course.

- **However**, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

Cont…

- **Ionic compounds** are solids that typically melt at high temperatures and boil at even higher temperatures.
- **For example**, sodium chloride melts at 801°C and boils at 1413°C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.)
- In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles).
- When molten, however, it can conduct electricity because its ions are able to move freely through the liquid.

Cont…

- In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions.
- Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions.
- We can use this observation to help us write the formula of an ionic compound.
- The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Cont…

- Many ionic compounds contain polyatomic ions as the cation, the anion, or both.
- For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$.

- This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups.
- The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3^-.
- The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

2.4.2. Formation of Molecular Compounds

- Many compounds do not contain ions but instead consist solely of discrete, neutral molecules.
- These molecular compounds (covalent compounds) result when atoms share rather than transfer (gains or losses), electrons.
- Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.
- Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals.

➢**Example 2.10**: Predict whether the following compounds are ionic or molecular:

(a) KI, the compound used as a source of iodine in table salt

(b) H_2O_2, the bleach and disinfectant hydrogen peroxide

(c) $CHCl_3$, the anesthetic chloroform

(d) Li_2CO_3, a source of lithium in antidepressants

2.5. Chemical Nomenclature

- **Nomenclatur**e, a collection of rules for naming things, is important in science and in many other situations.
- This portion describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4.
- The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids.

2.5.1. Ionic compounds

- To name an inorganic compound, we need to consider the answers to several questions.
  - First, is the compound ionic or molecular?
  - If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)?
  - Are the ions monatomic or polyatomic?
  - If the compound is molecular, does it contain hydrogen?
  - If so, does it also contain oxygen?
- From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

2.5.1.1. Compounds Containing Only Monatomic Ions

- The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix -ide). Some examples are given in Table 2.5.

- Table2.5: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

2.5.1.2. Compounds Containing Polyatomic Ions

- Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion.
- Examples are shown in Table 2.6.

Table2.6: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	NH_4Cl, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

2.5.1.3. Compounds Containing a Metal Ion with a Variable Charge

- Most of the transition metals and some main group metals can form two or more cations with different charges.
- Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal.
- The charge of the metal ion is determined from the formula of the compound and the charge of the anion.

➢Table2.8: Some Ionic Compounds with Variably Charged Metal Ions

Compound	Name
$FeCl_2$	iron(II) chloride
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

Cont…

- Out-of-date nomenclature used the suffixes –ic and –ous to designate metals with higher and lower charges, respectively:
- Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride.
- Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry.

- **For example**, you may see the words stannous fluoride on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

2.5.1.4. Ionic Hydrates

- Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**.
- The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning "not hydrated") compound that indicates the number of water molecules associated with each formula unit of the compound.
- The added word begins with a Greek prefix denoting the number of water molecules (see Table 2.9) and ends with "hydrate."

Cont…

- The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix –ide.
- The numbers of atoms of each element are designated by the Greek prefixes shown in Table 2.10.
- When only one atom of the first element is present, the prefix mono- is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide.

Cont…

- **For example**, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate.
- Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

➢ Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water.

➢ The two examples mentioned in the previous paragraph are represented by the formulas

- Copper(II) sulfate pentahydrate $CuSO_4 \cdot 5H_2O$
- Sodium carbonate decahydrate$Na_2CO_3 \cdot 10H_2O$

➢Table2.9: Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

Example 2.11: Name the following ionic compounds

(a) Fe_2S_3 (b) CuSe (c) GaN (d) $MgSO_4 \cdot 7H_2O$ (e) $Ti_2(SO_4)_3$

2.5.2. Molecular Compounds

- The bonding characteristics of inorganic molecular compounds are different from ionic compounds and they are named using a different system as well.
- The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas.
- However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Table2.10: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

2.5.2.1. Compounds Composed of Two Elements

- When two nonmetallic elements form a molecular compound, several combination ratios are often possible.

- **For example**, carbon and oxygen can form the compounds CO and CO_2.

- Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide).

- To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element.

Cont…

- There are a few common names that you will encounter as you continue your study of chemistry.
- For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide.
- Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.)
- You should commit to memory the common names of compounds as you encounter them.

2.5.2.2. Binary Acids

- Some compounds containing hydrogen are members of an important class of substances known as acids.
- Many acids release hydrogen ions, H+, when dissolved in water.
- If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word “hydrogen” is changed to the prefix hydro-
2. The other nonmetallic element name is modified by adding the suffix -ic
3. The word “acid” is added as a second word

- **For example**, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called hydrochloric acid. Several other examples of this nomenclature are shown in Table 2.11

Table2.11: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

2.5.2.3. Oxyacids

- Oxyacids is a compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound.
- Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion
3. Replace –ate with –ic, or –ite with –ous
4. Add “acid”

Cont…

- **For example**, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate").
- To name this correctly, "hydrogen" is omitted; the –ate of carbonate is replace with –ic; and acid is added-so its name is carbonic acid. Other examples are given in Table 2.12.

➢ There are some exceptions to the general naming method (e.g., H2SO4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfurous, acid).

Table 2.12: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	Acetate	acetic acid
HNO_3	Nitrate	nitric acid
HNO_2	Nitrite	nitrous acid
$HClO_4$	Perchlorate	perchloric acid
H_2CO_3	Carbonate	carbonic acid
H_2SO_4	Sulfate	sulfuric acid
H_2SO_3	Sulfite	sulfurous acid
H_3PO_4	Phosphate	phosphoric acid

CHAPTER THREE

Composition of Substances and Solutions

3.1. Formula Mass and Mole Concept

- Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

3.1.1. Formula Mass

- Is the mass of a substance obtained by summing the average atomic masses of all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

- For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance.
  - ✓ therefore, the formula mass may be correctly referred to as a molecular mass.
- Consider chloroform ($CHCl_3$), The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms.

- The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms.

Figure 3.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

- Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
				Molecular mass	206.27

Example 3.1: What is the molecular mass (amu) of Ibuprofen, $C_{13}H_{18}O_2$?

Solution

Molecules of this compound are composed of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms.

The average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
				Molecular mass	206.27

Formula Mass for Ionic Compounds

- Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter.
- The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds:
  - ✓ by summing the average atomic masses of all the atoms in the compound's formula.

Consider sodium chloride, NaCl, is an ionic compound composed of:

- sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

Example 3.2

What is the formula mass (amu) of Aluminum sulfate, $Al_2(SO_4)_3$?

Solution

The formula for this compound indicates it contains $Al^{3+}$and SO_4^{2-}ions combined in a 2:3 ratio. The formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14

3.1.2. The Mole Concept

- The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion.
- For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms.
    - However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties.

- The mole is an amount unit similar to familiar units like pair, dozen, gross, etc.
- It provides a specific measure of the number of atoms or molecules in a sample of matter.
- A mole of substance is that amount in which there are $6.02214076 \times 10^{23}$ discrete entities (atoms or molecules). This large number is a fundamental constant known as Avogadro's number (NA).

- This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being 6.022 X 10^{23} /mol.
- 1 mole of any element contains the same number of atoms as 1 mole of any other element.
- The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different.

➢The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol)

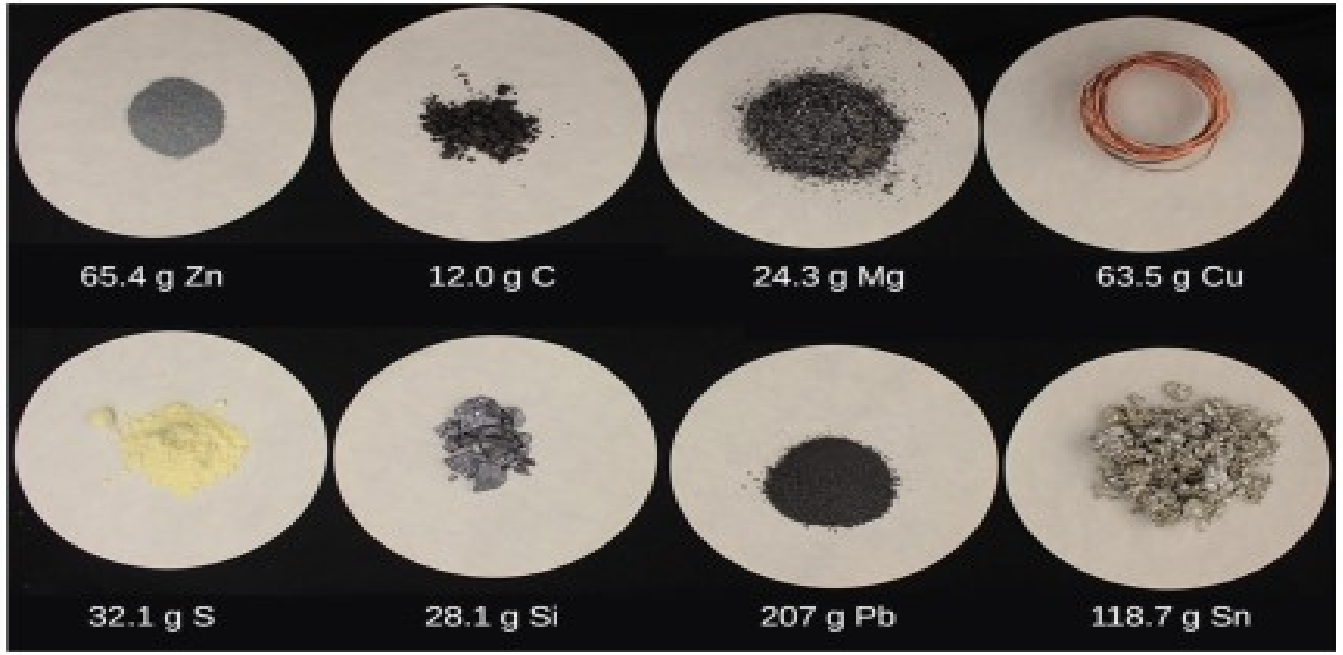


Figure 3.4: Each sample contains 6.022 X 10^{23} atoms 1.00 mol of atoms.

- The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu.
  - Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu).
  - A mole of ^{12}C weighs 12 g (its molar mass is 12 g/mol).
  - The molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu

Consider the following Figure 3.5 :



- Each sample contains 6.02 X 10^{23} molecules or formula units-1.00 mol of the compound or element.

Clock-wise from the upper left:

- 130.2 g of C_8H_{17} OH (1-octanol, formula mass 130.2 amu),
- 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu),
- 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and
- 256.5 g of S_8 (sulfur, formula mass 256.5 amu).

Example 3.3: Deriving Moles from Grams for an Element:

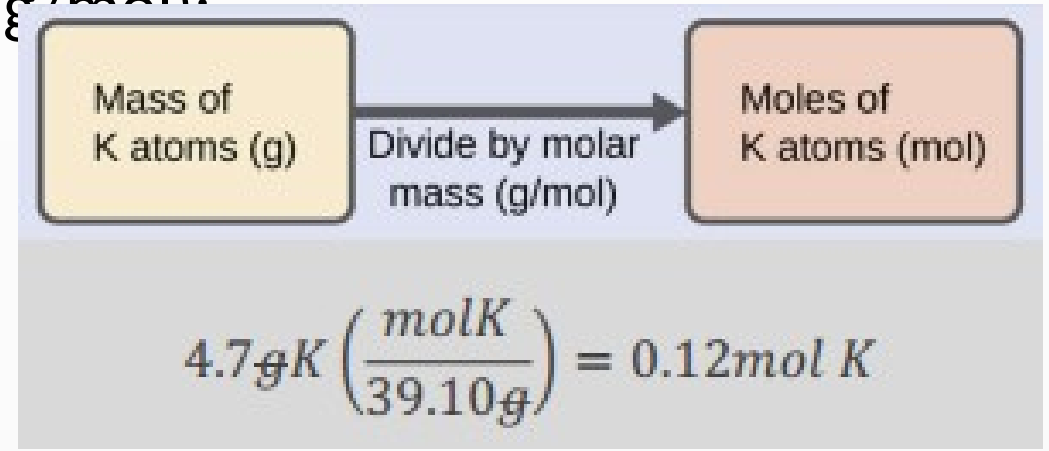
According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution:

The mass of K is provided, and the corresponding amount of K in moles is requested.

the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol and the given mass of K is 4.7 g.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



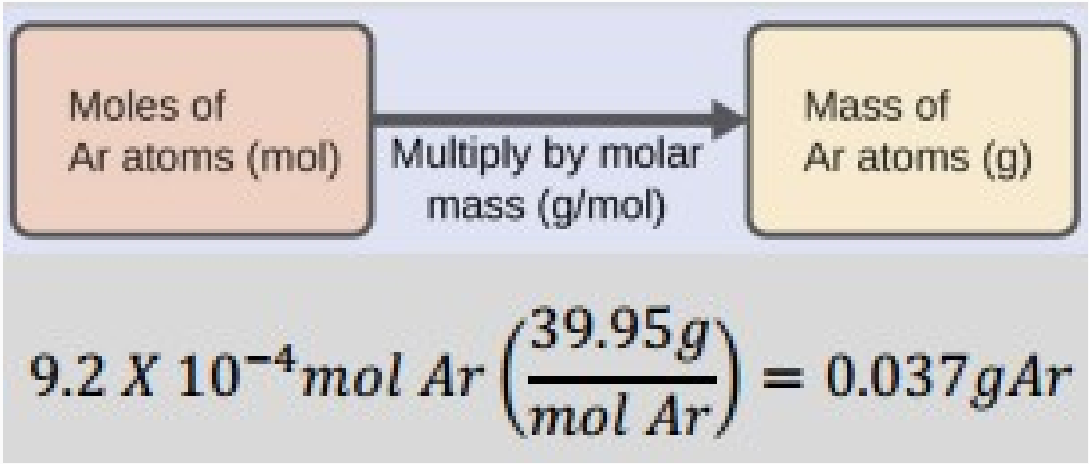
$$4.7\cancel{g}K\left(\frac{molK}{39.10\cancel{g}}\right) = 0.12mol\ K$$

Example 3.4: Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution:

Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g.



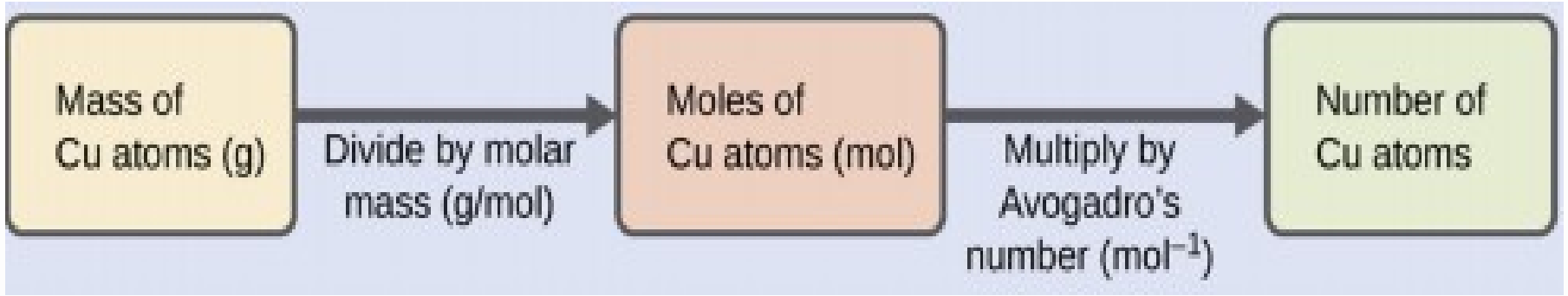
$$9.2\ X\ 10^{-4} mol\ Ar \left(\frac{39.95 g}{mol\ Ar}\right) = 0.037 g Ar$$

Example 3.5: Deriving Number of Atoms from Mass for an Element

Copper is commonly used to fabricate electrical wire. How many copper atoms are in 5.00 g of copper wire?

Solution:

The number of Cu atoms in the wire derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (NA).



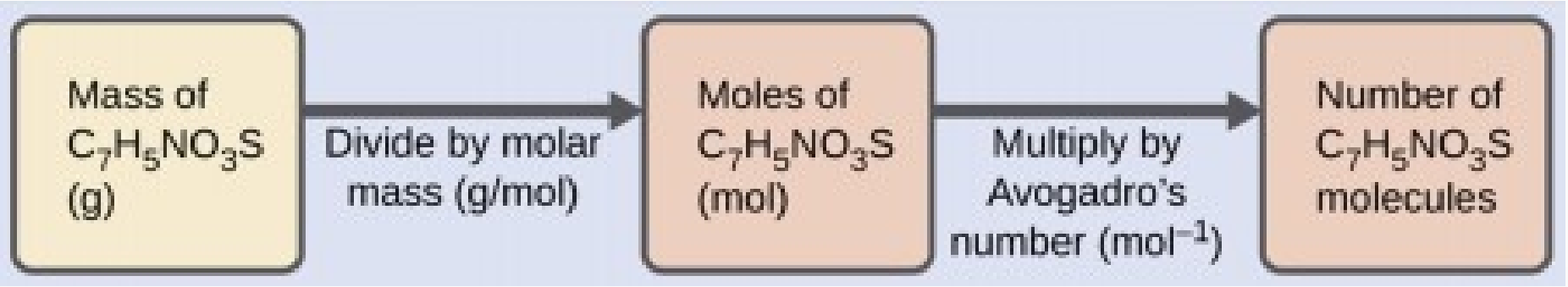
Carrying out the two-step computation yields:

$$5.00\cancel{g}\ Cu\left(\frac{\cancel{mol}\ Cu}{63.55\cancel{g}}\right)\left(\frac{6.022\ X10^{23}}{\cancel{mol}}atoms\right) \qquad 4.74\ X10^{22}\ atoms\ of\ Copper$$

Example 3.6: Deriving the Number of Atoms and Molecules from the Mass of a Compound

Given that saccharin, ($C_7H_5NO_3S$) has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution:



$$0.0400g\ C_7H_5NO_3S\left(\frac{\cancel{mol}\ {}_7H_5NO_3S}{183.18\cancel{g}C_7H_5NO_3S}\right)\left(\frac{6.022\ X10^{23}C_7H_5NO_3S\ molecules}{1\cancel{mol}\ C_7H_5NO_3S}\right)$$

$$= 1.31X10^{20}C_7H_5NO_3S\ molecules$$

- ✓ The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31X10^{20}C_7H_5NO_3S\ molecules\left(\frac{7\ C\ atoms}{1C_7H_5NO_3Smolecules}\right)$$

$$= 9.17X10^{20}\ C\ atom$$

3.2. Determining empirical and molecular formulas

3.2.1. Percent Composition

- The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup.
- When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally.

- For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%H = \frac{Mass\ of\ H}{Mass\ of\ compound}\ X\ 100\% \qquad \%C = \frac{Mass\ of\ C}{Mass\ of\ compound}\ X\ 100\%$$

- If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%H = \frac{2.5g\ H}{10.0g\ Compound}\ X\ 100\% = 25\%$$

$$\%C = \frac{7.5g\ C}{10.0g\ compound}\ X\ 100\% = 75\%$$

Example 3.7: Calculation of Percent Composition.

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution:

To calculate percent composition, divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%H = \frac{1.85gH}{12.04g\ compound}\ X\ 100\% = 15.4\%$$

$$\%N = \frac{2.85gN}{12.04g\ compound}\ X\ 100\% = 23.7\%$$

$$\%C = \frac{7.34gC}{12.04g\ compound}\ X\ 100\% = 61.0\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

Determining Percent Composition from Molecular or Empirical Formulas

- consider the common nitrogen containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O).

➢ The percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements.

➢ A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 × 1.008 amu) = 3.024

➢The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%N = \frac{14.01 amu N}{17.03 amu NH_3} X\ 100\% = 82.27\%$$

$$\%H = \frac{3.024 amu H}{17.03 amu NH_3} X\ 100\% = 17.76\%$$

Example 3.8 Determining Percent Composition from a Molecular Formula:

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

3.2.2. Determination of Empirical Formulas

- Empirical formulas are the simplest chemical formulas; they are written by reducing the subscripts in the molecular formulas to the smallest possible whole numbers.
- Molecular formulas are the true formulas of molecules. If we know the molecular formula, we also know the empirical formula, but the reverse is not true.

Example:

Consider the compound hydrazine (N_2H_4), the empirical formula of hydrazine is NH_2.

- ✓ Although the ratio of nitrogen to hydrogen is 1:2 in both the molecular formula (N_2H_4) and the empirical formula (NH_2),
- ✓ only the molecular formula tells us the actual number of N atoms (two) and H atoms (four) present in a hydrazine molecule.

- Empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element’s molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole number ratio of subscripts is obtained

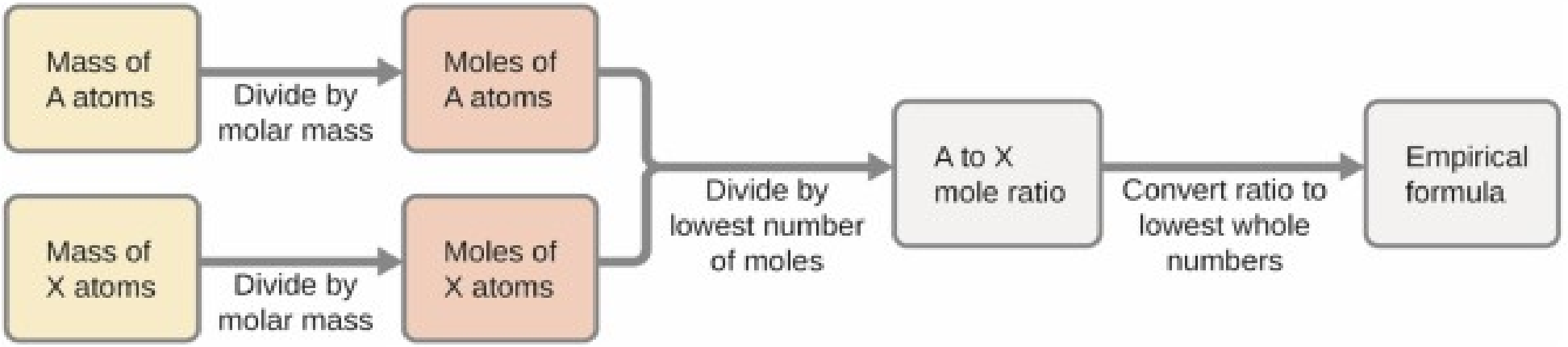


Figure 3.8: The empirical formula of a compound can be derived from the masses of all elements in the sample.

- For many molecules, the molecular formula and empirical formula are one and the same.
  - ✓ Some examples are water (H_2O), ammonia (NH_3), carbon dioxide (CO_2),and methane (CH_4).

Example 3.9:

Determining a Compound's Empirical Formula from the Masses of its Elements.

A sample of the black mineral hematite, an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?

Solution

This problem provides the mass in grams of each element. Begin by finding the moles of each:

$$34.97 g Fe \left(\frac{mol Fe}{55.85 g}\right) = 0.6261 mole\ Fe$$

$$15.03 g O \left(\frac{mol O}{16.00 g}\right) = 0.9394 mole\ O$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.00 moleFe$$

$$\frac{0.9394}{0.6261} = 1.500 moleO$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts.

$$2(Fe_1O_{1.5}) = Fe_2O_3$$

The empirical formula is Fe_2O_3.

Deriving Empirical Formulas from Percent Composition

- If the compound's percent composition is available rather than the absolute masses of the compound's constituent elements,
  - ✓ the percent composition can be used to calculate the masses of elements present in any convenient mass of compound;
  - ✓ these masses can then be used to derive the empirical formula in the usual fashion.

Example 3.10: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O. What is the empirical formula for this gas?

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g.

Assuming a 100 g sample of the compound we quickly convert 27.29% C to 27.29 g C and 72.71% O to 72.71 g O. Now we convert these to moles.

The molar amounts of carbon and oxygen in a 100 g sample are calculated by dividing each element's mass by its molar mass:

$$27.29gC\left(\frac{molC}{12.01g}\right) = 2.272mol\ C$$

$$72.71g\ O\left(\frac{molO}{16.00g}\right) = 4.544mol\ O$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ mol\ C}{2.272} = 1$$

$$\frac{4.544\ mol\ O}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

3.2.3. Determination of molecular formulas

- Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass.
- An empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula.
- If the molecular (or molar) mass of the substance is known, it may be divided by the empirical formula mass to yield the number of empirical formula units per molecule (n):

$$\frac{molecular\ or\ molar\ mass\ \left(amu\ or\ \frac{g}{mol}\right)}{empirical\ formula\ mass\ \left(amu\ or\ \frac{g}{mol}\right)} = n\ formula\ unit/molecule$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by n, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n = A_{nx}B_{ny}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O.

- ✓ The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom).
- ✓ If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180 amu/molecule}{30 \frac{amu}{formula\ unit}} = 6\ formula\ units/molecule$$

- Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6$$

Example 3.11: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula.

Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$74.02gC\left(\frac{1mol\ C}{12.01g\ C}\right) = 6.163\ mol\ C$$

$$8.710\ g\ H\left(\frac{1mol\ H}{1.01gH}\right) = 8.624\ mol\ H$$

$$17.27g\ N\left(\frac{1mol\ N}{14.01g\ N}\right) = 1.233\ mol\ N$$

Next, calculate the molar ratios of these elements relative to the least abundant element, N.

6.163molC/1.233molN=5

8.264molH/1.233molN=7

1.233molN/1.233molN=1

$$\frac{1.233}{1.233} = 1.000mol\ N$$

$$\frac{6.163}{1.233} = 4.998\ mol\ C$$

$$\frac{8.624}{1.233} = 6.994\ mol\ H$$

The molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

Calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57g\ nicotine}{0.2500\ mol\ nicotine} = \frac{162.3g}{mol}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3 g/mole}{81.13 \frac{g}{formula\ unit}} = 2\ formula\ units/molecule$$

Finally, derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

3.3. Molarity and Other Concentration Units

- The relative amount of a given solution component is known as its concentration.
- Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components.
  - This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or dissolved.
- A solution in which water is the solvent is called an aqueous solution.

- A solute is a component of a solution that is typically present at a much lower concentration than the solvent.
- Solute concentrations are often described with qualitative terms such as:-
  - dilute (of relatively low concentration) and
  - concentrated (of relatively high concentration).

➢Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications.

3.3.1. Molarity (M)

- Molarity (molar concentration) is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$Molarity = \frac{Mole\ of\ Solute}{L\ of\ Solution}$$

Example 3.12: Calculating Molar Concentrations.

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$Molarity = \frac{0.133\ mol}{355ml\frac{1L}{1000ml}} = 0.375\ \text{mol}\ /\text{L}$$

Example 3.13: Calculating Molar Concentrations from the Mass of Solute

A 0.500 L vinegar solution contains 25.2 g of acetic acid (CH_3CO_2H). What is the concentration of the acetic acid solution in units of molarity?

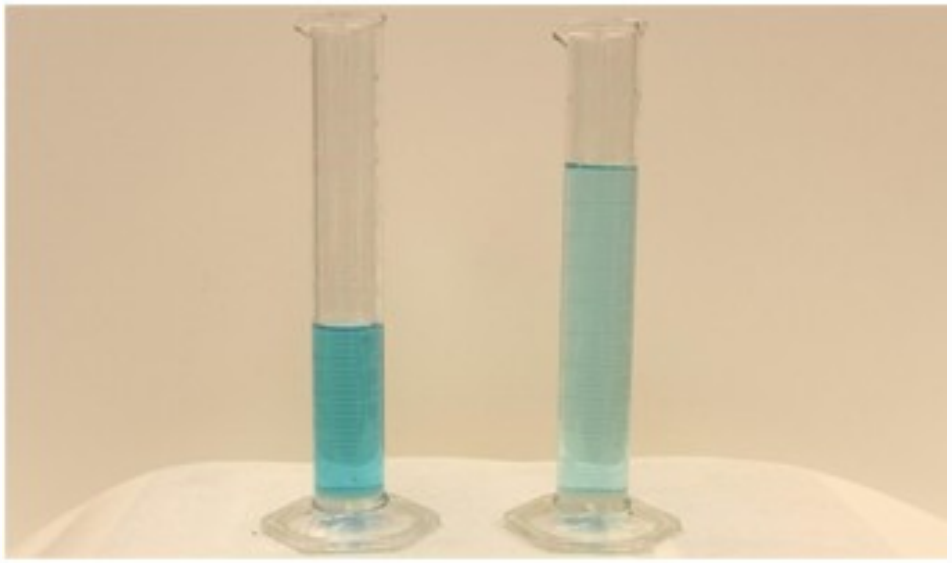
Solution

Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

$$\frac{25.2 g C\,H_3COOH\ X\ \frac{1\ mol\ C\,H_3COOH}{60.052 g C\,H_3COOH}}{0.500 L\ solution} = 0.839\ M$$

3.3.2. Dilution of Solutions

- Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent.
- For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste.



- Figure 3.9: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent.

The first has about half as much blue liquid as the second. The blue liquid is darker in the first cylinder than in the second.

- Dilution is also a common means of preparing solutions of a desired concentration.
- By adding solvent to a measured portion of a more concentrated stock solution, a solution of lesser concentration may be prepared.
- *For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application.*
  - *Before they can be used on crops, the pesticides must be diluted.*

- A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process.
- According to the definition of molarity, the number of moles of solute in a solution (n) is equal to the product of the solution's molarity (M) and its volume in liters (L):

$$n = ML$$

- Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1$$
$$n_2 = M_2 L_2$$

Where, the subscripts "1" and "2" refer to the solution before and after the dilution, respectively.

- Since the dilution process does not change the amount of solute in the solution, $n_1 = n_2$. Thus, these two equations may be set equal to one another. This relation is commonly referred to as the dilution equation.

$$M_1 L_1 = M_2 L_2 \quad \text{or} \quad C_1 V_1 = C_2 V_2$$

Example 3.14
Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00 M solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

The stock concentration, C_1, and volume, V_1, are provided as well as the volume of the diluted solution, V2.

Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution, C_2:

$$C_1V_1=C_2V_2 \qquad C_2=C_1V_1/V_2$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5 M.

$$C_2 = \frac{0.850L\ X\ 5.00mol/L}{1.80L} = 2.36M$$

3.3.3. Percentage (W/W, W/V and V/V)

3.3.3.1. Mass Percentage

- The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$Mass\ Percentage = \frac{mass\ of\ component}{mass\ of\ solution}\ X\ 100\%$$

- Mass percentage is also referred to by similar names such as percent mass, percent weight, weight/weight percent, and other variations on this theme.

- The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%.
- For example, the label of typical liquid bleach, an aqueous solution of sodium hypochlorite (NaOCl), bottle cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.

Example 3.15: Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains 3.75 mg of glucose in 5000 mg of fluid. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ glucose = \frac{3.75mg\ glucose \frac{1g}{1000mg}}{5.0g\ spinal\ fluid} = 0.075\%$$

Example 3.16: Calculations using Mass Percentage

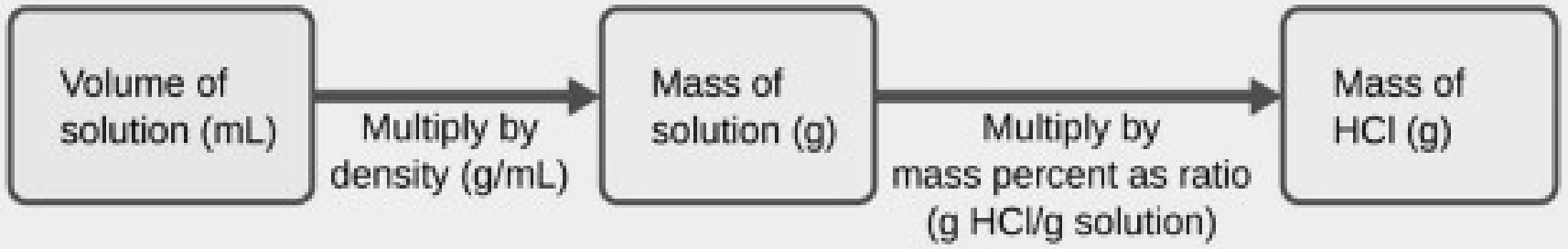
"Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

In order to derive the mass of solute in a solution from its mass percentage, the mass of the solution must be known.

Using the solution density given, convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mas.

This mathematical approach is outlined in this flowchart:



$$500ml\ solution\left(\frac{1.19g\ solution}{ml\ solution}\right)\left(\frac{37.2g\ HCl}{100g\ solution}\right) = 221\ g\ HCl$$

3.3.3.2. Volume Percentage

- The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as:
  - ✓a volume percentage,
  - ✓%vol or
  - ✓(v/v)%:

$$\text{Volume percentage} = \frac{\text{Volume solute}}{Volume\ of\ solution}\ X\ 100\%$$

Example 3.17: Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

The isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$(355ml\ solution)\left(\frac{70ml\ isopropyl\ acohol}{100ml\ solution}\right)\left(\frac{0.785g\ isopropyl\ alcohol}{1mL\ isopropyl\ alcohol}\right)$$
$$= 195g\ isopropyl\ alcohol$$

3.3.3.3. Mass-Volume Percentage

- *A mass-volume percentis a ratio of a solute's mass to the solution's volume expressed as a percentage.*
- For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution.

3.3.4. Parts per million (ppm) and Part per billion (ppb)

- Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb).
  - The mass-based definitions of ppm and ppb are given here:

$$ppm \quad \frac{mass\ solute}{mass\ solution} X10^{6} ppm \qquad ppb = \frac{mass\ solute}{mass\ solution} X10^{9} ppb$$

Example 3.18: Calculation of Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm.

$$15ppb\ X\ \frac{1ppm}{10^3ppb} = 0.015ppm$$

- The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided.
- Since the volume of solution (300 mL) is given, its density must be used to derive the corresponding mass.
- Assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL),

$$ppb = \frac{mass\ solute}{mass\ solution} X 10^9 ppb$$

$$mass\ of\ solute = \frac{ppb\ X\ mass\ solution}{10^9 ppb}$$

$$mass\ solute = \frac{15ppb\ X\ 300mL\ X\ \frac{1.00g}{ml}}{10^9 ppb} = 4.5\ X\ 10^{-6} g$$

Finally, convert this mass to the requested unit of micrograms:

$$4.4\ X\ 10^{-6} g\ X\ \frac{1\mu g}{10^{-6} g} = 4.5\mu g$$

CHAPTER FOUR

Stoichiometry of Chemical Reaction

- **Stoichiometry** (pronounced “stoy-keyom-e-tree” from the Greek stoicheion, "element or part, "and metron, "measure") is the calculation of the quantities of reactants and products involved in a chemical reaction
- It is the quantitative study of reactants and products in a chemical reaction or the study of quantities of materials consumed and produced in chemical reactions
- It is based on the chemical equation and on the relationship between mass and moles

- **Stoichiometric coefficients:** The numbers multiplying the chemical formulas in a balanced chemical equation tells us the number of moles of each substance that is consumed or is produced in the reaction

- **Subscript -** shows how many atoms of an element are in a molecule

Writing Chemical Equations

- Shorthand form for writing what reactants are used and what products are formed in a chemical reaction is called **chemical equations**

- A chemical reaction cannot be seen; it occurs on the Submicroscopic Level!

Since reactions can't be seen, we use a chemical equation to represent a chemical reaction.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O(l)$$

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

❑ The chemical equation for a reaction gives some important types of information:

A. Identities of the reactants and products

B. Relative amounts of the reactants and products or the relative numbers of each atoms

C. Physical states(solid, liquid and gas) of the reactants and products

- **The fundamental aspects of any chemical equation:**

  1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation

  2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation

3. Plus signs (+) separate individual reactant and product formulas, and an arrow (⟶) separates the reactant and product (left and right) sides of the equation

From the previous reactions:

I. *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules

II. *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules

III. *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of

- A chemical equation is balanced when the same number of atoms of each element appears on both sides of the arrow
- Because of the principle of the conservation of matter, an equation must be balanced
- It must have the same number of atoms of the same kind on both sides
- We insert coefficients (not subscripts) in front of the chemical formulas to make the number of atom in the reactants equal to the number of atom in the products

Rules for balancing

1.Begin with atoms that appear in only one compound on the left and right

2.If an atom occurs as a free element, balance it last

3.Change only coefficients (not formulas)

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

Elements	Reactants	Products	Balanced?
C	1×1 = 1	1 × 1 = 1	1 = 1, yes
H	4×1 = 4	2 × 2 = 4	4 = 4, yes
O	2×2 = 4	(1×2) + (2×1) = 4	4 = 4, yes

Ex: $H_2O \longrightarrow H_2 + O_2$ (unbalanced)(**Trial 1**)

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Elements	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$, no

- **$2H_2O \longrightarrow H_2 + O_2$** (unbalanced) (**Trial 2**)

Elements	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$1 \neq 2$, no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

- The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2

❑ **$2H_2O$** ⟶ $2H_2$ + **O_2** (balanced) (**Trial 3**)

Elements	Reactants	Products	Balanced?
H	2 × 2 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 1 = 2	2 × 1 = 2	2 = 2, yes

Ex: Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide,

❖(N_2 + O_2 ⟶ N_2O_5 (unbalanced))

Example: Consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \longrightarrow H_2O + CO_2 \text{ (unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown: $C_2H_6 + O_2 \longrightarrow 3H_2O + 2CO_2$ (unbalanced)

$$C_2H_6 + 7/2O_2 \longrightarrow 3H_2O + 2CO_2 \text{ (balanced)}$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2C_2H_6 + 7O_2 \longrightarrow 6H_2O + 4CO_2$$

- When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl:

$$CaCl_2(aq) + 2AgNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2AgCl(s)$$

- **This is molecular equation** because it doesn't represent the ionic species that are present in solution

- When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution

EX. $CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$

$2AgNO_3(aq) \longrightarrow 2Ag^+(aq) + 2NO^{3-}(aq)$

$Ca(NO_3)_2(aq) \longrightarrow Ca^{2+}(aq) + 2NO^{3-}(aq)$

- Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation (*s)*
- The formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

  $Ca^{2+}(aq) + 2Cl^{-}(aq) + 2Ag^{+}(aq) + 2NO^{3-}(aq) \longrightarrow Ca^{2+}(aq) + 2NO^{3-}(aq) + 2AgCl(s)$
- Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, Ca^{2+} (*aq*) and NO^{3-} (aq) which is called **spectator ions—**ions whose presence is required to maintain charge neutrality

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$CO_2(aq) + NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$ (unbalanced)

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$CO_2(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

$CO_2(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$

- Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$CO_2(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$$

$$CO_2(aq) + 2OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$$

EX1; Balance the oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ in acid solution.

1. Write the unbalanced equation for the reaction in ionic form.

$$Fe^{2+} + Cr_2O_7^{2-} \qquad Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2}} \longrightarrow \overset{+3}{Cr^{3+}}$

3. Balance the atoms other than O and H in each half reaction.

$Cr_2O_7^{2-}$ $2Cr^{3+}$

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

$Cr_2O_7^{2-}$ $2Cr^{3+} + 7H_2O$

$14H^+ + Cr_2O_7^{2-}$ $2Cr^{3+} + 7H_2O$

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

Fe^{2+} $Fe^{3+} + 1e^-$

$6e^- + 14H^+ + Cr_2O_7^{2-}$ $2Cr^{3+} + 7H_2O$

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

$$6Fe^{2+} \qquad 6Fe^{3+} + 6e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \qquad 2Cr^{3+} + 7H_2O$$

7. Add the two half-reactions together and balance the final equation by inspection.

The number of electrons on both sides must cancel

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Verify that the number of atoms and the charges are balanced

$$14x1 - 2 + 6x2 = 24 = 6x3 + 2x3$$

- **EX;** Here is a second half-reaction, also in basic solution:

$$MnO_4^- \text{ ---> } MnO_2$$

- Step One: Balance the half-reaction as if it were in acid solution.

$$3e^- + 4H^+ + MnO_4^- \text{ ---> } MnO_2 + 2H_2O$$

- Step Two: Convert all H^+ to H_2O.

$$3e^- + 4H_2O + MnO_4^- \text{ ---> } MnO_2 + 2H_2O + 4OH^-$$

- Step Three: Remove any duplicate molecules or ions.

$$3e^- + 2H_2O + MnO_4^- \text{ ---> } MnO_2 + 4OH^-$$

Classification of chemical reactions

1. Acid-base reactions

An acid-base reaction (also called a neutralization reaction) occurs when an acid reacts with a base

The complete reaction of a strong acid and a strong base produces a neutral solution, thus, this type of reaction is called a **neutralization reaction**

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

Why acid-base reactions are called neutralization reactions?

✓The complete reaction of an acid with a base creates solution of a salt in water.

This solution has a neutral pH . It is neither acidic nor basic

❖Acids that completely react are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong

❖ A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions

❖A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO\text{-}(aq) + H_3O^+(aq)$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, CH_3COO^-

- Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrobromic acid
HI	hydrobromic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

- A **base** is a substance that will dissolve in water to yield hydroxide ions, OH^-
- The most common bases are ionic compounds composed of alkali or alkaline earth metal cations combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$
- Unlike the acid compounds, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution
- For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+} respectively) and hydroxide ions, OH-
- These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**

- Consider as an example the dissolution of sodium hydroxide in water:

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

- This equation confirms that sodium hydroxide is a base
- When dissolved in water, NaOH dissociates to yield Na^{+} and OH^{-} ions
- Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases
- Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules
- In all cases, these compounds react only partially and so are classified as **weak bases**

- When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

- This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules

- A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a **salt** and water

  Acid + base ⟶ salt + water

EX: Write balanced chemical equations for the acid-base reactions described here:

(a) The weak acid hydrogen hypochlorite reacts with water

(b) A solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O

Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

- A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely
- b) The two reactants are provided, $Ba(OH)_2$ and HNO_3
- Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO3-)
- $Ba(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

2. Precipitation reactions and solubility rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products

- Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions
- Substances with relatively large solubility are said to be **soluble**
- A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility
- Substances with relatively low solubility are said to be **insoluble**, and these are the substances that readily precipitate from solution

Table: patterns of solubility of some ionic compounds

Soluble ionic Cpds	Contain these ions	Exceptions
	group I cations: Li^+ , Na^+, K^+ Rb^+, Cs^+	None
	Cl^-, Br^-,I^-	CPds with Ag^+, Hg^{2+} , and Pb^{2+}
	F^-	Cpds with group 2 metal cations, Pb^{2+} and Fe^{3+}
	$C_2H_3O^{2-}$, HCO^{3-} , NO^{3-} , ClO^{3-}	None
	SO_4^{2-}	Cpds with Ag^+, Ba^{2+}, Ca^{2+} , Hg^{2+}, Pb^{2+} and Sr^{2+}
Insoluble ionic Cpds	Contain these ions	Exceptions
	CO_3^{2-}, CrO_4^{2-}, PO_4^{3-}, S^{2-}	Cpds with group 1 cations and NH_4^+
	OH^-	Cpds with group 1 cations and Ba^{2+}

- Example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

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

- This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts
- The net ionic equation representing this reaction is:

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

- **Ex: Predicting Precipitation Reactions**

  Predict the result of mixing reasonably concentrated solutions of the following ionic compounds

  If precipitation is expected, write a balanced net ionic equation for the reaction.

  (a) potassium sulfate and barium nitrate

  (b) lithium chloride and silver acetate

  (c) lead nitrate and ammonium carbonate

Solution

(a)The two possible products for this combination are KNO_3 and $BaSO_4$

- The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected

- The net ionic equation for this reaction is

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

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl

- The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected
- The net ionic equation for this reaction is

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3

- The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected
- The net ionic equation for this reaction is

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow PbCO_3(s)$$

- The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*
- Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

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

- It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of beach reactant in the form of an equation called a **half-reaction**: $\mathbf{2Na(s) \longrightarrow 2Na^+(s) + 2e^-}$

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound

For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

Oxidation = loss of electrons

Reduction = gain of electrons

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine

- Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium

  reducing agent = species that is oxidized

  oxidizing agent = species that is reduced

- Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl: **$H_2(g)$ + $Cl_2(g) \longrightarrow 2HCl(g)$**

- The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved

The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*

- The following guidelines are used to assign oxidation numbers to each element in a molecule or ion

  1. The oxidation number of an atom in an elemental substance is zero

  2. The oxidation number of a monatomic ion is equal to the ion's charge

  3. Oxidation numbers for common nonmetals are usually assigned as follows:

  ¬ Hydrogen: +1 when combined with nonmetals, -1 when combined with metals

  ¬ Oxygen: -2 in most compounds, sometimes -1 (so-called peroxides, O_2^{2-}), very rarely -1/2 (so-called superoxides, O^{2-}), positive values when combined with F (values vary)

- Halogens: -1 for F always, -1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion

EX: Assigning Oxidation Numbers

- Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

(a) H_2S (b) SO_3^{2-} (c) Na_2SO_4

Solution

- (a) According to guideline 1, the oxidation number for H is +1.
- Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:
- Charge on $H_2S = 0 = (2\times+1) + (1\times x)$

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

(b) Guideline 3 suggests the oxidation number for oxygen is -2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

charge on $SO_3^{2-} = -2 = (3\times-2) + (1\times x)$

$$x = -2-(3\times-2) = +4$$

c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately

According to guideline 2, the oxidation number for sodium is +1

Assuming the usual oxidation number for oxygen (-2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

Charge on SO_4^{2-} = -2 = (4×-2)+(1×x), x = -2-(4×-2) = +6

Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number

Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

Oxidation = increase in oxidation number

- In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to -1 in NaCl)
- In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to -1 in HCl)

EX: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

(a) $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

(b) $2Ga(l) + 3Br_2(l) \longrightarrow 2GaBr_3(s)$

(c) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(d) $BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2KCl(aq)$

(e) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

- **Solution**

  (a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements

  (b) This is a redox reaction

- Gallium is oxidized, its oxidation number increasing from 0 in Ga(*l*) to +3 in $GaBr_3(s)$

- The reducing agent is Ga(*l*)

- Bromine is reduced, its oxidation number decreasing from 0 in $Br_2(l)$ to -1 in $GaBr_3(s)$

- The oxidizing agent is $Br_2(l)$

(c) This is a redox reaction

- It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*
- Oxygen is oxidized, its oxidation number increasing from -1 in $H_2O_2(aq)$ to 0 in $O_2(g)$
- Oxygen is also reduced, its oxidation number decreasing from -1 in $H_2O_2(aq)$ to -2 in $H_2O(l)$
- For disproportionation reactions, the same substance functions as an oxidant and a reductant

(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from -2 in $C_2H_4(g)$ to +4 in $CO_2(g)$

- The reducing agent (fuel) is $C_2H_4(g)$
- Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to -2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products

One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each

- 7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation

  8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:

  a. Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.

  b. On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.

  c. Simplify the equation by removing any redundant water molecules.

  9. Finally, check to see that both the number of atoms and the total charges1 are balanced

EX: Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$

Solution

Step 1: *Write the two half-reactions*.

Each half-reaction will contain one reactant and one product with one element in common.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Step 2: *Balance all elements except oxygen and hydrogen*.

The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right

- Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

Step 3: *Balance oxygen atoms by adding* H_2O *molecules*.

The iron half-reaction does not contain O atoms

The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

Step 4: *Balance hydrogen atoms by adding* H^+ *ions*.

The iron half-reaction does not contain H atoms

- The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Step 5: *Balance charge by adding electrons*.

The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion)

Adding one electron to the right side brings that side's total charge to (3+) + (1-) = 2+, and charge balance is achieved

The chromium half-reaction shows a total charge of (1 × 2-) + (14 × 1+) = 12+ on the left side (1$Cr_2O_7^{2-}$ ion and 14 H^+ ions)

- The total charge on the right side is (2 × 3+) = 6 + (2Cr^{3+} ions)
- Adding six electrons to the left side will bring that side's total charge to (12+ + 6-) = 6+, and charge balance is achieved

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

- Step 6: *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction*.

  To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

  $6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$

  $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

- Step 7: *Add the balanced half-reactions and cancel species that appear on both sides of the equation*.

  $Cr_2O_7^{2-} + 6e^- + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 6e^- + 7H^2O$

  only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

  $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

  A final check of atom and charge balance confirms the equation is balanced

Reaction stoichiometry

- It is based on the chemical equation and on the relationship between mass and moles.
- **Stoichiometric coefficients:** The numbers multiplying the chemical formulas in a balanced chemical equation tells us the number of moles of each substance that is consumed or is produced in the reaction
- The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity

- **$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$**

  This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,\mathbf{NH_3\ molecules}}{3\,\mathbf{H_2\ molecules}} \quad \text{Or} \quad \frac{2\mathbf{doz\ NH_3\ molecules}}{3\mathbf{doz\ H_2\ molecules}} \quad \text{Or} \quad \frac{2\mathbf{mol\ NH_3\ molecules}}{3\mathbf{mol\ H_2\ molecules}}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecule

EX: Moles of reactant required in a reaction

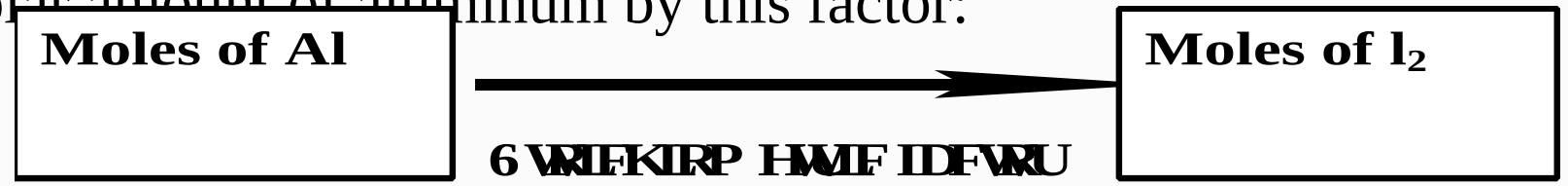
How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation?

$$2Al + 3I_2 \longrightarrow 2AlI_3$$

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is 3mol I_2/ 2mol Al

The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\text{mol } I_2 = 0.429 \text{ mol Al} \times 3 \text{ mol } I_2/2\text{mol Al} = 0.644 \text{ mol } I_2$$

Example: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Solution

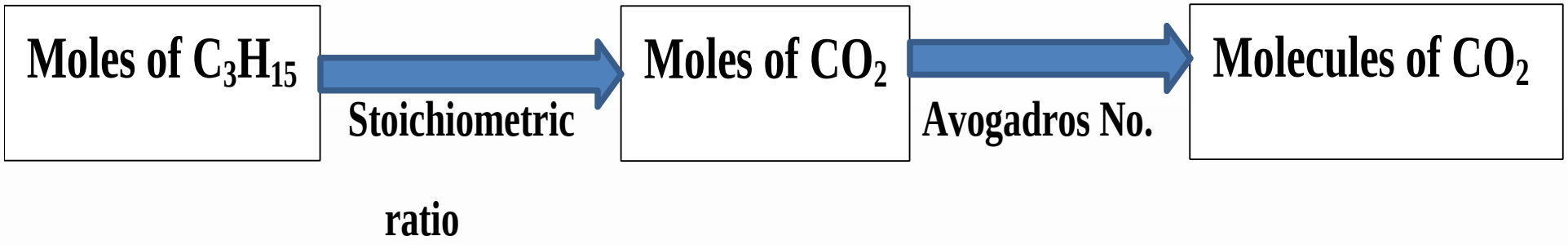
The approach here is the same as for Example, though the absolute number of molecules is requested, not the number of moles of molecules

This will simply require use of the moles-tonumbers conversion factor, Avogadro's number

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$3\ \text{mol}CO_2/1\ \text{mol}C_3H_8$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75 mol C_3H_8 \times 3 mol CO_2 / 1 mol C_3H_8 \times 6.022 \times 1023 CO_2 molecules / mol CO_2 = 1.4 \times 1024 CO_2 \text{ molecules}$$

Example: Relating Masses of Reactants and Products

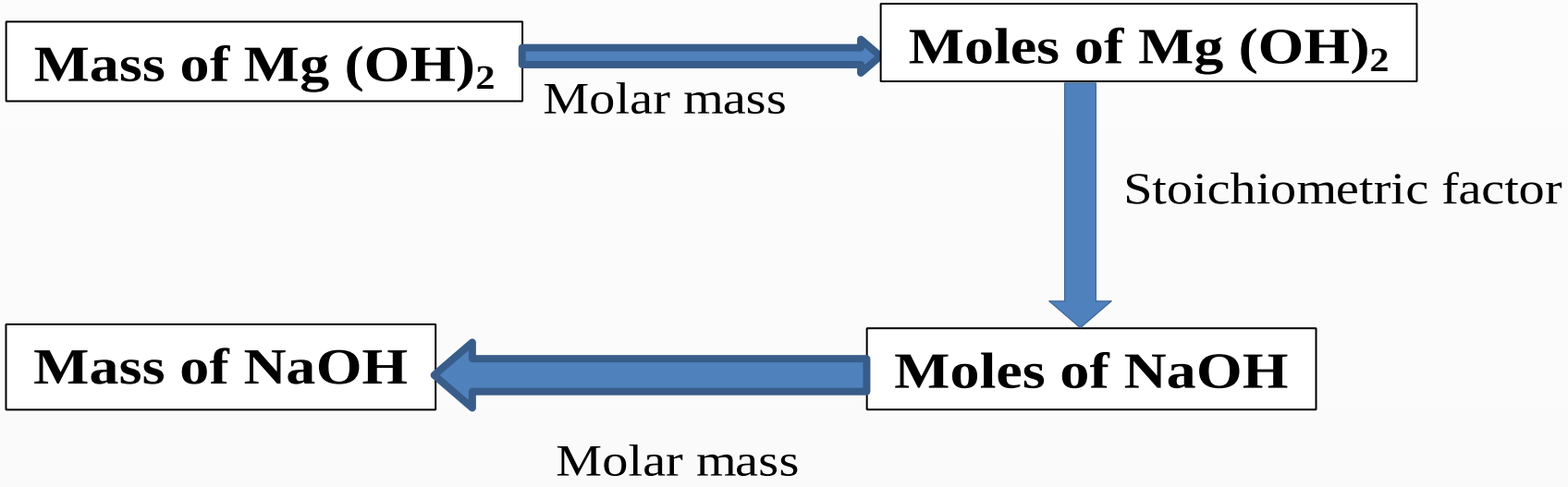
What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$$

Solution

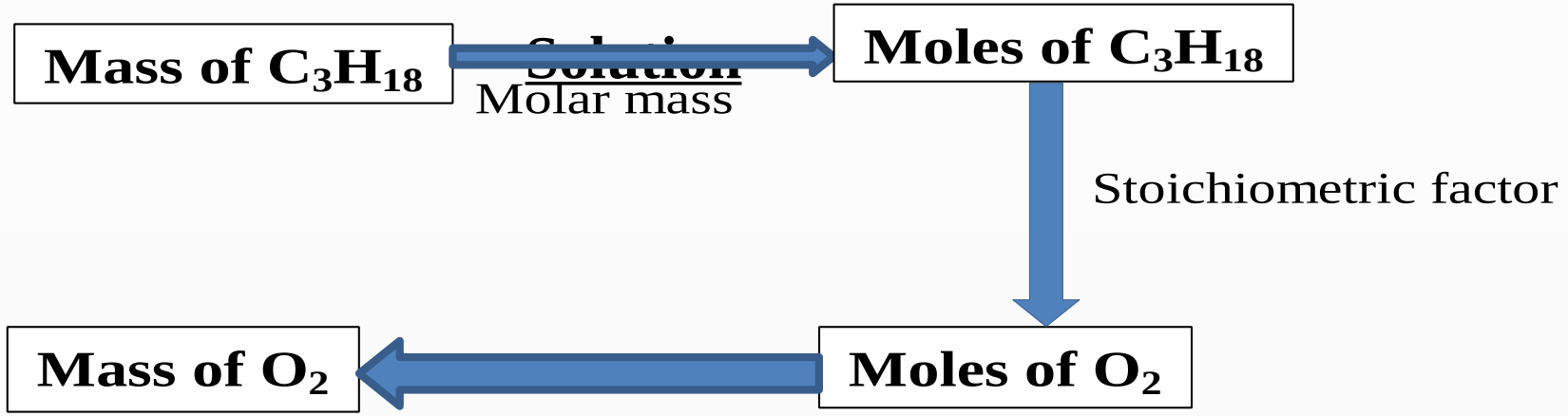
First we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest

In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



- 6g $Mg(OH)_2$×1mol $Mg(OH)_2$/58.3g $Mg(OH)_2$×2mol NaOH/1mol $Mg(OH)_2$×40.0 g NaOH/mol NaOH = 22 g NaOH

EX: What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline? $2C_8H_{18} + 25O_2 \longrightarrow 16CO2 + 18H_2O_2$



702g C_8H_{18}×1molC_8H_{18} /114.23gC_8H_{18}×25molO_2/2molC_8H_{18}×32.00 gO_2/molO_2=2.46×103gO_2

- **Reaction Yield**

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*

All the exercises of the preceding module involved stoichiometric amounts of reactants

Limiting Reactant

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

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

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio

- If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated
- This substance is the **limiting reactant**, and the other substance is the **excess reactant**
- Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation
- For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2

- This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1
- Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant
- Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted
- Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry
  The reactant yielding the lesser amount of product is the limiting reactant
- For the example in the previous paragraph, complete reaction of the hydrogen would yield

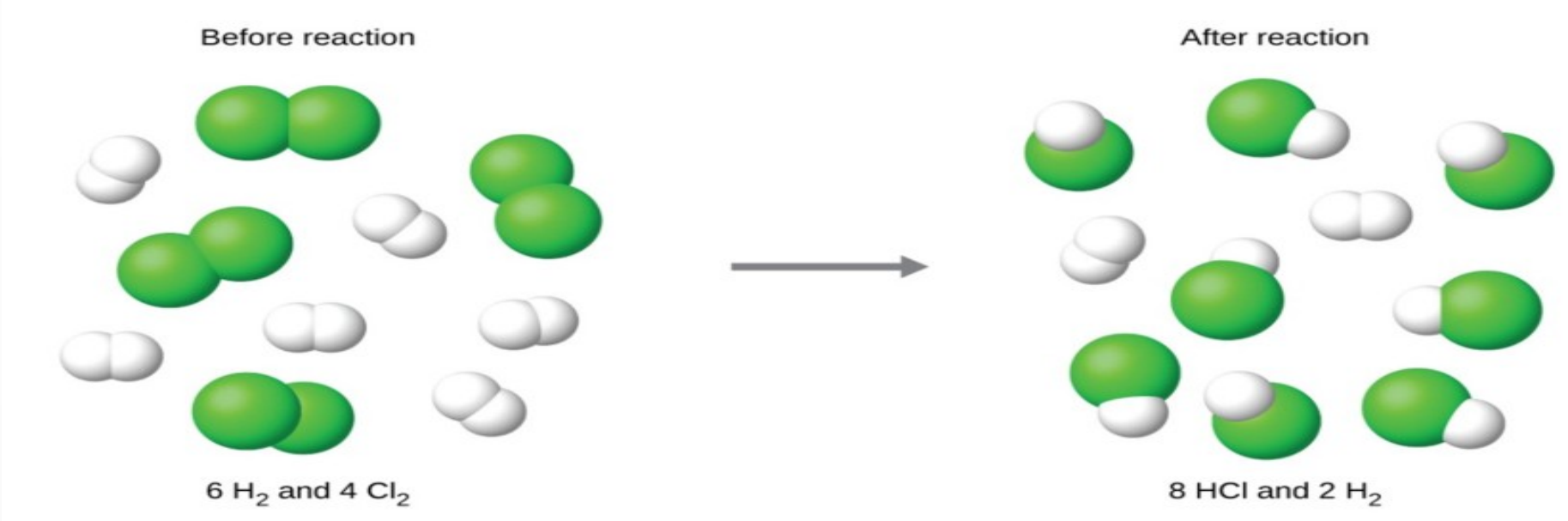
mol HCl produced = 3molH_2×2 mol HCl/1 molH_2 = 6 mol HCl

Complete reaction of the provided chlorine would produce

mol HCl produced = 2 molCl_2×2 mol HCl/1 molCl_2= 4 mol HCl

The chlorine will be completely consumed once 4 moles of HCl have been produced

- Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete



- **EX: Identifying the Limiting Reactant**

  Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines

- It is prepared according to the following equation:

$$3Si(s) + 2N_2(g) \longrightarrow Si_3N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant

mol Si = 2.00g Si×1 mol Si/28.09g Si = 0.0712 mol Si

$molN_2 = 1.50gN_2 \times 1molN_2/28.02gN_2 = 0.0535$ mol N_2

- The provided $Si:N_2$ molar ratio is:

  $0.0712\ mol\ Si/0.0535\ mol N_2 = 1.33\ mol\ Si/1 mol N_2$

  The stoichiometric $Si:N_2$ ratio is:

  $3\ mol\ Si/2\ mol N_2 = 1.5\ mol\ Si/1\ mol N_2$

  Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant

  Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants

- The 0.0712 moles of silicon would yield

$Mol\ Si_3N_4\ produced = 0.0712\ mol\ Si \times 1 mol Si3N_4/3 mol Si = 0.0237\ mol Si_3N_4$

while the 0.0535 moles of nitrogen would produce

$mol Si_3N_4\ produced = 0.0535 mol N_2 \times 1 mol Si_3N_4/2 mol N_2 = 0.0268\ mol Si_3N_4$

Since silicon yields the lesser amount of product, it is the limiting reactant

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction

In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reason

Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products

Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield

- The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

$$\textbf{Percent yields} = \frac{}{} \times 100\ \%$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas)

As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated

EX: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4\,(aq) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$1.274 g CuSO_4 \times 1 mol CuSO_4 / 159.62 g CuSO_4 \times 1 mol Cu / 1 mol CuSO_4 \times 63.55 g\ Cu / 1 mol\ Cu = 0.5072 g Cu$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be percent yield = (actual yield/theoretical yield)×100

$$\text{Percent yield} = (0.392\ g\ Cu / 0.5072\ g\ Cu) \times 100 = 77.3\%$$

Quantitative Chemical Analysis

A. Acid-base Titration

The test of vinegar with potassium carbonate is one type of **quantitative analysis**-the determination of the amount or concentration of a substance in a sample

In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution

$$\mathbf{2CH_3CO_2H(aq) + K_2CO_3(s) \longrightarrow 2CH_3CO_2K(aq) + CO_2(g) + H_2O(l)}$$

The bubbling was due to the production of CO_2

The described approach to measuring vinegar strength was an early

- A typical titration analysis involves the use of a **buret** to make incremental additions of a solution containing a known concentration of some substance (the **titrant**) to a sample solution containing the substance whose concentration is to be measured (the **analyte**)
- The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for
  complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration
- The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction

- The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration
- Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration
- Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible

- Though any type of chemical reaction may serve as the basis for a titration analysis, precipitation, acid-base, and redox titrations are the most common

EX: The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant

The titration reaction is: $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

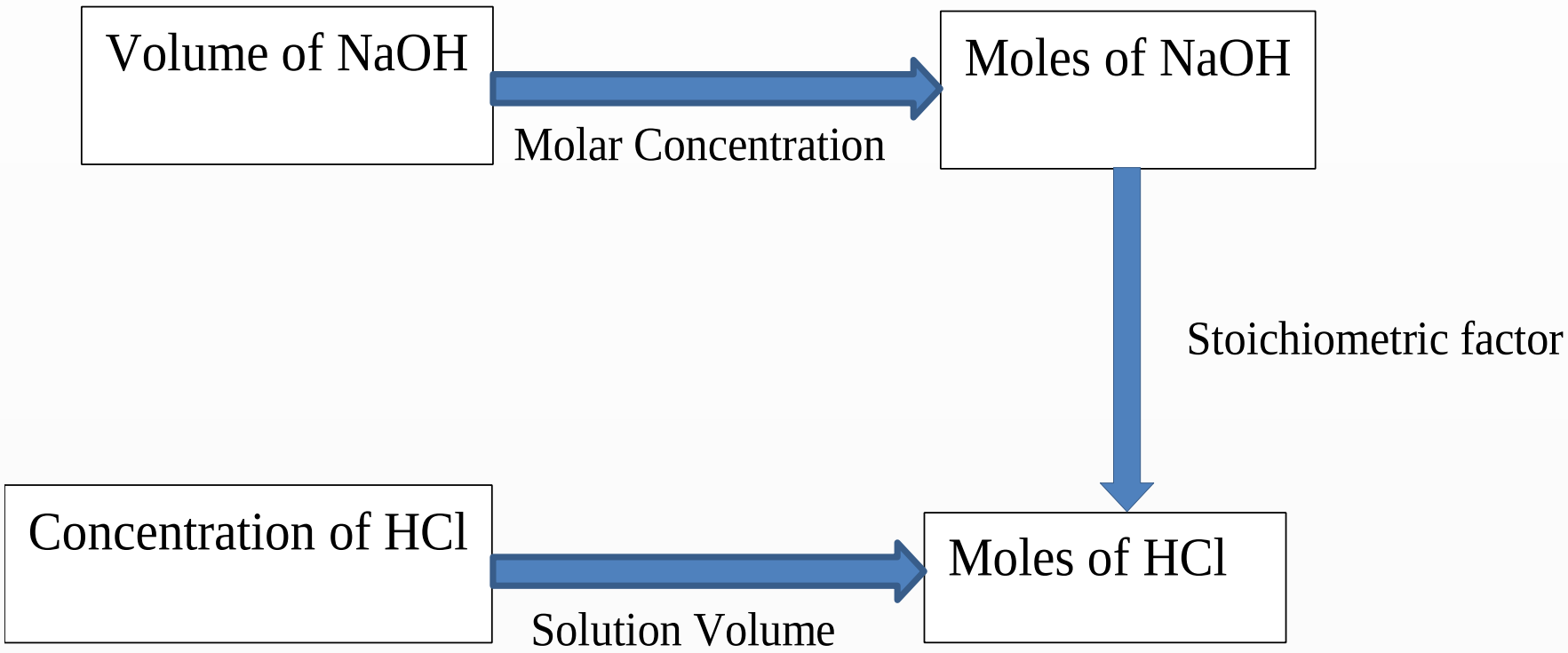
What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation

The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations

For this exercise, the calculation will follow the following outlined steps:



- The molar amount of HCl is calculated to be:

  35.23 mLNaOH × 1L/1000 mL× 0.250 mol NaOH/1L × 1 mol HCl/1mol NaOH = 8.81×10^{-3} mol HCl

  Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

  M = mol HCl / L solution

  M = 8.81×10^{-3} mol HCl / 50.00mL × 1L / 1000 mL

  M = 0.176 M

- Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{mol\ solute}{L\ solution}\ X\ \frac{\frac{10^3 mmol}{mol}}{\frac{10^3 mL}{L}} = \frac{mmol\ solute}{mL\ solution}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23mL\ NaOH\ X\ \frac{0.250mmol\ NaOH}{mL\ NaOH}\ X\ \frac{1mmolHCl}{1mmol\ NaOH}}{50.00mL\ solution} = 0.176MHCl$$

Gravimetric Analysis

A **gravimetric analysis** is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample

Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration

Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory

- The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes
- For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water
- The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed

EX: A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$

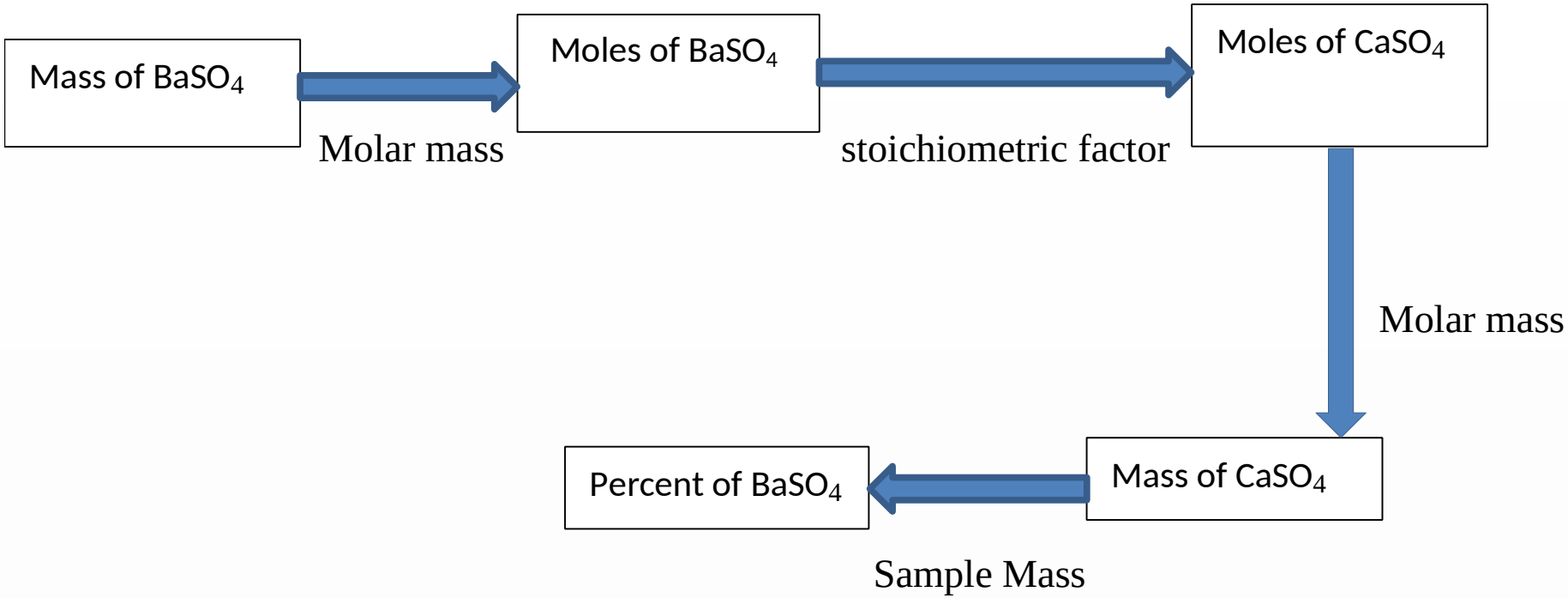
$MgSO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$

What is the concentration (mass percent) of MgSO4 in the mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of $BaSO_4$ and $MgSO_4$ through their stoichiometric factor

- Once the mass of $MgSO_4$ is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration



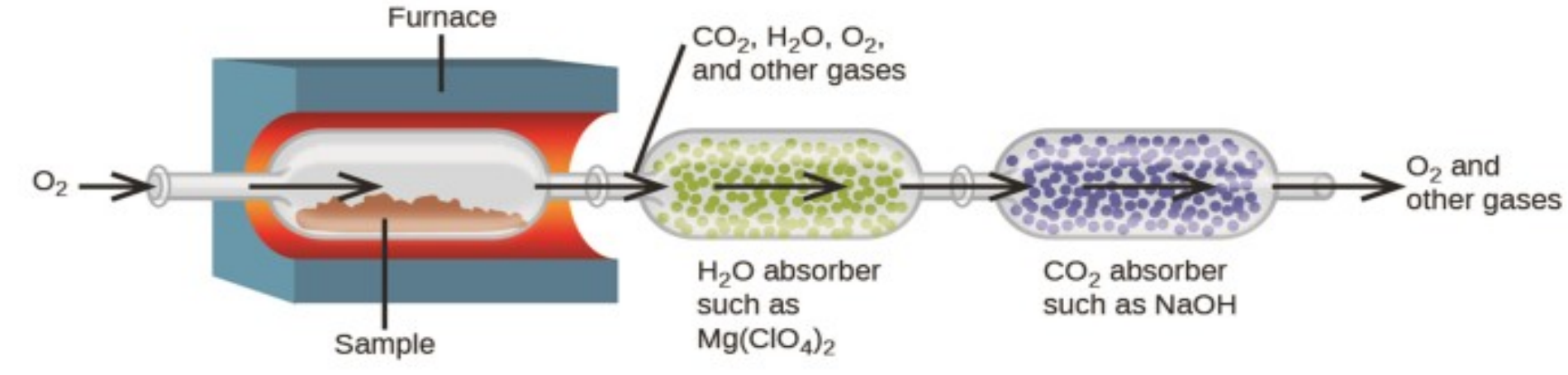
The mass of $MgSO_4$ that would yield the provided precipitate mass is 0.6168g $BaSO_4$×1mol $BaSO_4$/233.43g $BaSO_4$×1mol $MgSO_4$/1mol $BaSO_4$×120.37g $MgSO_4$/1mol $MgSO_4$

= 0.3181g $MgSO_4$

The concentration of $MgSO_4$ in the sample mixture is then calculated to be Percent $MgSO_4$ = mass $MgSO_4$ / mass sample ×100% 0.3181g / 0.4550g × 100% = 69.91%

- The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as **combustion analysis**
- In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities
- The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products

The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element



EX: Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O. What is the empirical formula of polyethylene?

Solution

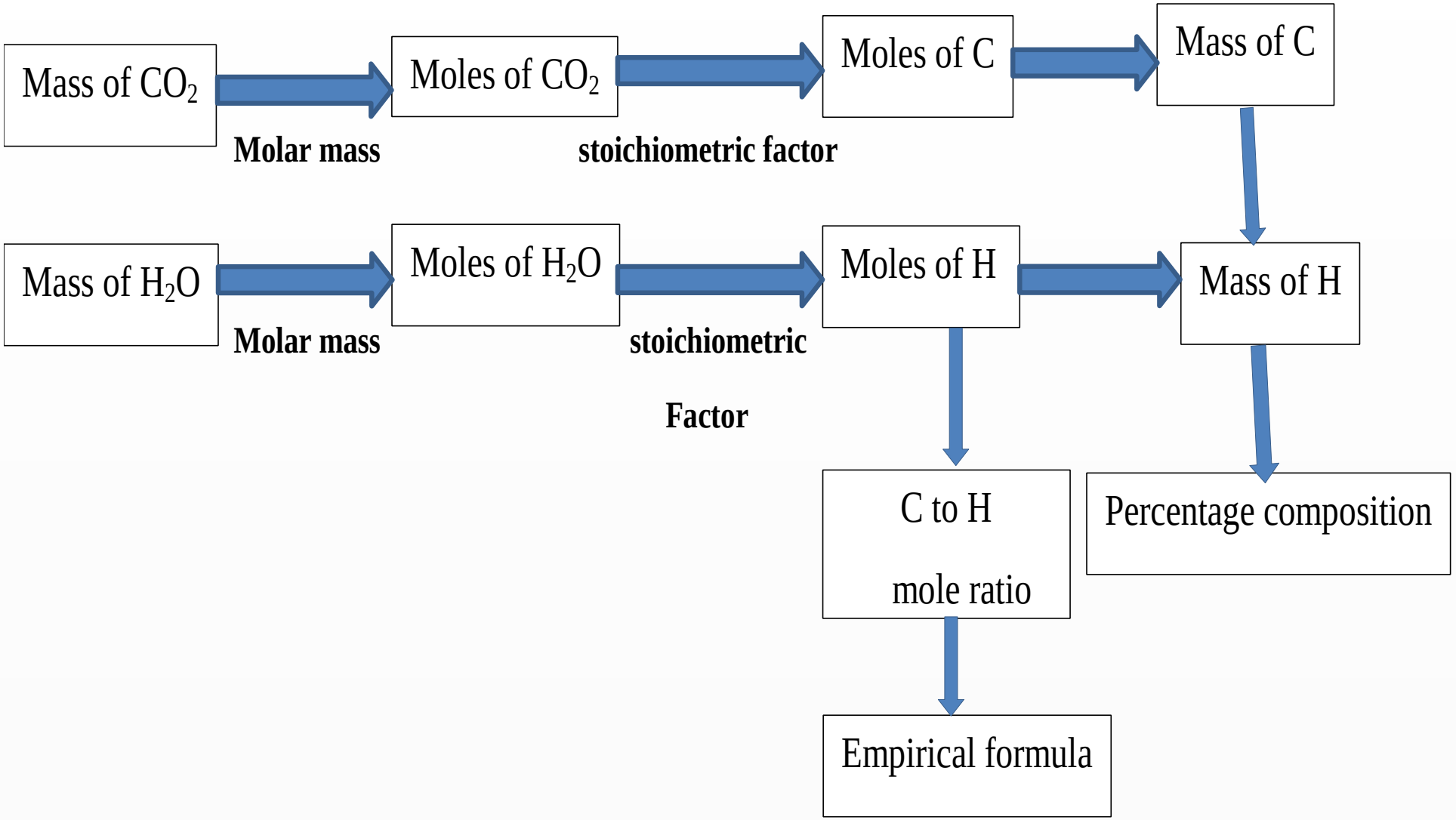
The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

$C_xH_y(s)$+ excess $O_2(g) \longrightarrow xCO_2(g) + y2H_2O(g)$

- Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts x and y are needed

  First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively

An outline of this approach is given in the following flow chart:



mol C = 0.00394g CO_2×1mol CO_2/44.01 g×1mol C/1mol CO_2=8.95×10-5molC mol H = 0.00161g H_2O×1mol H_2O /18.02g× 2mol H/1mol H_2O =1.79×10-4molH

The empirical formula for the compound is then derived by identifying the smallest whole number multiples for these molar amounts

The H-to-C molar ratio is molH / mol C =1.79×10^{-4} mol H / 8.95×10^{-5} mol C = 2mol H / 1molC and the empirical formula for polyethylene is CH_2

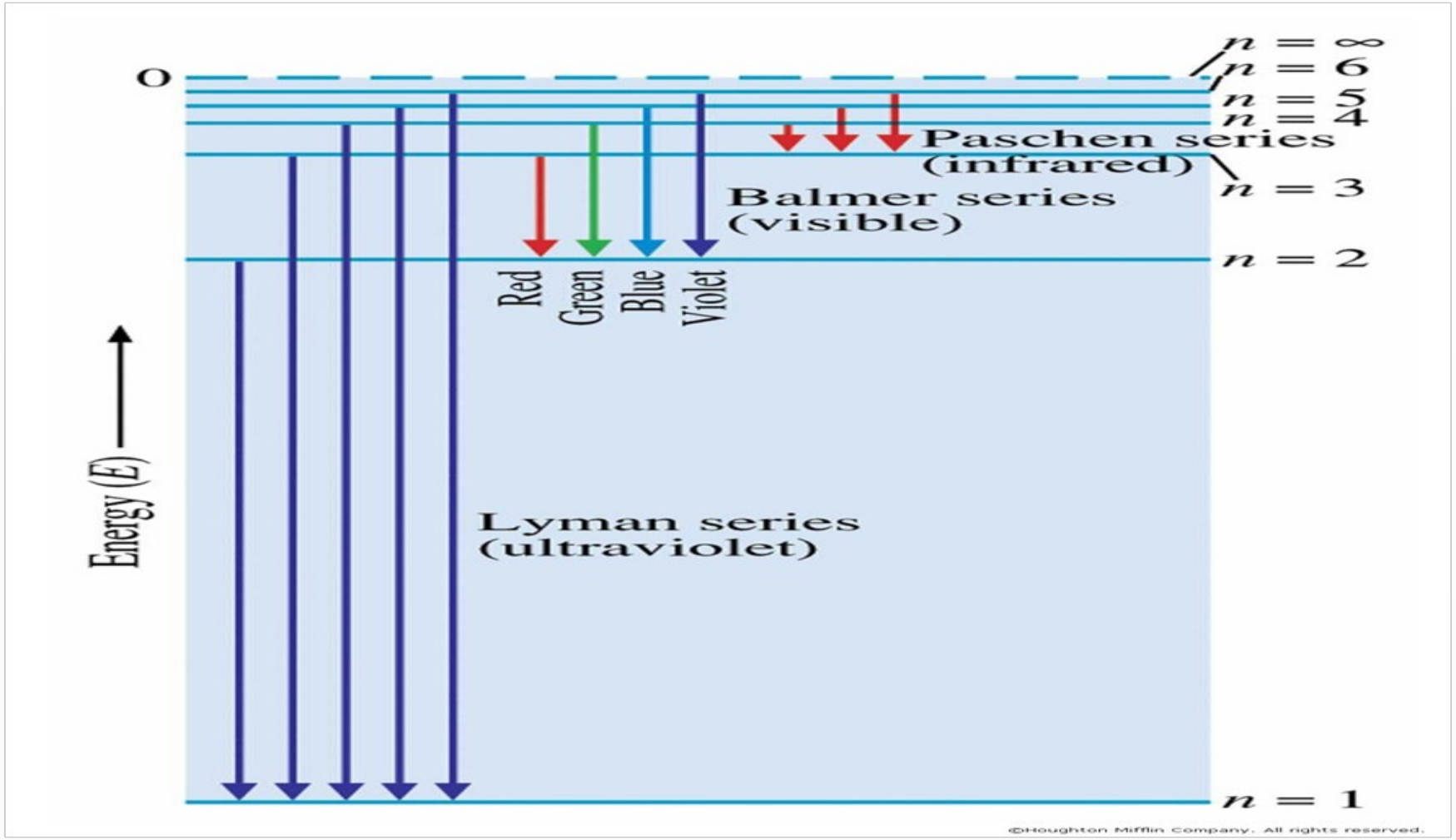
CHAPTER –FIVE
ELECTRONIC STRUCTURE AND THE PERIODIC PROPERTIES

Spectra

- The abs. & emission spectra of an element are complementary.
- The absorption spectrum shows dark lines against a bright background.
- The dark lines are at wavelengths where light is absorbed, and thus not seen.
- The emission spectrum shows bright lines against a dark background.
- Line spectra were studied for many years without adequate explanation.
- A # of scientists focused on the spectrum of H, which appeared the simplest.
- By recording the emission spectrum of H on light sensitive film, scientists were able to "see" not only the visible emission lines, but also emission lines in the UV and IR regions of the EM spectrum.

Atomic spectra…

The series of lines falling in the different regions are shown in the following figure.



Atomic spectra…

Atomic spectra…

- All of the observed spectral series of the H atom were found to obey the ff generalized Rydberg equation.

$$\mathbf{1/\lambda = RH\,(1/n_1^2 - 1/n_2^2)}$$

$$\mathbf{E = 2.176\ X\ 10^{-18}(1/n_1^2 - 1/n_2^2)}$$

- Where, RH is a constant with value $1.09678\ X\ 10^{-2}\ nm^{-1}$ and n_1 and n_2 are energy levels.
- The unified fit of the H spectrum provided by this equation suggested a regular internal structure to the atom that is changed in some way by interaction with light.

E.g. What is the frequency of the photon required to promote the e from the n = 1 level to the n = 4 level in the H atom?

Solution. **$E = 2.176 \times 10^{-18}(1/n_1^2 - 1/n_2^2)$**

The energy of the required photon is $2.176 \times 10^{-18}(1 - 1/16) = 2.04 \times 10^{-18}$ J. Since $E = h\nu$,

$\nu = E/h = 2.04 \times 10^{-18}\ J/6.626 \times 10^{-34}\ J\text{-}s = 3.08 \times 10^{15}\ s^{-1}$

Bohr model of the atom

Bohr was able to use his model hydrogen to:

-Account for the observed spectral lines.

-Calculate the radius for hydrogen atoms.

His model did not account for:

-atoms other than hydrogen

-Why the energy is quantized

His concept of es moving in fixed orbitals was later abandoned.

Dual nature of electron (de Broglie theory)

- He suggested that the e, normally considered a particle, might behave sometimes as a wave!
- There was absolutely no experimental evidence at the time to justify it. However, he was able to put it on a quantitative basis by making an analogy to a photon, for which the r/n ship b/n wavelength and momentum, p, is given in the ff equation: ¬ = **h/p**

de Broglie suggested that the e is governed by a similar equation.

Substituting the product of mass & velocity for momentum: ¬ = **h/mv**

- He then proceeded to show that Bohr's theory of the H atom was a consequence of this equation!
- His reasoning was (probably) something as follows. The allowed orbits of the H atom are those in which an integral # of e ¬ s exactly fit the circumference of the orbit. **n¬ = 2 r**
- Where ‘n’ is an integer and ‘r’ is the orbit radius.

Cont'd

Substituting for the electron wavelength from the previous equation:

$n h / 2\pi = mvr$

It is important to realize that although de Broglie's result for the H atom is the same as Bohr's.

de Broglie's approach is more satisfying, because the quantum number 'n' arises quite naturally from the requirement that the e be a standing wave that just fits the circumference of the orbit.

E.g. The electron in the n = 1 level of the H atom travels at 2.19×10^6 m/s. What wavelength is associated with the electron?

Solution.

$\lambda = h/mv = 6.626 \times 10^{-34}$ J-sec/$(9.11 \times 10^{-31}$ kg$)(2.19 \times 10^6$ m/s) = 3.32×10^{-10} m = 3.32×10^{-8} cm.

Cont'd

- by reciprocating the above equation (¬ = h/mv) both sides: **1/¬ = mv/h = p/h**
- **1/¬** is called wave # which is the number of wave cycles that occur per unit length (m or cm) and symbolized by 'k'.
- So, p = hk which is similar in form to equation E = h⊏ (for light)
- P(momentum) used as particle and 'k' as wave characteristics respectively.

Wave theory of the electron

1924 De Broglie suggested that es have wave properties to account for why their energy was quantized.

He reasoned that the e in the H atom was fixed in the space around the nucleus.

He felt that the e would best be represented as a standing wave.

As a standing wave, each electron's path must equal a whole number times the wavelength.

De Broglie wave

De Broglie proposed that all particles have a wavelength as related by:

$\lambda = h/mv$ where λ = wavelength, meters

h = plank's constant m = mass, Kg v = frequency, m/s

The Heisenberg Uncertainty Principle

- The modern quantum theory says that we can not know the exact location of the electron in the H atom (or of any e in any atom).
- We can know at best only the probability that the electron will be found in a particular region.
- This lack of exact knowledge is the Uncertainty Principle, proposed by Werner Heisenberg in 1927.
- It is not possible to simultaneously know exactly both the position and the momentum of an electron (or of any other small "particle").
- This is difficult to accept because at the macroscopic scale, we of course are able to know both quantities at the same time.

Cont'd

- Very small particles simply do not behave in the same way as large ones. This is not something that can be explained; it simply is.

$$(\Delta p)X(\Delta x) > h/2\,\bar{}$$

- In words, product of the uncertainty in momentum and the uncertainty in position must exceed a fundamental minimum value given by $h/2\,\bar{}$.
- This minimum value is so small that we do not observe the Uncertainty Principle working at the macroscopic scale.

E.g. An e is accelerated through a potential difference of 1 volt, which causes it to acquire KE. The max. KE that the e could acquire is 1 e-volt, or 1.6×10^{-19} J. Calculate the uncertainty in the position of the e.

Cont'd

Solution.

The KE of the e is somewhere between 0 and 1.6×10^{-19} J. Let's calculate the momentum of a 1.6×10^{-19} J e. This will be the maximum possible momentum.

The minimum momentum possible is 0. **$KE = 1/2\ mv^2$, $p = mv$**

Thus $p^2 = 2mKE$, and $p = (2mKE)^{1/2}$.

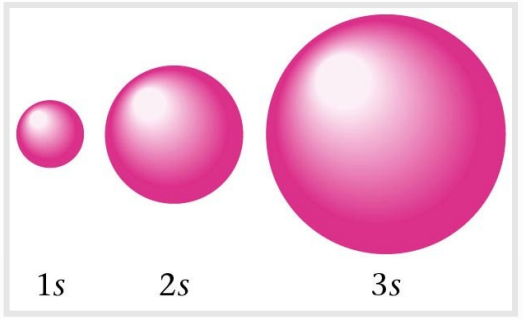
We calculate that $p = 5.40 \times 10^{-25}$ kg-m/s. Because the momentum lies somewhere between 0 and this value, the uncertainty in p is roughly 10^{-25} kg-m/s.

Applying the Heisenberg principle, the uncertainty in position is

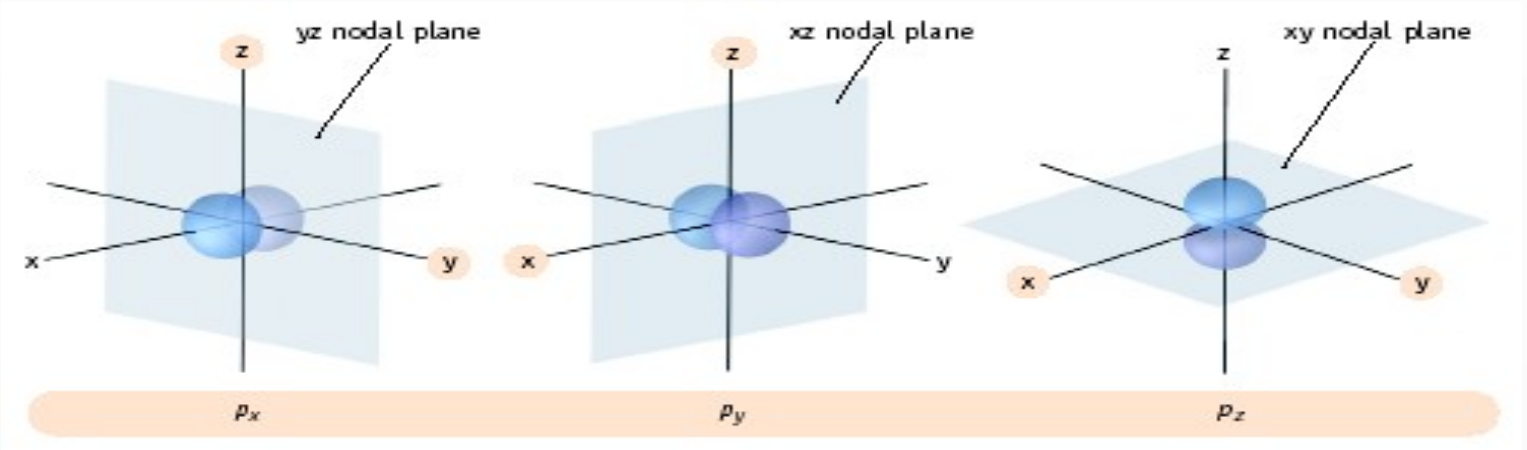
$\Delta x = h/2\pi\ \Delta p = 6.6 \times 10^{-34}$ joule-s/$(2\pi)(10^{-25}$ kg-m/s) = 1.0×10^{-9} m

- The e- will be found within a fairly easily defined region of space quite close to the nucleus. Such a region of space is called an ***orbital.***
- You can think of an orbital as being the region of space in which the electron lives.

s-orbitals (spherical in shape) **:**

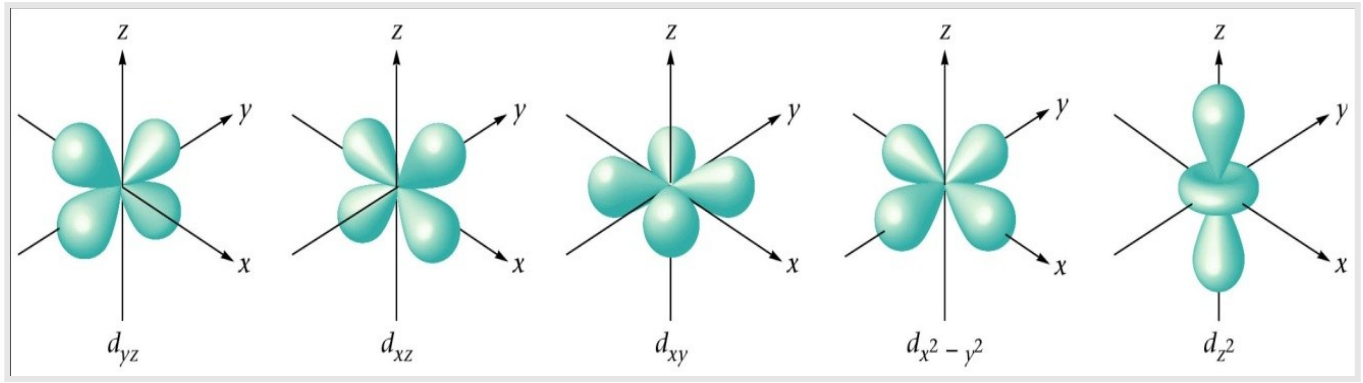


p-orbita;sls (dumbbell-shaped)**:**

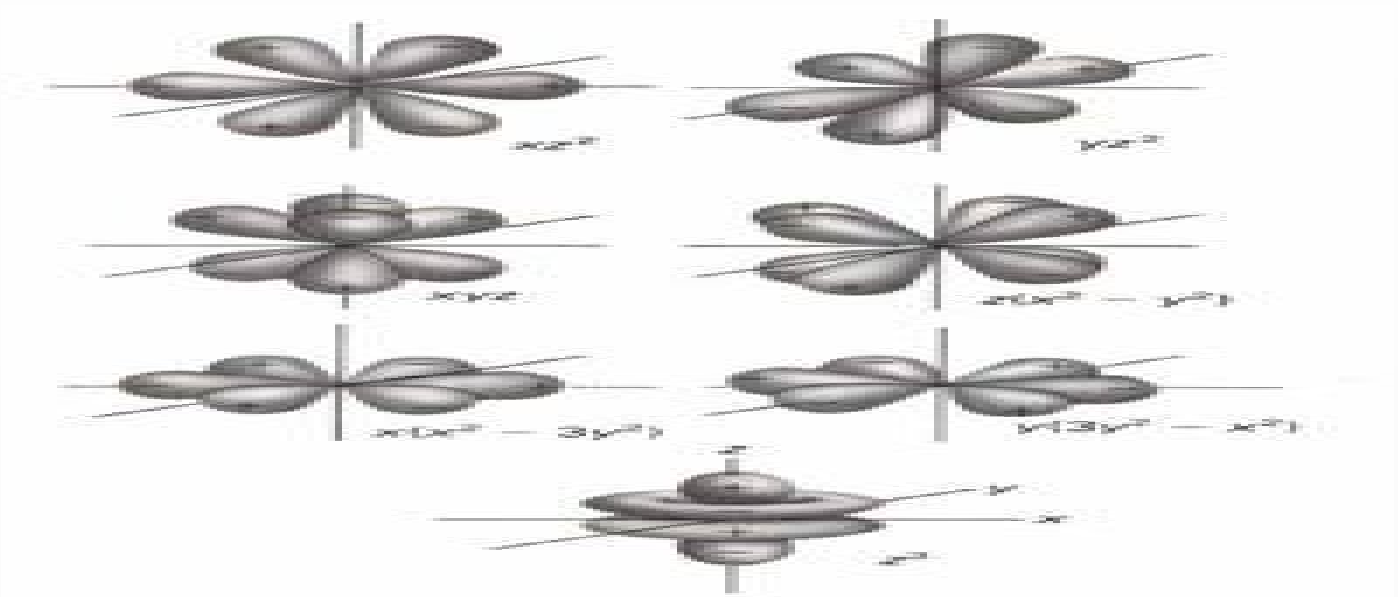


Cont'd

d-orbitals:



f-orbitals:



quantum numbers

- The first three (***n, l, m***$_l$) specify the particular orbital of interest, and the fourth (***m***$_s$) specifies how many es can occupy that orbital.

i. Principal Quantum Number (*n*): *n* = 1, 2, 3, …, ∞

- Specifies the **energy** of an electron and the **size** of the orbital.
- All orbitals that have the same value of *n* are said to be in the same **shell** (**level**).
- For a H atom with *n*=1, the e is in its ***ground state***; if the e is in the *n*=2 orbital, it is in an ***excited state***.
- The total number of orbitals for a given *n* value is n^2.

ii. Angular Momentum (Azimunthal) Quantum # (*l*): *l* =0,..., *n*-1

- Specifies the **shape** of an orbital with a particular principal quantum #.
- This quantum number divides the shells into smaller groups of orbitals called **subshells** (**sublevels**).

Cont'd

- Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3
Letter	s	p	d	f

- The subshell with n=2 and l=1 is the 2p subshell; if n=3 and l=0, it is the 3s subshell, and so on.
- The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l ($s < p < d < f$).

iii. Magnetic Quantum Number (m_l): $m_l = -l, ..., 0, ..., +l$

- Describes the orientation that the orbital projects in space.
- This number divides the subshell into individual **orbitals** which hold the electrons;
- There are **2*l*+1** orbitals in each subshell. Thus the *s* subshell has only one orbital, the *p* subshell has three orbitals, & so on.

Cont’d

n	l	ml	subshell level	# of orbitals
1	0	0	1s	1
2	0	0	2s	1
	1	-1,0,1	2p	3
	0	0	3s	1
3	1	-1,0,1	3p	3
	2	-2,-1,0,1,2	3d	5
	0	0	4s	1
	1	-1,0,1	4p	3
4	2	-2,-1,0,1,2	4d	5
	3	-3,-2,-1,0,1,2,3	4f	7

Cont'd

iv. Spin Quantum Number (m_s): m_s = +½ or -½

- Specifies the **direction of the spin axis** of an electron.
- An e can spin in only one of 2 directions (called *up* and *down*).

How electrons fill the orbitals

- Each atom has an infinite # of possible electronic configurations.
- We are here only concerned with the ground-state electronic configuration, which has the lowest energy.
- The ground-state electronic configuration of an atom can be determined by the ff three principles.

1. Pauli Exclusion Principle

- It states that no more than two electrons can occupy each orbital, and if two electrons are present, their spins must be paired

Electron Spin and the Pauli Exclusion Principle

- ✓ In 1925, Wolfgang Pauli proposed the most important rules, called the Exclusion Principle:
- ✓ At most 2 electrons may simultaneously occupy an atomic orbital.
- ✓ However, the motion of these electrons should be different
- ✓ The quantum number associated with this motion is the electron spin quantum number and symbolized by m_s.
- ✓ This quantum number has only two values: +1/2 and -1/2.
- ✓ These 2 values are referred to as "up spin" and "down spin", respectively
- ✓ 2 es in the same orbital might have the same values of n, l, & m_l.
- ✓ However, they have opposite spins (one "up", the other "down"), then they will differ in at least 1 of the 4 quantum #s that characterize them. As a result, Pauli Principle restated :
- ✓ *Two es in an atom must differ in at least one of the 4 quantum #s.*

- The distribution of electrons among the orbitals is called the electron-configuration of the atom.
- Shell energy increases as ‘n’ increases ($n_2 > n_1$)
- The subshells within a main shell have different energies

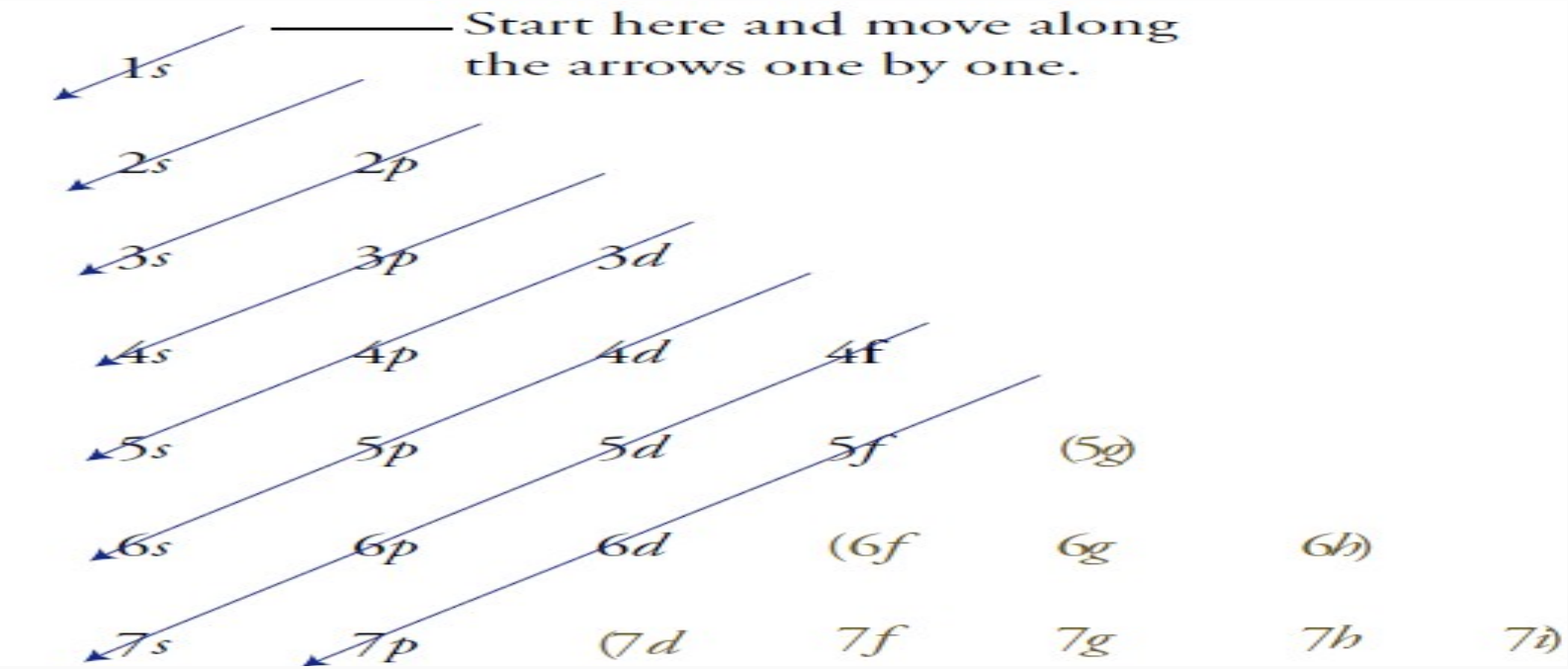
  ns < np < nd < nf

- The orbitals within a subshell all have exactly the same energy (are said to be degenerate)
- The maximum # of es that can enter a subshell is determined by the 2-per-orbital rule:

Subshell	maximum number of electrons
s	2 electrons(1 orbital, 2 per orbital)
p	6 electrons (3 orbitals, 2 per orbital)
d	10 electrons (5 orbitals, 2 per orbital)
f	14 electrons (7 orbitals, 2 per orbital)

2. Aufbau approach

- We can use this approach to ‘build’ atoms and describe their electron configurations.
- For any element, you know the # of es in the neutral atom equals the atomic number. Start filling orbitals, from lowest to highest.
- If 2/more orbitals exist at the same energy level, they are degenerate. Do not pair the electrons until you have to.



Cont'd

- Note that there is some overlap of the high energy subshell of n = 3, 3d, with the low-energy subshell of n = 4, 4s.
- Similar overlaps occur more frequently as n increases.

Exceptions to the Aufbau principle

- remember d and f orbitals require large amount of energy.
- If we can't fill these sublevels, then the next best thing is to be half full (one electron in each orbital in the sublevel).
- There are many exceptions, but the most common ones are d^4 & d^9 for the purpose of this class, we are going to assume that all atoms(ions) that end in d^4 or d^9 are exceptions to the rule.
- This may or may not be true, it just depends on the atom.

- d^4 is one e short of being half full in order to become more stable.
- one of the closest s e will actually go into the d, making it d^5 instead of d^4.
- for example: Cr would be [Ar] $4s^2 3d^4$,but since this ends exactly with a d^4 it is an exception to the rule thus, Cr should be [Ar] $4s^1 3d^5$
- Procedure : find the closest s orbital, steal one e from it, and add it to the d.
- Ok, so this helps the d, but what about the poor s orbital that loses an electron?
- Remember, half full is good… and when an s loses 1, it too becomes half full.
- So …having the s half full and the d half full is usually lower in energy than having the s full and the d to have one empty orbital

Cont'd

- d^9 is one e short of being full just like d^4,one of the closest s es will go into the d, this time making it d^{10} instead of d^9

E.g: Au would be [Xe] $6s^2 4f^{14} 5d^9$,but since this ends exactly with a d^9 it is an exception to the rule. Thus, Au should be [Xe] $6s^1 4f^{14} 5d^{10}$

- Procedure : same as before! find the closest s orbital, steal one e from it, and add it to the d.

3. Hund's rule

- when putting es into orbitals with the same energy(degenerate),
- place 1 e in each orbital before putting 2 in any one.
- The existence of unpaired es can be tested for since each acts like a tiny electromagnet.
- Paramagnetic-attracted to magnetic field. indicates the presence of unpaired es
- diamagnetic-pushed out of a magnetic field. indicates that all es are paired

Writing electron configuration

O:- $1s^2 2s^2 2p^4$ core format [He] $2s^2 2p^4$

Ti :-$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ [Ar] $3d^2 4s^2$

Br:-$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ [Ar] $3d^{10} 4s^2 4p^5$

-Ve ions: Add e(s): S^{-2} ion (16 + 2) e:$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

+Ve ions: Remove e(s): Mg^{+2} ion (12-2) electrons: $1s^2$, $2s^2$, $2p^6$

Electrons are divided between core and valence electrons

B $1s^2 2s^2 2p^1$

Core =[He], valence = $2s^2 2p^1$

Br [Ar] $3d^{10} 4s^2 4p^5$ Core = [Ar] valence **$4s^2 4p^5$**

Valence electrons:-are es which are found in the outermost electronic shell of atoms and es which participate in the formation of chemical bonding(chemical rxns).

Ground-State Electron Configurations of Atoms $Z = 1$ to 36

Z	Element	Configuration	Z	Element	Configuration
1	H	$1s^1$	19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
2	He	$1s^2$	20	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
3	Li	$1s^2 2s^1$	21	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
4	Be	$1s^2 2s^2$	22	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
5	B	$1s^2 2s^2 2p^1$	23	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
6	C	$1s^2 2s^2 2p^2$	24	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
7	N	$1s^2 2s^2 2p^3$	25	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
8	O	$1s^2 2s^2 2p^4$	26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
9	F	$1s^2 2s^2 2p^5$	27	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
10	Ne	$1s^2 2s^2 2p^6$	28	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
11	Na	$1s^2 2s^2 2p^6 3s^1$	29	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
12	Mg	$1s^2 2s^2 2p^6 3s^2$	30	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	31	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	32	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	33	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	34	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	35	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

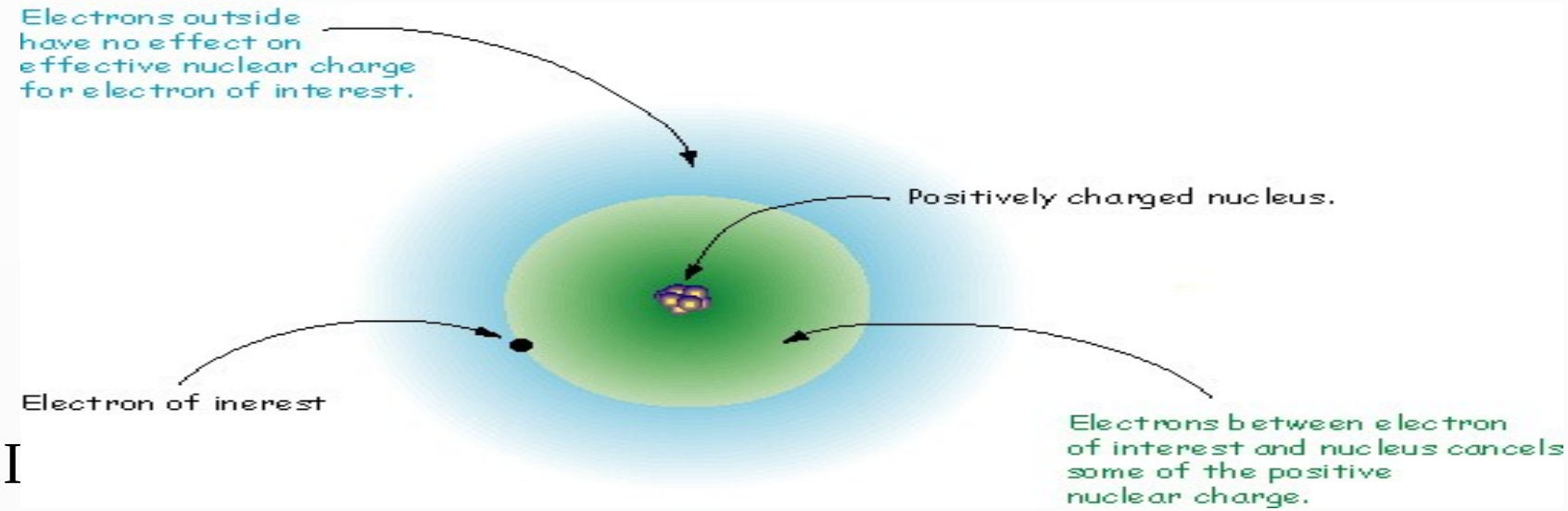
Periodic table

- Mendeleev arranged the elements into the first periodic table.
- He 1st arranged the elements in columns in order of increasing atomic mass and put elements with the most similar properties side by side.
- However, Henry Moseley determined the atomic number of the atoms of the elements, and the periodic table was arranged according to atomic number, not mass.
- Therefore, the periodic table is divided into groups and periods.
- From e configuration one can understand or identify the group and period numbers of the elements.
- The # of valence e-s tells the groups and the energy level (n) tells the periods.

Some properties

A. Electron Shielding and Effective Nuclear Charge

- In an atom with one e, that e experiences the full charge of the +ve nucleus. In this case, the Z_{eff} can be calculated from Coulomb's law.
- However, in an atom with many es the outer es are simultaneously attracted to the +ve nucleus and repelled by the -vely charged es.
- The effective nuclear charge on such an e is given by the ff equation: $Z_{eff} = Z - S$, where S is the shielding constant



- I

- ‘S’ is shielding factor
- we will discuss core charge, Z_{core}, which is roughly parallels to Z_{eff} .
- The core charge of an atom is the difference between the number of protons in the nucleus and the number of core electrons.
- Core electrons are those in completely filled shells below the valence shell.
- The core charge therefore measures the net positive charge pulling on the valence electrons.

For example, the core charge for lithium is its atomic number (the # of protons) minus the # of electrons in filled shells (the atomic # of the preceding noble gas): $Z_{core}(Li) = 3 - 2 = 1$.

Cont…

- consider an atom of He and for all other many e atoms, we need to consider not just the proton - e attractions, but also the e - e repulsions.
- Because of this repulsion, each e experiences a nuclear charge that is somewhat less than the actual nuclear charge.
- Essentially, one e **shields**, or screens the other e from the nucleus.
- The +ve charge that an e actually experiences is called the **effective nuclear charge**, $\mathbf{Z_{eff}}$,
- Z_{eff} is always somewhat less than the actual nuclear charge.
- The term "effective" is used because the shielding effect of -ve charged es prevents higher orbital es from experiencing the full nuclear charge by the repelling effect of inner-layer es.
- The Z_{eff} experienced by the outer shell e is also called the core charge.

Cont'd

Similarly, the core charges for C&F are 6-2 = 4&9-2 = 7, respectively.

Element	Z	# of core electrons	Z_{core}
Na	11	10	1
Mg	12	10	2
Al	13	10	3
Si	14	10	4
P	15	10	5
S	16	10	6
Cl	17	10	7
Ar	18	10	8

P

Across a row, Z_{core} increases that results shrinkage of the e cloud on other hands atomic size decreases across a period.

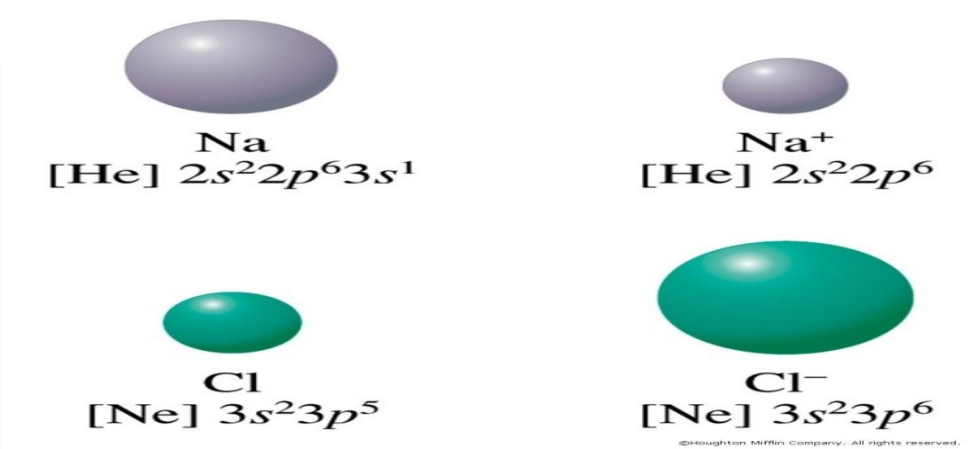
The elements of a family (column) of the PT have the same # of es in the outer most shells. Thus the core charge is the same for all members of a family. However, atomic size increases down a group due to increasing of distance from the nucleus 'n'.

C. Ionic radius

- Ions may be larger or smaller than the neutral atom, depending on the ion's charge.
- When an atom loses an e to form a cation, the lost e no longer contributes to shielding the other es from the charge of the nucleus; consequently, the other es are more strongly attracted to the nucleus, and the radius of the atom gets smaller.

+ve ions smaller than their neutral atoms

- Similarly, when an e is added to an atom, forming an anion, the added e repels other es, with the result that the size of the atom increases. -ve ions larger than their atoms



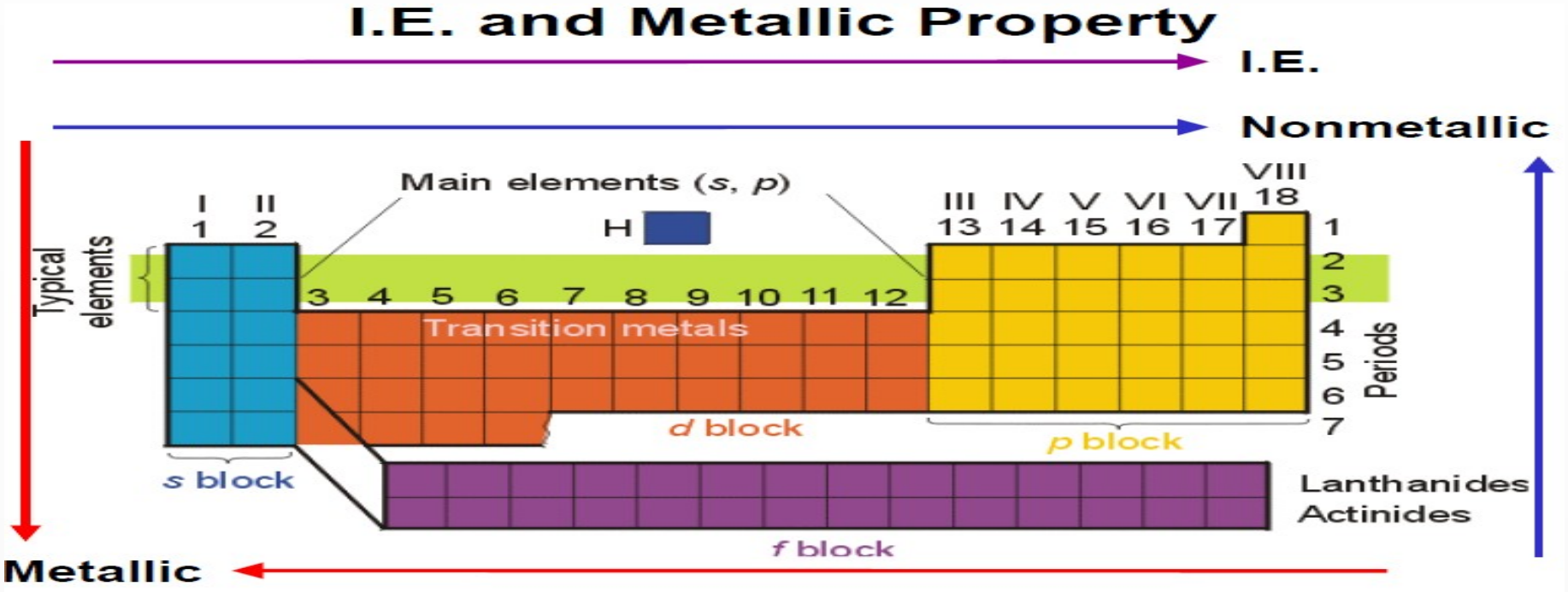
D. Ionization Energy (I)

- ✓ The energy required to remove the least tightly held e of an atom in the gas phase. **$Li(g) \rightarrow Li^{+}(g) + e^{-}$ Energy required = I > 0**
- ✓ The electron removed in this case is the single 2s valence electron.
- ✓ The force exerted on the outer e by the core charge is given by Coulombs Law: **$F = -Z_{core}e^2/r^2$**
- ✓ Here Z_{core} is the core charge, ‘e’ is the charge of the outermost electron, and ‘r’ is the average distance of this e from the nucleus.
- ✓ From equation that the force increases as Z_{core} increases.
- ✓ Z_{core} increases from left to right across a period.
- ✓ Thus F and I are expected to increase also.
- ✓ Similarly, the force decreases as ‘r’ increases. Since ‘r’ increases with increasing ‘n’ down a family, I decreases down the group.

$E(g) \rightarrow E^{+}(g) + e$, 1st ionization energy (I_1)
$E^{+}(g) \rightarrow E^{2+}(g) + e$, 2nd ionization energy (I_2)
$E^{2+}(g) \rightarrow E^{3+}(g) + e$, 3rd ionization energy (I_3)

Cont'd

- Always, $I_3 > I_2 > I_1 > 0$.
- When the 1st e is removed, the remaining es are pulled in more tightly to the nucleus because there is now a net +ve charge of 1 unit on the atom.
- The 2nd e is therefore harder to remove because it must be pulled away from the +ve ion, E^+.
- For the same reason, the 3rd e is even harder to remove than the 2nd.



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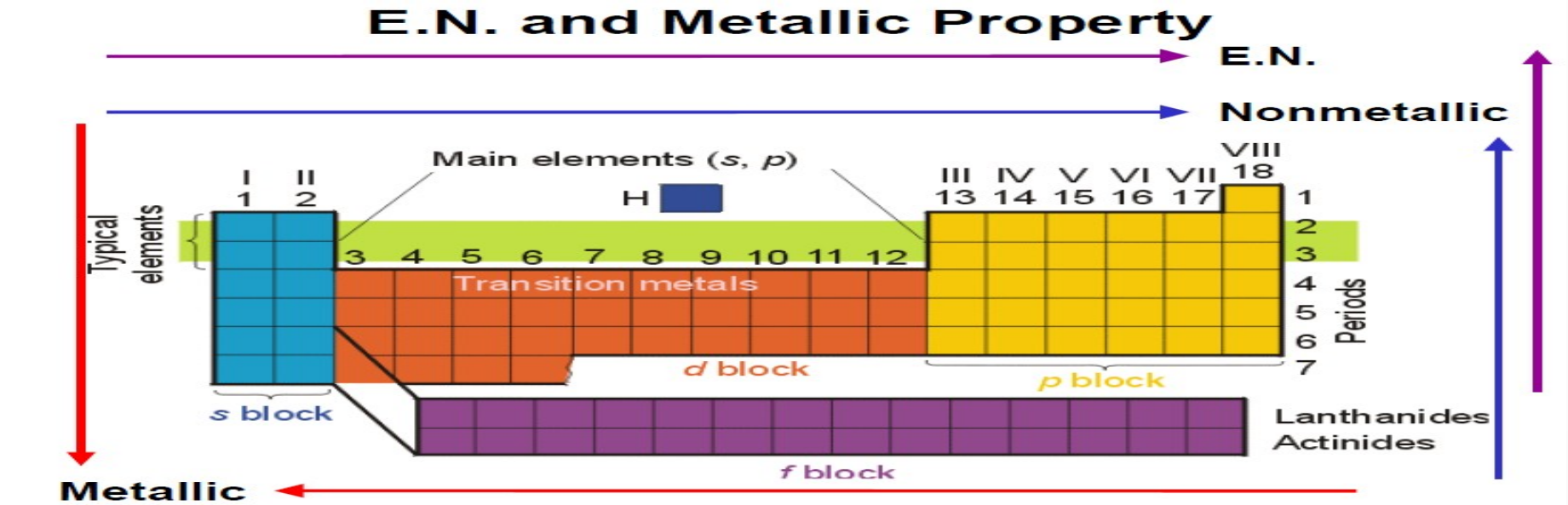
E. Electron Affinity (EA)

- The EA is the energy required/released to add one e to an atom. For example: $Cl\ (g) + e^- \longrightarrow Cl^-\ (g)$ [D E = - 349 kJ/mol]
- Energy released when an electron is added to an atom.
- D E < 0 Favorable (energy is released, products more stable than reactants).EA is the opposite process to ionization energy.
- A measure of the tendency of an atom to gain, rather than lose an e.
- The same trends as IE, increases from lower left corner to the upper right corner Metals have low "EA" but nonmetals have high "EA").
- EA(just like IE) is a measure of how stable the products are with respect to the reactants. If the products are much more stable, a large amount of energy will be released during the process and EA will be a large -ve number.
- At the other extreme, if the reactants are much more stable than the products, then it becomes very difficult to add an e and the EA will be +ve.

Cont'd

F. Electronegativity (E.N.)

- EN is a measure of the ability of an atom in a molecule to attract electrons to itself.
- *In a group:* Atoms with fewer energy levels can attract electrons better (less shielding). So, EN increases UP a group of elements.
- *In a period:* more protons, while the energy levels are the same, means atoms can better attract electrons. So, EN increases right in a period of elements.



Chemical properties and the periodic table

- Electron configurations helps us understand changes in atomic radii, ionization energies and electron affinities.

Various trends in reactivity can be observed

- ✓ Main group metals becomes more reactive as you go down a group
- ✓ Reactivity of nonmetals decreases as you go down a group
- ✓ Transition metals becomes less reactive as you go down a group

Hydrogen

- Hydrogen is a nonmetal under normal conditions. While it may lose an electron to form H^+. It also can gain an electron to form H^-.

$$2Na(s) + H_2 \xrightarrow{>200^0c} 2NaH(s)$$

Hydrogen is commonly placed either in the G-1A or G-VIIA

Nobel Gases

- Each of these has filled s and p sublevels except for helium(s only).
- All are very unreactive.
- A limited # of cpds have been produced using xenon and krypton.

$$Xe(g) + F_2(g) \xrightarrow{> 250^0c} XeF_2(g)$$

- The noble gases are noted for their chemical stability and existence as monatomic molecules.
- Except for helium, they share a common e configuration that is very stable. This configuration has 8 valence shell electrons.

Alkali metals

- The group 1A metals all have an outer electron configuration of ns^1.
- Lose of an e to form a 1+ ion is the basis of almost all rxns of the alkali metals. $M \longrightarrow M^+ + e^-$
- The reactivity of the elements increases from top to bottom of the group.

Alkaline earth metals

- The group IIA(2) metals are not as reactive as the alkali metals
- They need to lose 2 es in order to achieve a noble gas configuration.

$$M \longrightarrow M^{2+} + 2e^-$$

- Reactivity increases as you go from the top to the bottom of the group.

Halogens

- The common group VIIA(17) elements are all nonmetals.
- each only needs a single e to achieve a noble gas configuration. When reacting with metals, they form1- ions

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

When reacting with nonmetals, they share electrons.

$$O_2(g) + F_2(g) \longrightarrow 2OF_2$$

CHAPTER SIX

CHEMICAL BONDING AND MOLECULAR GEOMETRY

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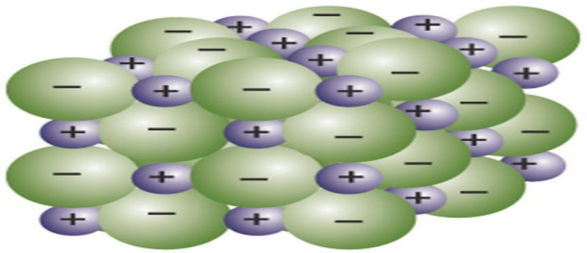
Chapter-6:Chemical Bond

Formation of compounds

- Transfer or sharing of valence electron(s) takes place.
- Atoms achieve the electronic configuration of the nearest noble gas in the Periodic Table
- Atoms are joined together by chemical bonds
- Three types of chemical bonds

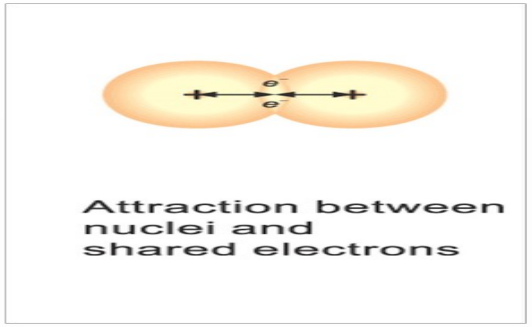
1.Ionic bond:

Electrostatic attraction between positively charged particles and negatively charged particles.



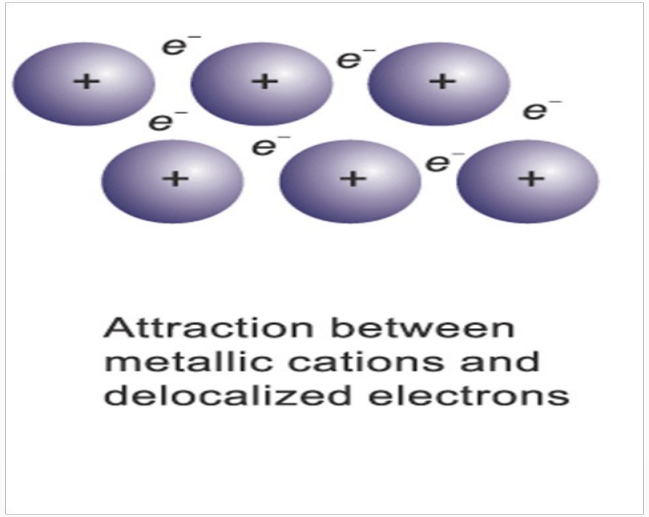
2. covalent bond:

Electrostatic attraction between nuclei and shared electrons.



3. Metallic bond:

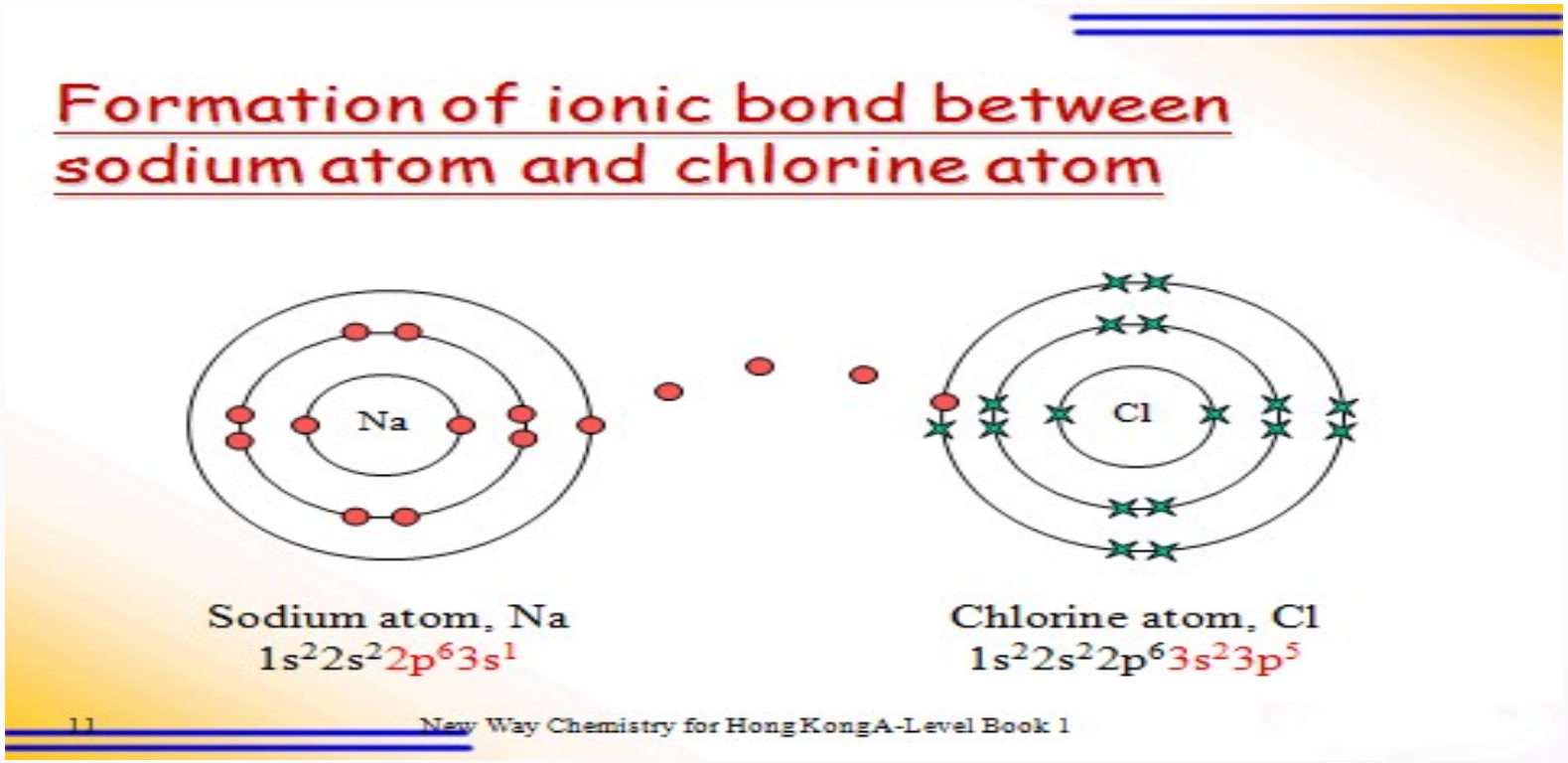
Electrostatic attraction between metallic cations and delocalized electrons (electrons that have no fixed positions)



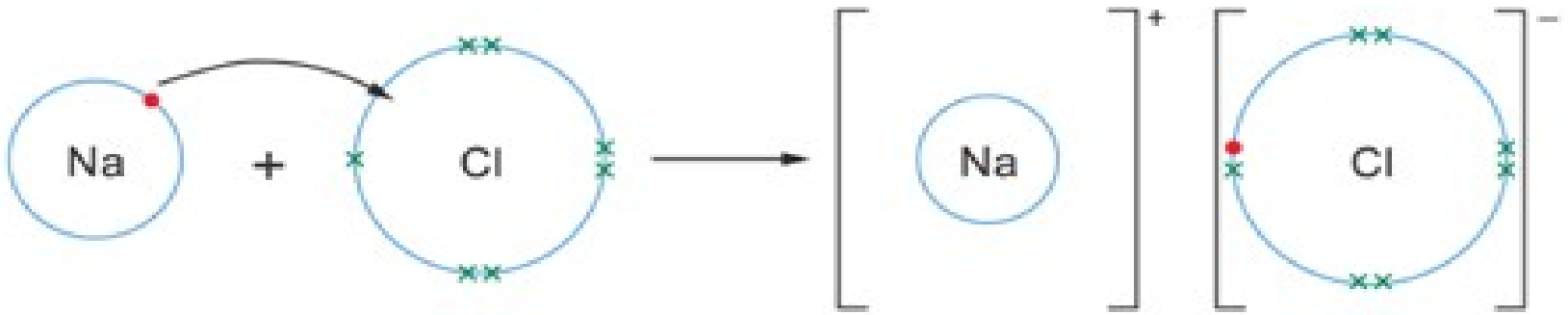
Formation of Ionic Bonds:

Ionic bonds are the strong non-directional electrostatic attraction between ions of opposite charges.

- Formed by a transfer of electrons from metallic atoms to non-metallic atoms. E.g. formation of sodium chloride
- Both the sodium ion and chloride ion attain the electronic configurations of noble gases which give rise to stability.



Ionic Bonds: Donating and Accepting Electrons



Sodium atom $1s^2 2s^2 2p^6 3s^1$

Chlorine atom $1s^2 2s^2 2p^6 3s^2 3p^5$

Sodium ion $1s^2 2s^2 2p^6$ (Electronic configuration of neon)

Chloride ion $1s^2 2s^2 2p^6 3s^2 3p^6$ (Electronic configuration of argon)

Energetics of Formation of Ionic Compounds

Consider the formation of the ionic cpd via a serious of steps.

1. the conversion of the elements to the gaseous atoms(standard enthalpy change of atomization, ΔH^{o}_{atom})

$$Na(s) \xrightarrow{\Delta H^{o}_{atom}} Na(g)$$

$$^{1}/_{2}Cl_{2}(g) \xrightarrow{\Delta H^{o}_{atom}} Cl(g)$$

2.The conversation of the gaseous atoms to gaseous ions(ionization enthalpy, $\Delta H_{I.E}$ and electron affinity, $\Delta H_{E.A}$)

$$Na(s) \xrightarrow{\Delta H^{o}_{atom}} Na(g) \xrightarrow{\Delta H_{I.E}} Na^{+}(g)$$

$$^{1}/_{2}Cl_{2}(g) \xrightarrow{\Delta H^{o}_{atom}} Cl(g) \xrightarrow{\Delta H_{E.A}} Cl^{-}(g)$$

3. The combination of the gaseous ions to form ionic crystal(lattice enthalpy, $\Delta H^{o}_{lattice}$)

$$Na(s) \xrightarrow{\Delta H^{o}_{atom}} Na(g) \xrightarrow{\Delta H_{I.E}} Na^{+}(g) \xrightarrow{\Delta H^{o}_{lattice}} NaCl(s)$$

$$^{1}/_{2}Cl_{2}(g) \xrightarrow{\Delta H^{o}_{atom}} Cl(g) \xrightarrow{\Delta H_{E.A}} Cl^{-}(g)$$

1. Standard enthalpy change of formation(ΔH^o_f)

The enthalpy change when one mole of the ionic cpd is formed from its constituent elements(in their standard states) under standard conditions. $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$ $\Delta H^o_f = -411 KJmol^{-1}$

2. Standard Enthalpy change of atomization (ΔH^o_{atom})

The enthalpy change when one mole of gaseous atoms is formed from an element in the standard state under standard conditions.

$Na(s) \rightarrow Na(g)$ $\Delta H^o_{atom}[Na(s)] = +109 KJmol^{-1}$

$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ $\Delta H^o_{atom}[Cl_2(g)] = +121 KJmol^{-1}$

3. Ionization Enthalpy ($\Delta H_{I.E}$)

The energy required to remove one mole of electrons from one mole of atoms or ions in the gaseous state.

$Na(g) \rightarrow Na^+(g) + e^-$ $\Delta H_{I.E}[Na(g)] = +494 KJmol^{-1}$

$Mg(g) \rightarrow Mg^+(g) + e^-$ $\Delta H_{I.E}[Mg(g)] = +736 KJmol^{-1}$

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ $\Delta H_{I.E}[Mg^+(g)] = +1450 KJmol^{-1}$

4. Electron affinity ($\Delta H_{E.A}$)

The enthalpy change when one mole of electrons is added to one mole of atoms or ions in the gaseous state.

1st electron affinity of O(g)

$$O(g) + e^- \longrightarrow O^-(g) \quad \Delta H_{E.A}[O(g)] = -142 KJmol^{-1}$$

2nd electron affinity of O(g)

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \quad \Delta H_{E.A}[O(g)] = -844 KJmol^{-1}$$

5. Lattice enthalpy ($\Delta H^o_{lattice}$)

The enthalpy change when one mole of an ionic crystal is formed from its constituent ions in the gaseous state under standard conditions.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \quad \Delta H^o_{lattice}[Na^+Cl^-(s)] \ (+ve \text{ or } -ve)$$

Lattice enthalpy can be calculated from the values of other experimentally determined enthalpy changes by constructing a Born-Haber cycle and applying Hess's law.

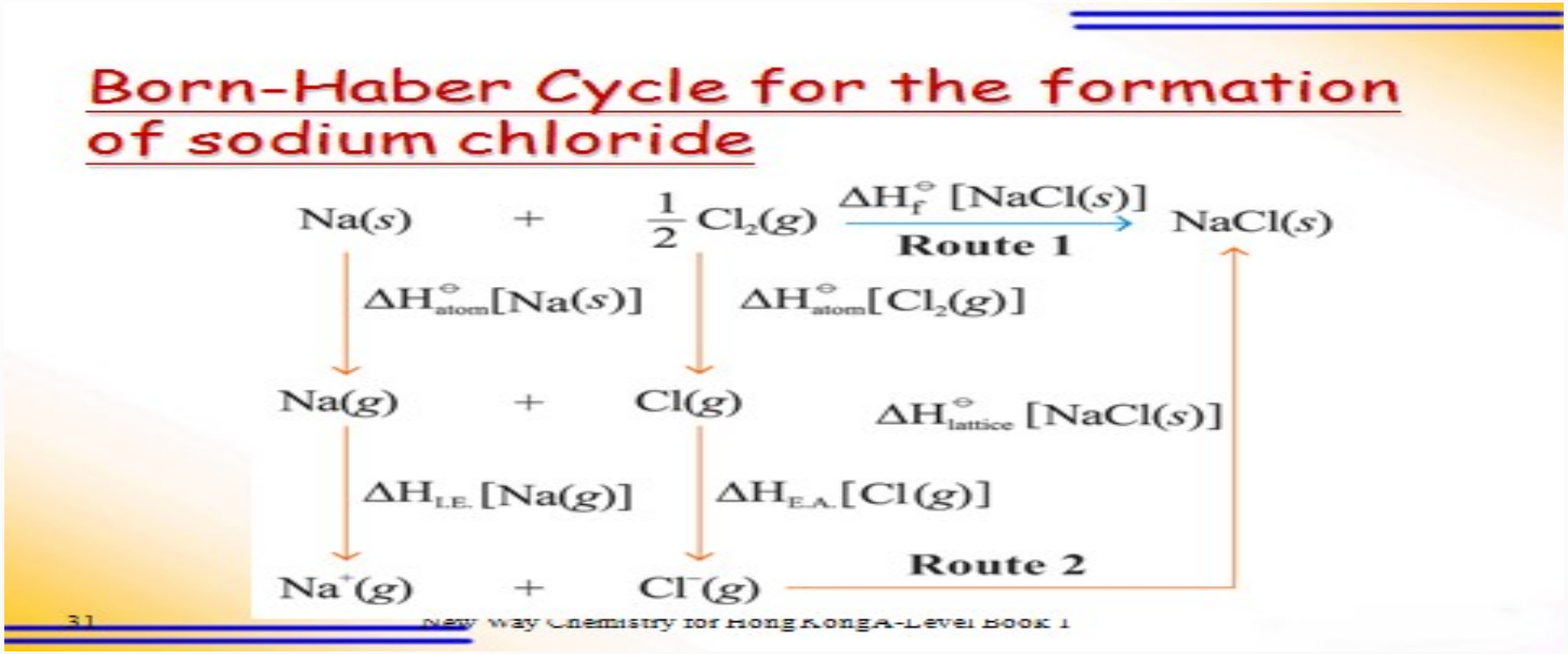
Born-Haber cycle

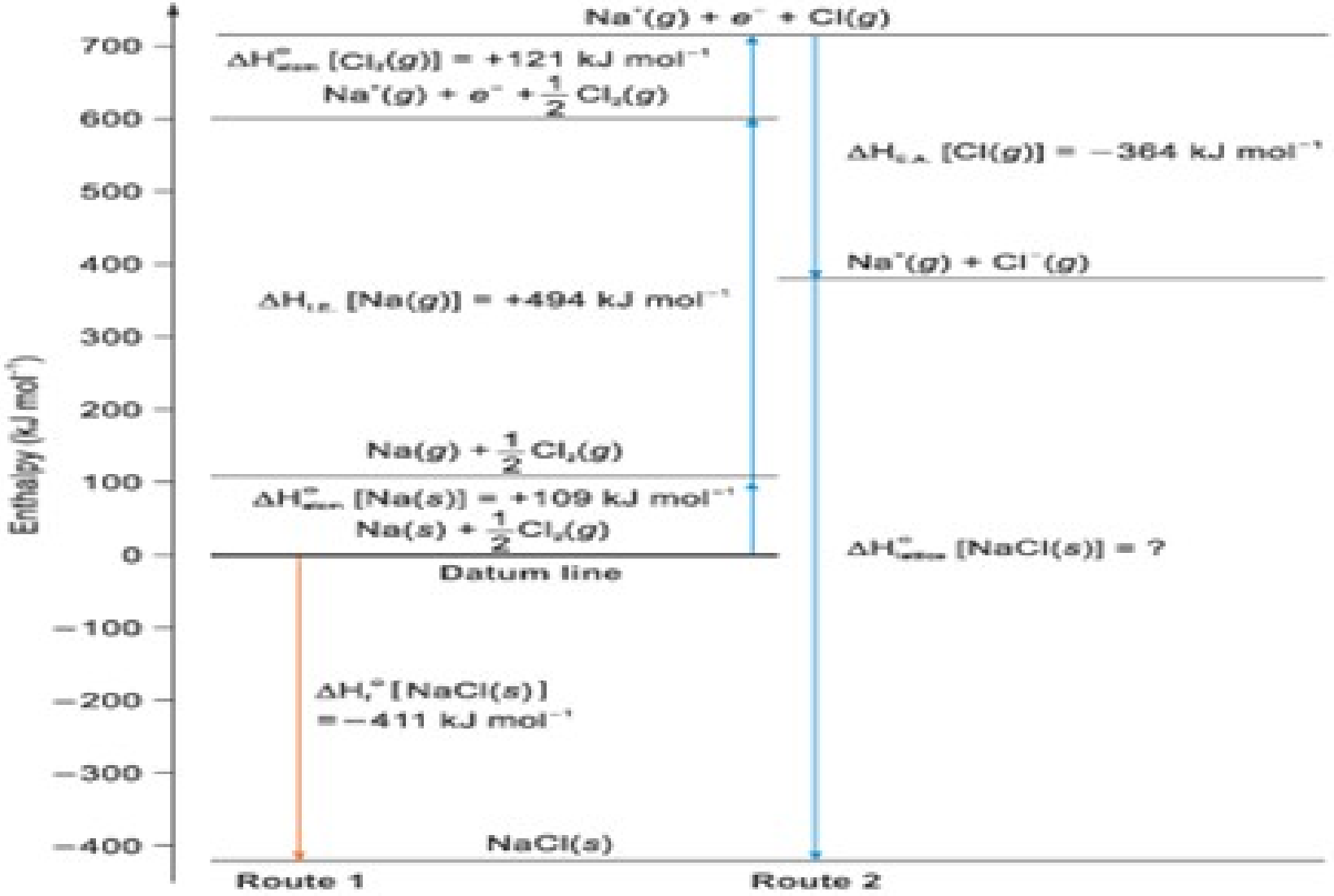
A simplified enthalpy level diagram used to calculate the lattice enthalpy of an ionic cpd.

-two different routes to form an ionic pd

Route 1: direct single-step rxn of the elements to form the ionic cpd.

Route 2: consists of a number of steps. The enthalpy change of each step can be found from experiments. Except the lattice enthalpy




Na⁺(g) + e⁻ + Cl(g)
ΔH°sub [Cl₂(g)] = +121 kJ mol⁻¹
Na⁺(g) + e⁻ + ½Cl₂(g)
ΔH°e.a. [Cl(g)] = −364 kJ mol⁻¹
Na⁺(g) + Cl⁻(g)
ΔHi.e. [Na(g)] = +494 kJ mol⁻¹
Na(g) + ½Cl₂(g)
ΔH°sub [Na(s)] = +109 kJ mol⁻¹
Na(s) + ½Cl₂(g)
ΔH°f [NaCl(s)] = ?
Datum line
ΔH°f [NaCl(s)]
= −411 kJ mol⁻¹
NaCl(s)
Route 1
Route 2
Enthalpy (kJ mol⁻¹)
700
600
500
400
300
200
100
0
−100
−200
−300
−400

Example 7-2

Lewis formula of ionic compounds

- Electron-dot diagrams (Lewis structures) can represent the valence electron arrangement in elements, compounds, and ions.



atom ion molecular cpd ionic cpd

- When metals lose es to form ions, they lose all their valence es. The Lewis Dot Structure of a metal ion has no dots. The charge indicates how many es were lost.



Magnesium atom Magnesium ion

- When nonmetals gain es, they fill up their valence shell with a complete octet (except H.) The ion is placed in brackets with the charge outside the brackets.



A '+' metal ion is attracted to a ' –' nonmetal ion (opposites attract) forming an ionic cpd. We can use Lewis dot structures to represent ionic cpds.



The formula for magnesium fluoride is MgF_2

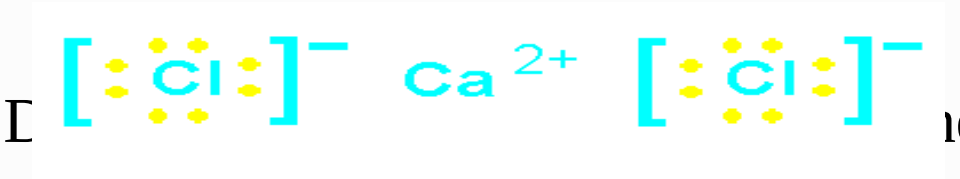
Draw the e-dot (Lewis) structure of an atom of calcium.



Draw the e-dot (Lewis) structure of an atom of Cl.



Draw the e-dot (Lewis) structure of $CaCl_2$.



Draw the e-dot (Lewis) structure of the ff substances:

Calcium oxide(an ionic cpd)



Hydrogen bromide





Covalent bond

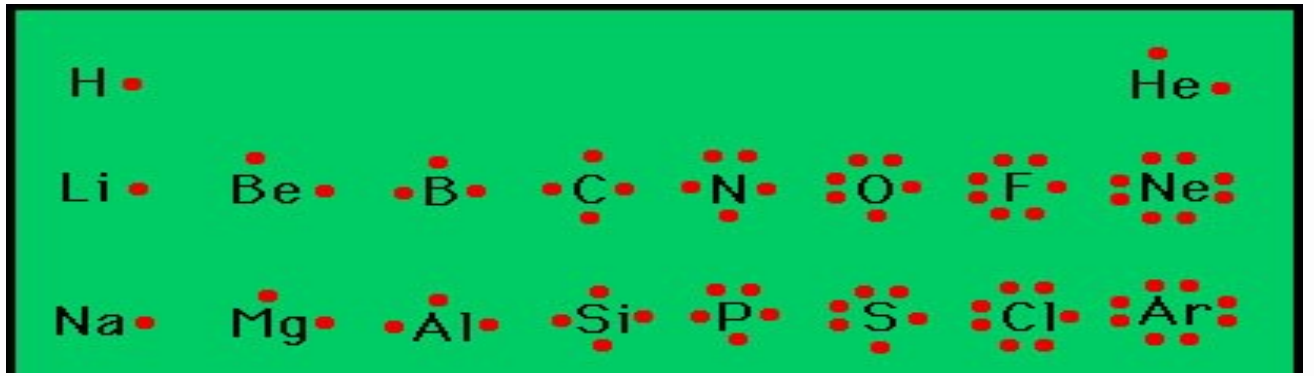
Covalent Bonding results from the sharing of two es between two atoms (usually non-metals) resulting in molecules ***Octet Rule applies***

Triple bond

Each Covalent Bond contains three electrons

Drawing *molecules* using Lewis Dot Structures

- Symbol represents the KERNEL of the atom (nucleus and inner e-)
- dots represent valence e-



- Always remember atoms are trying to complete their outer shell!
- The # of es the atoms needs is the total # of bonds they can make.
- G7A elements (e.g. F) have one valence e for covalent bonding, so to achieve octet

G6A elements (e.g. O) use two valence es for covalent bonding, so to achieve octet

G5A elements (e.g. N) use three valence es for covalent bonding, so to achieve octet

Cont…

G4A elements (e.g. C) use four valence es for covalent bonding, so to achieve octet

Carbon dioxide, CO_2 Total # of valence es = 4 + (2 x 6) = 16

Double bonds

Rules for Drawing Lewis Structures

- ***First sum the number of valence electrons from each atom.***
- ***The central atom is usually written first in the formula.***
- ***Complete the octets of atoms bonded to the central atom (remember that H can only have two electrons)***
- ***Place any left over es on the central atom, even if doing so it results in more than an octet.***
- ***If there are not enough es to give the central atom an octet , try multiple bonds***

Cont...

E.g. PCl_3 Total Number of valence es = 5 + (3 x 7) = 26

E.g.; $CHBr_3$:-Total # of valence es = 4 +1+ (3 x 7) = 26

Exceptions to the Octet Rule in Covalent Bonding

1.Molecules with an odd number of electrons

2.Other Natural Radicals, which do not obey Lewis Structures (e.g. O2)

3.Molecules in which an atom has less than an octet

4.Molecules in which an atom has more than an octet

1. Odd Number of Electrons

NO **# of valence es = 11**

***Resonance* occurs when more than one valid Lewis structure can be written for a particular molecule (i.e. rearrange electrons)**

NO_2 # of valence es = 17

Molecules and atoms which are neutral (contain no formal charge) and with an unpaired electron are called Radicals

O_2

2. Less than an Octet

Includes Lewis acids such as halides of B, Al and compounds of Be

BCl_3

Group 3A atom only has six es around it

However, Lewis acids "accept" a pair of electrons readily from Lewis bases to establish a stable octet.

AlX_3

Aluminium chloride is an ionic solid in which Al^{3+} is surrounded by six Cl^-. However, it sublimes at 192°C to vapour Al_2Cl_6 molecules

B_2H_6 **A Lewis structure cannot be written for diborane. This is explained by a three-centre bond – single e is delocalized over a B-H-B**

3. More than an Octet

Elements from the third Period and beyond, have *n*s, *n*p and unfilled *n*d orbitals which can be used in bonding

PCl_5 **P : (Ne) $3s^2\ 3p^3\ 3d^0$ # of valence es = 5 + (5 x 7) = 40**

10 es around the phosphorus

SF_4 **S : (Ne) $3s^2\ 3p^4\ 3d^0$ # of valence es = 6 + (4 x 7) = 34**

The Larger the central atom, the more atoms you can bond to it – usually small atoms such as F, Cl and O allow central atoms such as P and S to expand their valency.

Intramolecular Bonds

- ✓ Intramolecular Bonds are attractive forces *within* a compound.

  The bond b/n O & H in a H_2O molecule is an intramolecular bond.

  The bond between Na^{+1} and Cl^{-1} is an intramolecular Bond.

- ✓ an *intermolecular bond* is an attraction *between different* molecules.
- ✓ The 3 major types of intramolecular bond can be described by the EN difference:
- ✓ Non-Polar Covalent – Bonds which occur between atoms with little or no electronegativity difference (Den = 0.0).
- ✓ Polar Covalent – Bonds which occur between atoms with a definite electronegativity difference (0.0 < Den < 2.0).
- ✓ Ionic – Bonds which occur between atoms with a large EN difference (Den > 2.0), where electron transfer can occur.

E.g. F-F (4.0 – 4.0 = 0) is *non-polar covalent*

H-F (4.0 – 2.1 = 1.9) is *polar covalent*, LiF (4.0 – 1.0 = 3.0) is ionic

Cont…

The Relationship between Electronegativity and Bond Type

Electronegativity difference between the bonding atoms	Bond type	Covalent character	Ionic character
zero ↓ intermediate ↓ large	covalent ↓ polar covalent ↓ ionic		

$$I^{\delta+} --- Cl^{\delta-}$$

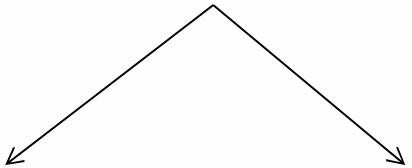
- NON-Polar bonds -Electrons shared evenly in the bond
  - EN difference is zero
  - Between identical atoms diatomic molecules
  - Sometimes the **bonds** within a molecule are polar and yet the **molecule** is non-polar because its shape is symmetrical. CH_4
- Polar bond -Electrons unevenly shared
  - EN difference greater than zero but less than 2.0
  - closer to 2.0 more polar more "ionic character"
- Not equal on all sides
  - Polar bond between 2 atoms makes a polar molecule
  - asymmetrical shape of molecule

✓ Place these molecules in order of increasing **bond** polarity which is least and which is most?

- HCl, CH_4 , CO_2 , NH_3 , N_2 , HF

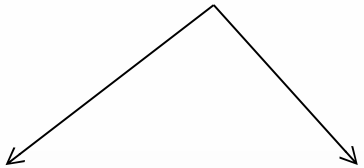
Summary of polarity

BONDS



Non-polar	Polar
Identical	different
e.g. CH_4	

MOLECULES

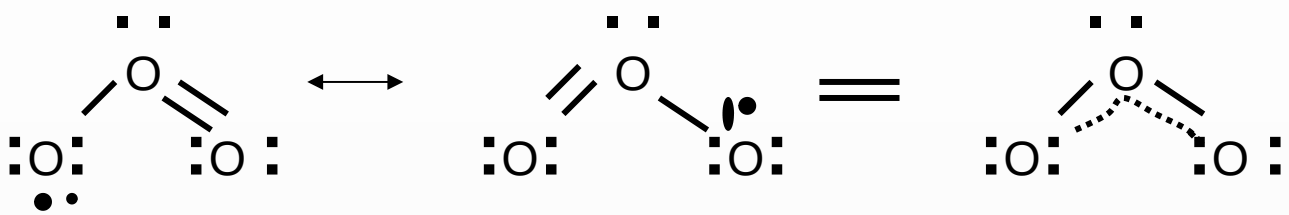


Non-polar	Polar
Symmetrical	Asymmetrical
e.g.	$_{27}^{+}$ H-Cl $_{27}^{-}$

Resonance

When several structures with different e distributions among the bonds are possible, all structures contribute to the electronic structure of the molecule. These structures are called resonance structures.

When two or more plausible Lewis structures can be written but the "correct" structure cannot be written is called resonance. For example:



NO Number of valence electrons = 11

Resonance **occurs when more than one valid Lewis structure can be written for a particular molecule (i.e. rearrange electrons)**

NO_2 Number of valence electrons = 17

Molecules and atoms which are neutral (contain no formal charge) and with an unpaired electron are called ***Radicals***

O_2

Formal charge

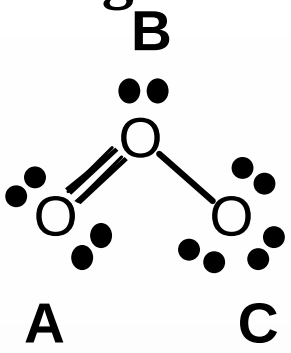
- **Formal charge** is the charge calculated for an atom in a Lewis structure on the basis of an equal sharing of bonded electron pairs.

$$\text{FORMAL CHARGE} = \left(\begin{array}{c}\text{Number of}\\ \text{valence electrons}\\ \text{in free atom}\end{array}\right) - \frac{1}{2}\left(\begin{array}{c}\text{Number of}\\ \text{bonding}\\ \text{electrons}\end{array}\right) - \left(\begin{array}{c}\text{Number of}\\ \text{nonbonding}\\ \text{electrons}\end{array}\right)$$

- Formal charge can be used to determine the most plausible Lewis Structure when more than one possibility exists for a compound.
- **4 criteria for choosing the more important resonance structure:**

1. Smaller formal charges (either +ve/-ve) are preferable to larger charges;
2. A more -ve formal charge should exist on an atom with a larger electronegative (EN) value.
3. Get unlike charges as close together as possible
4. Avoid like charges (+ + or - -) on adjacent atoms

Q. Calculate the formal charge of each oxygen atoms in ozone?



For O_B

valence e^- = 6

nonbonding e^- = 2

bonding e^- = 6 X 1/2 = 3

Formal charge = +1

For O_A

valence e^- = 6

nonbonding e^- = 4

bonding e^- = 4 X 1/2 = 2

Formal charge = 0

For O_C

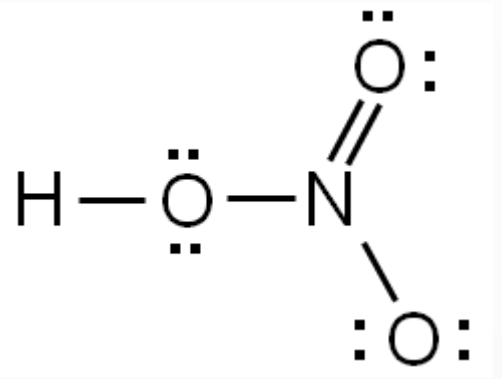
valence e^- = 6

nonbonding e^- = 6

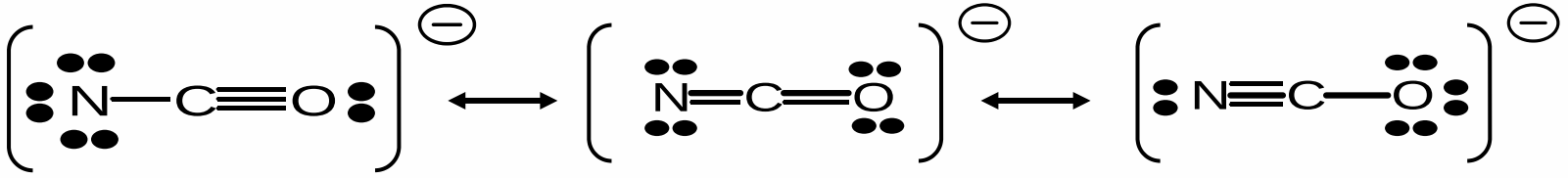
bonding e^- = 2 X 1/2 = 1

Formal charge = -1

Q. Calculate the formal charge of each atoms on nitric acid?

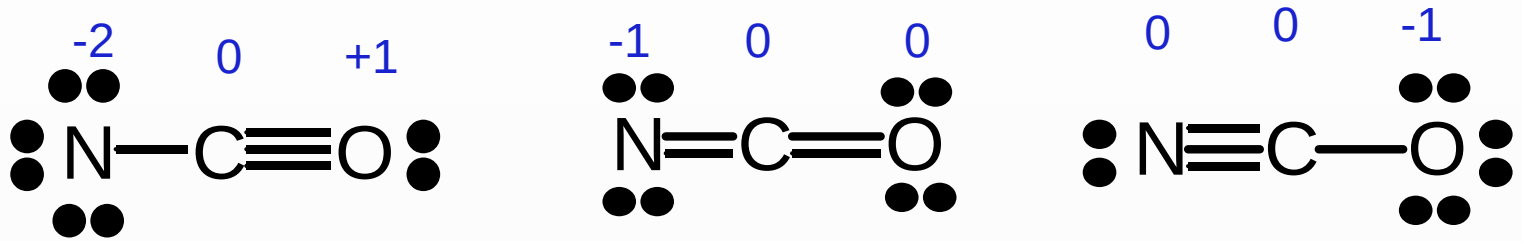


EXAMPLE: NCO^- has 3 possible resonance forms and determine which resonance structure is most plausible Lewis structure ?



A **B** **C**

Now Determine Formal Charges



Forms B and C have smaller formal charges; this makes them more important than form A. (rule 1)

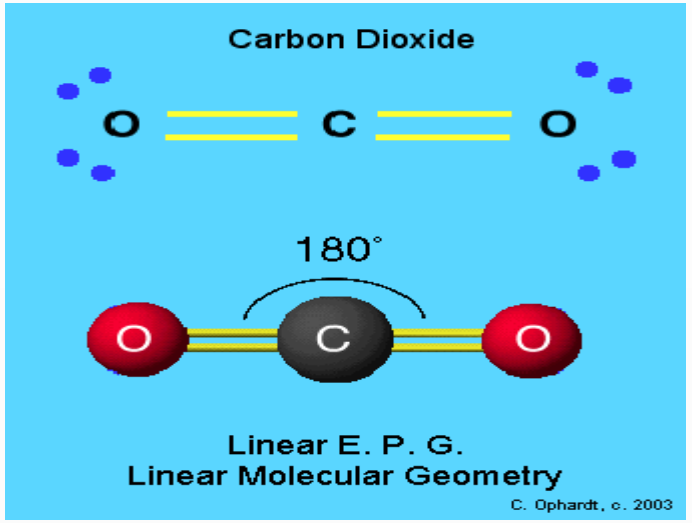
Form C has a negative charge on O which is the more EN element, therefore C contributes the most to the resonance hybrid. (rule 2)

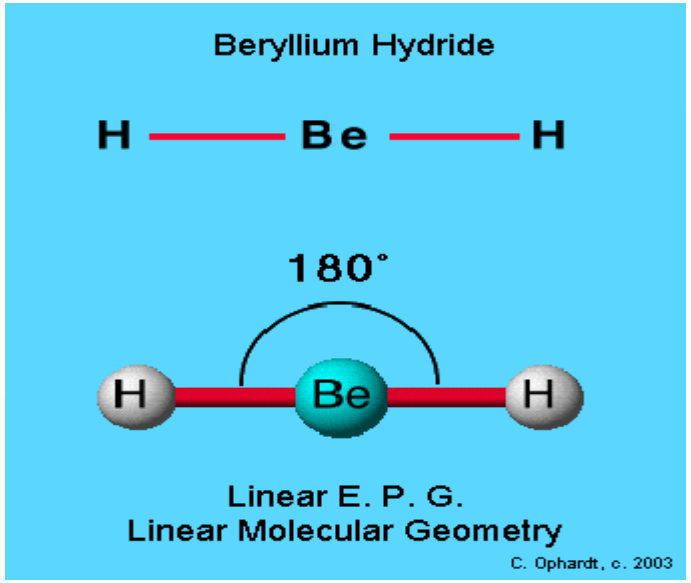
Shapes of Molecules

We use Lewis structures to account for formula of covalent cpds.
Lewis structures also account for the number of covalent bonds.
Lewis structures however don't account for the shapes of molecules.
Molecules of AB_n have shapes dependent on the value of *n*

AB_2 must be either linear or bent:

Examples of Linear molecules





Linear - No non-bonding electrons

Linear Molecules have a bond angle = 180°

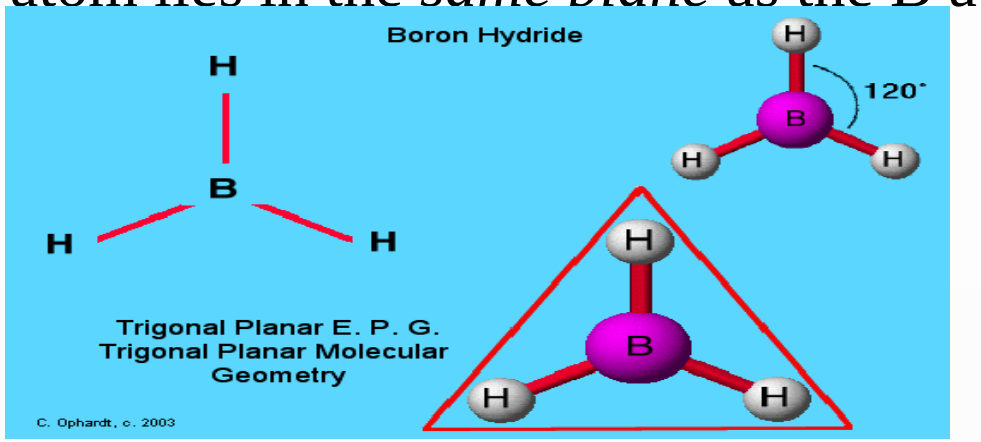
Bent molecules have a bond angle ≠ 180° **Bent**

AB_3 most common shapes place the B atoms at the corners of an equilateral triangle:

Trigonal Planar: the A atom lies in the *same plane* as the B atoms (Flat)

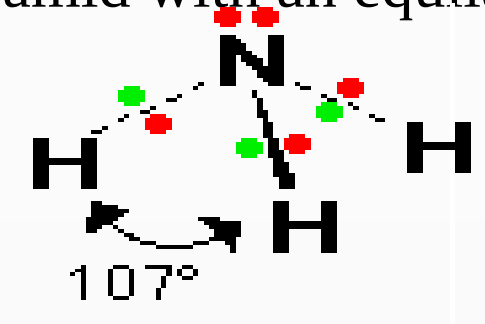
Bond angle = 120°

No non-bonding es



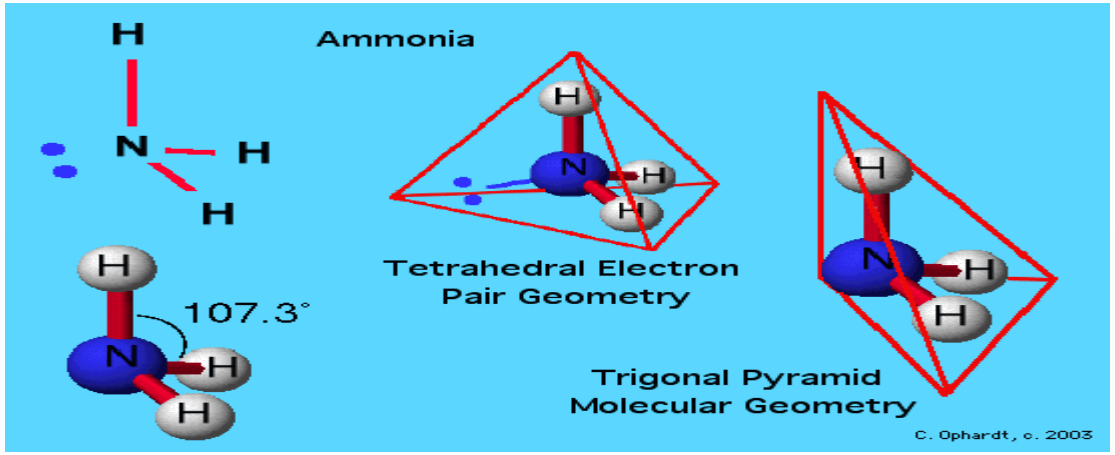
Trigonal Pyramidal:-The A atom lies above the plane of the B atom.

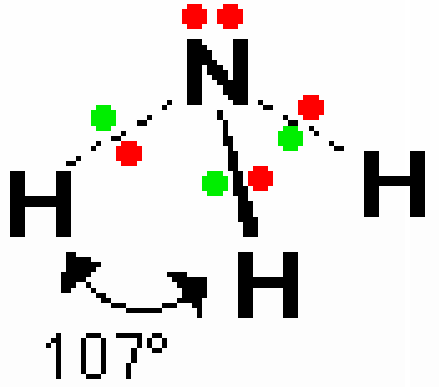
Pyramid with an equilateral triangle as the base.





- **The ideal tetrahedron has a bond angle = 109.5°**

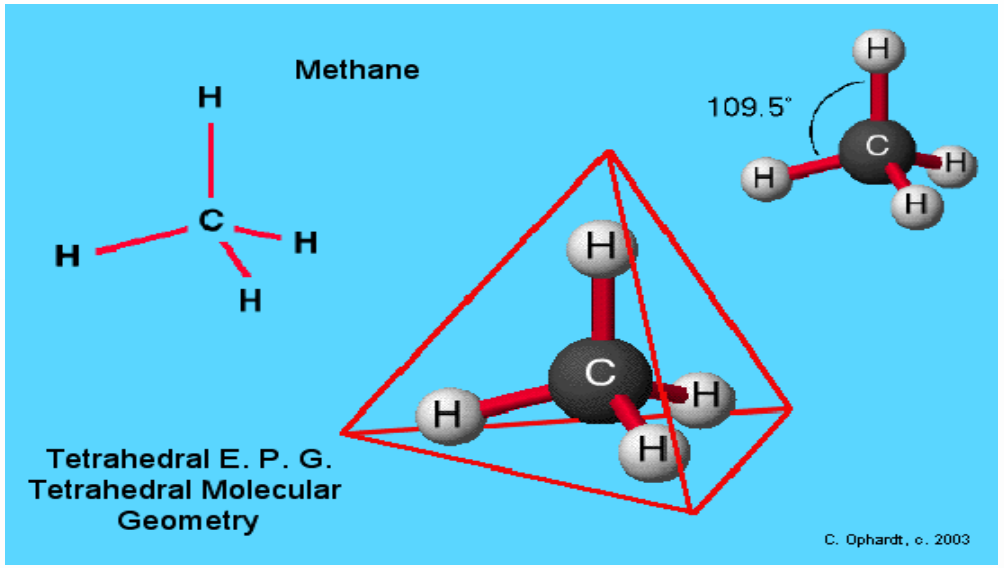




- The lone e pair exerts a little extra repulsion on the three bonding H atoms to create a slight compression to a 107° bond angle.
- Less repulsion is exerted by a bonding pair of electrons because they feel attraction from two nuclei, while a non-bonding pair feels attraction from only one nucleus.
- *Non-bonding pairs spread out more*!

Tetrahedral

AB_4 is Tetrahedral



The C has 4 valence es and thus needs 4 more es from four H atoms to complete its octet.

The hydrogen atoms are as far apart as possible at 109° bond angle. This is tetrahedral geometry. The molecule is three dimensional.

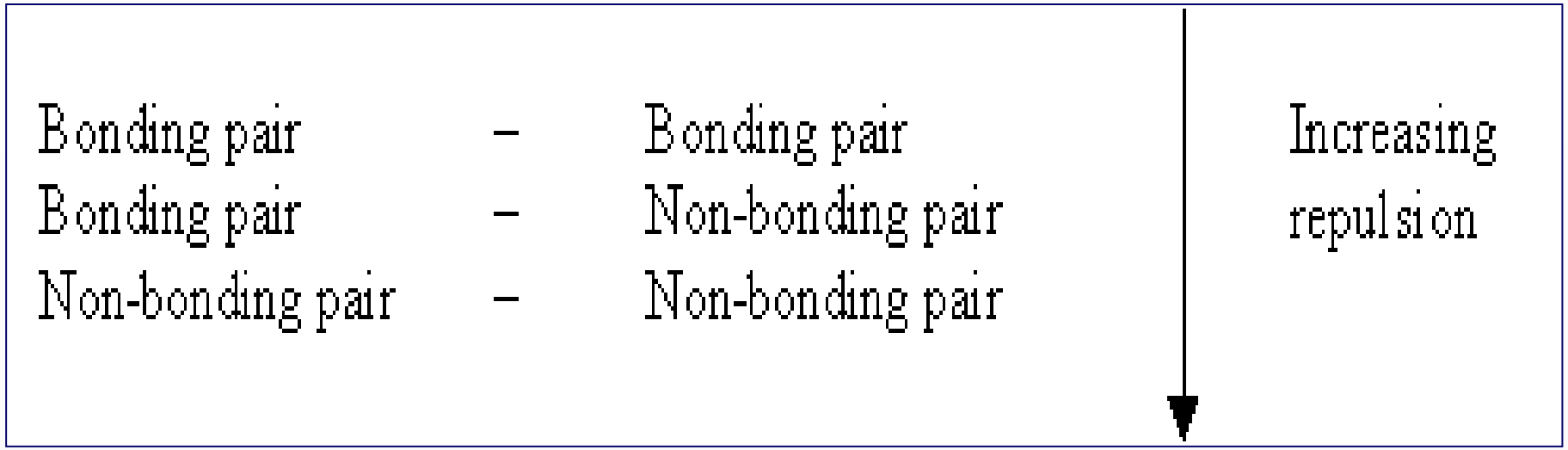
In molecules there are 2 types of electron

1. Bonding Pairs 2. Non-bonding or lone pairs

The combinations of these determine the shape of the molecule

Single bonds have a big impact on shape, double bonds have little effect

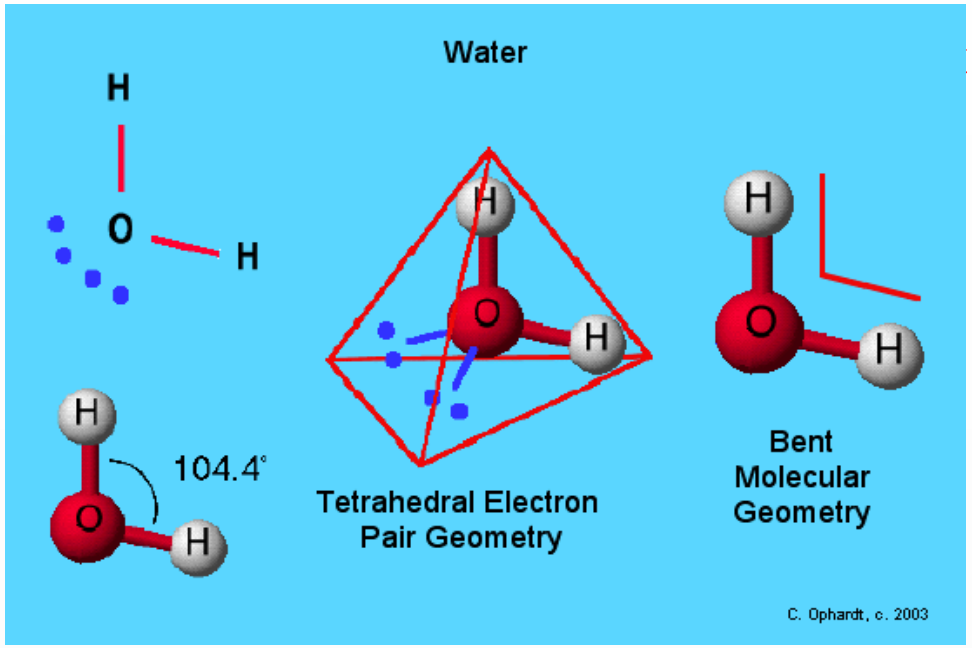
The outer pairs of es around a covalently bonded atom minimize repulsions between them by moving as far apart as possible



Cont…

Water is a bent molecule with bond angles of 104.5°

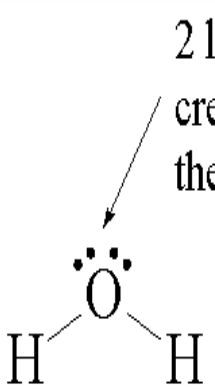
The bond angle decreases as the # of non-bonding pairs increases



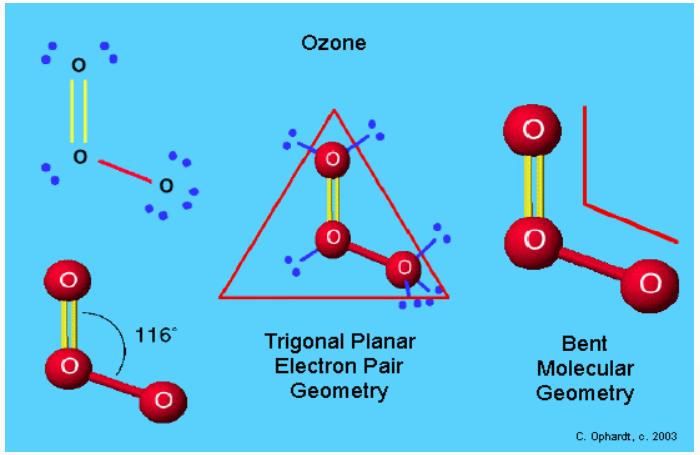
lassification

H_2O

2 lone pairs on the oxygen create a repulsion, *bending* the molecule



O_3 ; # of valence es = 18



AB_3 - classification

1. sum the total # of valence es. Drawing the Lewis Structure

2.The atom usually written first in the chemical formula is the Central atom in the Lewis structure

3. Complete the octet bonded to the Central atom. However, elements

in the third row have empty d-orbitals which can be used for bonding.

4. If there are not enough es to give the central atom an octet try multiple bonds. Predicting the Shape of the Molecule

5. sum the # of e domains around the central atom in the Lewis structure; single = double = triple bonds = non-bonding lone pair of es = one e domain

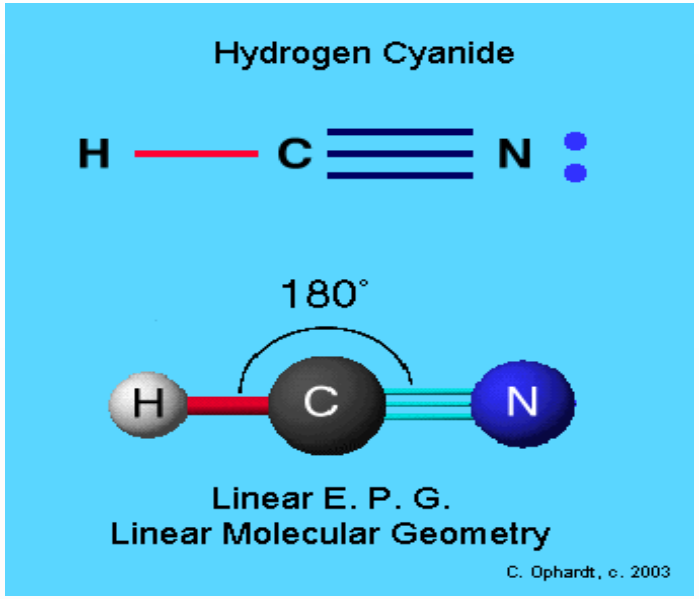
6. from the total # of e domains, predict the geometry and bond

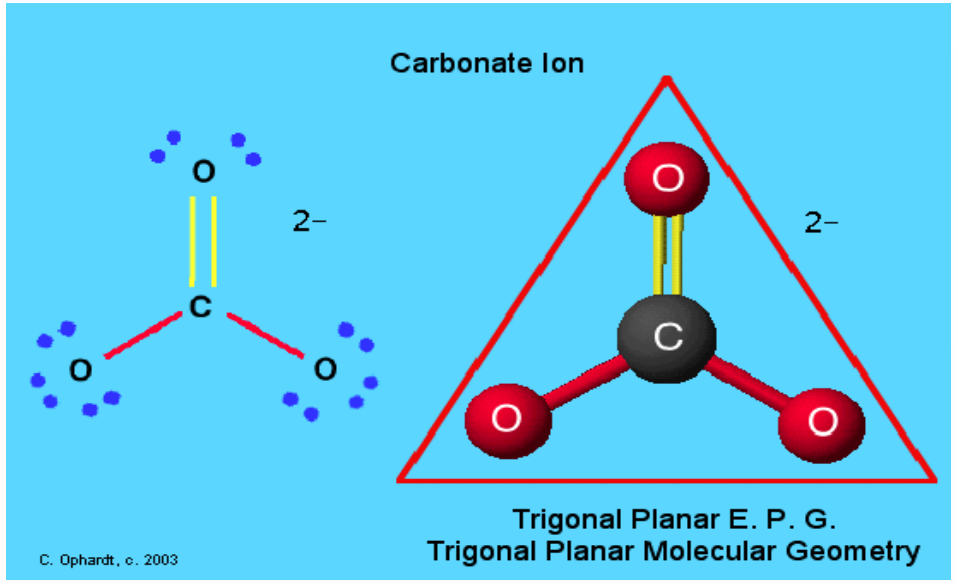
angle(s); 2 (linear = 180º); 3 (trigonal planar = 120º); 4 (tetrahedral =

109.5º); 5 (trigonal bipyramidal = 120º and 90º); 6 (octahedral = 90º)

Cont…

7. lone pair e domains exert a greater repulsive force than bonding domains. e domains of multiple bonds exert a greater repulsive force than single bonds. thus they tend to compress the bond angle.





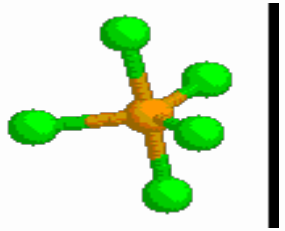
Shape	Bonding-pairs	Non-bonding pairs	Bond angle / ⁰	Examples
Linear	2	0	180	$BeCl_2$, CO_2, HCN, C_2H_2
Trigonal planar	3	0	120	BF_3, SO_3, NO_3^-, CO_3^{2-}, C_2H_4
Tetrahedral	4	0	109.5	NH_4^+, SO_4^{2-}, PO_4^{3-}, $Ni(CO)_4$, CH_4
Trigonal pyramidal	3	1	107	PH_3, SO_3^{2-}, NH_3
Non-linear (Crooked)	2	2	105	H_2S, SO_2, H_2O

Molecules with Expanded Valence Shells

When the central atom of a molecule is from the third period of the Periodic Table and beyond, that atom may have more than four pairs of electrons around it

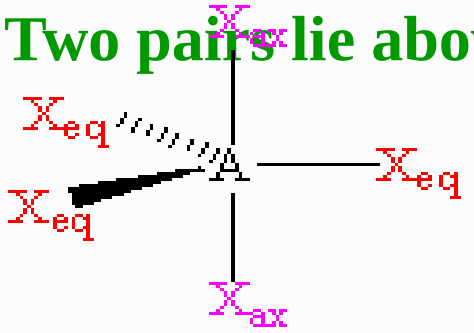
Five pairs of electrons around the central atom are based on the Trigonal Bipyramidal structure.

AB_5: e.g. PCl_5



Three pairs define an Equatorial Triangle (Equatorial electrons)

Two pairs lie above and below the triangle plane (Axial electrons)



axial positions are 90° from 3 equatorial positions

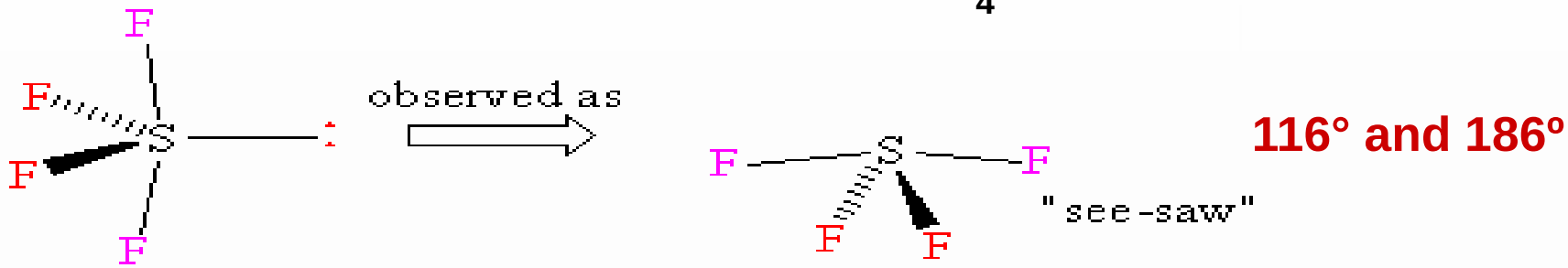
equatorial positions are 90° from 2 axial positions

The repulsion between pairs located 90° apart are *much* greater than for those 120° apart;

Cont…

Because repulsion is greater for non-bonding than for bonding electron pairs, then non-bonding pairs occupy equatorial positions on the Trigonal Bipyramidal structure

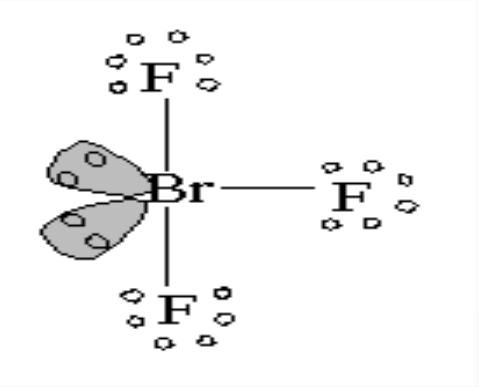
SF_4 :



116° and 186°

The non-bonding pair occupies an equatorial position. The axial and equatorial S-F bonds are slightly bent back because of the larger repulsive effect of the lone pair.

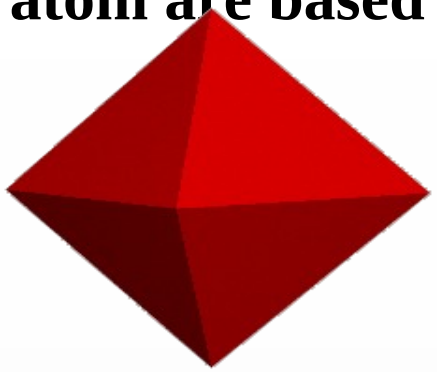
BrF_3 : T-shaped



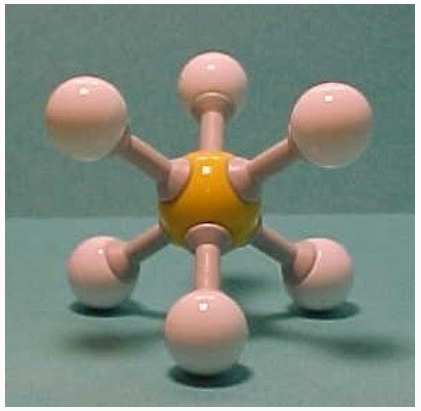
90°

Six pairs of electrons around the central atom are based on the Octahedron structure.

AB_6 : e.g. SF_6



The central atom can be visualized as being at the centre of an octahedron, with the 6 es pointing to the 6 vertices – all bond angles are 90°



Octahedral

90°

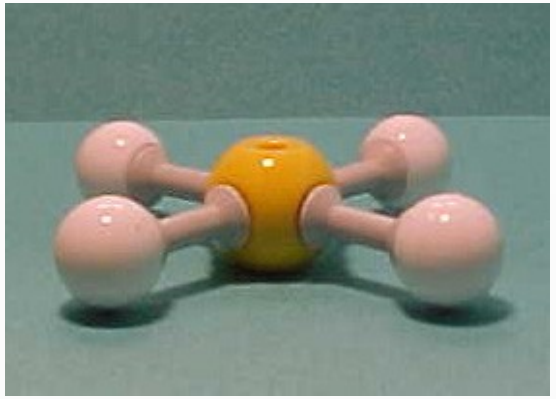
E.g. BrF_5



Square Pyramidal

Should be less than 90º

E.g. XeF_4



Square Planar

CHAPTER-SEVEN
EQILLIBRUM CONCEPTS AND ACID-BASE EQUILIBRIUM

The Concept of Equilibrium

Consider colorless frozen N_2O_4. At room temperature, it decomposes to brown NO_2: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

At some time, the color stops changing and we have a mixture of N_2O_4 and NO_2.

Chemical equilibrium is the point at which the rate of the forward reaction is equal to the rate of the reverse reaction.

At that point, the concentrations of all species are constant.

Using the collision model:

- as the amount of NO_2 builds up, there is a chance that two NO_2 molecules will collide to form N_2O_4.
- At the beginning of the reaction, there is no NO_2 so the reverse reaction ($2NO_2(g) \rightleftharpoons N_2O_4(g)$) does not occur.

As the substance warms it begins to decompose:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The Concept of Equilibrium

When enough NO_2 is formed, it can react to form N_2O_4:

$2NO_2(g) \rightleftharpoons N_2O_4(g)$.

At equilibrium, as much N_2O_4 reacts to form NO_2 as NO_2 reacts to re-form N_2O_4

The double arrow $\rightleftharpoons$ implies the process is dynamic.

As the reaction progresses

- [A] decreases to a constant,
- [B] increases from zero to a constant.
- When [A] and [B] are constant, equilibrium is achieved.

No matter the starting composition of reactants and products, the same ratio of concentrations is achieved at equilibrium.

The Equilibrium Constant

For a general reaction

the equilibrium constant expression is

where K_c is the equilibrium constant.

K_c is based on the molarities of reactants and products at equilibrium.

We generally omit the units of the equilibrium constant.

Note that the equilibrium constant expression has products over reactants.

Write the equilibrium expression for the following reaction:

The Equilibrium Constant in Terms of Pressure

If K_P is the equilibrium constant for reactions involving gases, we can write:

K_P is based on partial pressures measured in atmospheres.

Relationship between K_c and K_p

From the ideal gas law we know that

PV = nRT $P = \frac{n}{V}RT$ = Pressure in terms of conc.

$P_A = \frac{n_A}{V}RT = [A]\,RT$ Substituting P=[A]RT into the expression for K_p for each substance, the relationship between K_c and K_p becomes $K_p = K_c\,(RT)^{\Delta n}$

Where

Δn = (moles of gaseous product) – (moles of gaseous reactant)

The Magnitude of Equilibrium Constants

- The equilibrium constant, K, is the ratio of products to reactants.
- Therefore, the larger K the more products are present at equilibrium.
- Conversely, the smaller K the more reactants are present at equilibrium.
- If $K >> 1$, then products dominate at equilibrium and equilibrium lies to the right.
- If $K << 1$, then reactants dominate at equilibrium and the equilibrium lies to the left.
- An equilibrium can be approached from any direction.

Example:

The Magnitude of Equilibrium Constants

However,

The equilibrium constant for a rxn in one direction is the reciprocal of the equilibrium constant of the rxn in the opposite direction.

Heterogeneous Equilibria

- When all reactants and products are in one phase, the equilibrium is homogeneous.
- If one or more reactants or products are in a different phase, the equilibrium is heterogeneous.

Consider:

- experimentally, the amount of CO_2 does not seem to depend on the amounts of CaO and $CaCO_3$. Why?

Heterogeneous Equilibria

- Neither density nor molar mass is a variable, the concs of solids and pure liquids are constant. (You can't find the conc. of something that isn't a solution!)
- We ignore the concentrations of pure liquids and pure solids in equilibrium constant expressions.
- The amount of CO_2 formed will not depend greatly on the amounts of CaO and $CaCO_3$ present.

$$\mathbf{K_c = [CO_2]}$$

- Concentrations of liquids and solids can be obtained by dividing the density of the substance by its molar mass and both of these are constants at constant temperature.

$$\frac{density}{molar\ mass} = \frac{g/L}{g/mol} = \frac{mol}{L}$$

Calculating Equilibrium Constants

Steps to Solving Problems:

1. Write an equilibrium expression for the balanced reaction.
2. Write an ICE table. Fill in the given amounts.
3. Use stoichiometry (mole ratios) on the change in conc. line.
4. Deduce the equilibrium concentrations of all species.

Usually, the initial conc. of products is 0.(This is not always the case.) Example-1:1.00 mol of H_2 gas &1.00 mol of I_2 vapor are introduced into a 5.00-liter sealed flask. The mixture is heated to a certain temp. and the ff rxn occurs until equilibrium is established.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, the mixture is found to contain 1.580 mole of HI. (a) What are the concentrations of H_2, I_2 and HI at equilibrium? (b) Calculate the equilibrium constant K_c.

Calculating Equilibrium Constants

	$H_2(g)$	+	$F_2(g)$	⇌	2 HF(g)
Initial [ ], M:	0.200		0.200		0.000
Change in [ ], M:	-0.158		-0.158		+ 0.316
Equilibrium [ ], M	0.042		0.042		0.316

$$K_c = \qquad = \qquad = 57$$

Example-2: 0.500 mole of HI is introduced into a 1.00 L sealed flask and heated to a certain temp.. Under this condition HI decomposes to produce H_2 and I_2 until an equilibrium is established. An analysis of the equilibrium mixture shows that 0.105 mol of HI has decomposed. Calculate the equilibrium concentrations of H_2, I_2 and HI, and the equilibrium constant K_c for the ff rxn: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$,

	$H_2(g)$	+	$I_2(g)$	⇌	2HI(g)
Initial [ ], *M*:	0.000		0.000		0.500
Change in [ ], *M*:	+0.0525		+0.0525		-0.105
Equil [ ], *M*	0.0525		0.0525		0.395

$$K_c = \qquad = 56.6$$

Calculating Equilibrium Constant

The decomposition of HI at low temp. was studied by injecting 2.5 mol of HI into a 10.32 L vessel at 25^0c.what is $[H_2]$ at equilibrium for the rxn $2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$; $K_c = 1.26 \times 10^{-3}$?

- calculate M. Starting conc. of HI: 2.5 mol/10.32 L = 0.242 M

	$2\ HI(g)$	$H_2(g) + I_2(g)$	
Initial:	0.242 M	0	0
Change:	-2x	+x	+x
Equil:	0.242-2x	x	x

What we are asked for here is the equilibrium concentration of H_2 ...

... otherwise known as x. So, we need to solve this beast for x.

And yes, it's a *quadratic equation.* Doing a bit of rearranging:

Calculating Equilibrium Constants

$$x = 0.00802 \text{ or } -0.00925$$

Since we are using this to model a real, physical system, we reject the -ve root. The $[H_2]$ at equil. is 0.00802 M.

Calculating Equilibrium Constants

The atmospheric oxidation on nitric oxide, $2NO + O_2 \rightleftharpoons 2 NO_2$ was studied at 184^0c with initial pressures of 1.0 atm of NO and 1.0 atm of O_2. at equilibrium $Po_2 = 0.506$ atm. Calculate K_p.

This type of problem is typically tackled using the "three line" approach:

	$2 NO$	$+ O_2$	$\rightleftharpoons 2 NO_2$
Initial:			
Change:			
Equilibrium:			

If Keq is really small the rxn will not proceed to the right very far, meaning the equil concs will be nearly the same as the initial concs of your reactants. $0.20 - x$ is just about 0.20 is x is really dinky.

If the difference between Keq and initial concs is around 3 orders of magnitude or more, go for it. Otherwise, you have to use the quadratic.

Calculating Equilibrium Constants

In a study of halogen bond strengths, 0.50mol of I_2 was heated in a 2.5 L vessel, and the ff rxn occurred: $I_2(g) \rightleftharpoons 2I(g)$

(a) Calculate $[I_2]$ and [I] at equilibrium at 600 K: Kc = 2.94×10^{-10}

(b) Calculate $[I_2]$ and [I] at equilibrium at 2000 K: Kc = 0.209

Initial Concentration of I_2: 0.50 mol/2.5L = 0.20 M :

	$I_2(g)$	$\rightleftharpoons$	$2I(g)$
Initial:	0.20		0
Change:	-x		+2x
Equilibrium:	0.20-x		2x

more than 3 orders of mag b/n these #. The simplification will work here.

With an equilibrium constant that small, whatever x is, it's near dink, and 0.20 minus dink is 0.20 (like a million dollars minus a nickel is still a million dollars). 0.20 – x is the same as 0.20

$x = 3.83 \times 10^{-6}$ M

Calculating Equilibrium Constants

In a study of halogen bond strengths, 0.50mol of I_2 was heated in a 2.5 L vessel, and the ff rxn occurred: $I_2(g) \rightleftharpoons 2I(g)$

(a) Calculate $[I_2]$ and [I] at equilibrium at 600 K: Kc = 2.94×10^{-10}

(b) Calculate $[I_2]$ and [I] at equilibrium at 2000 K: Kc = 0.209

Initial Concentration of I_2: 0.50 mol/2.5L = 0.20 M

	$I_2(g)$	$\rightleftharpoons$	$2I(g)$
Initial:	0.20		0
Change:	-x		+2x
Equilibrium:	0.20-x		2x

These are too close to each other 0.20-x will not be trivially close to 0.20 here.

Looks like this one has to proceed through the quadratic ...

Applications of Equilibrium Constants

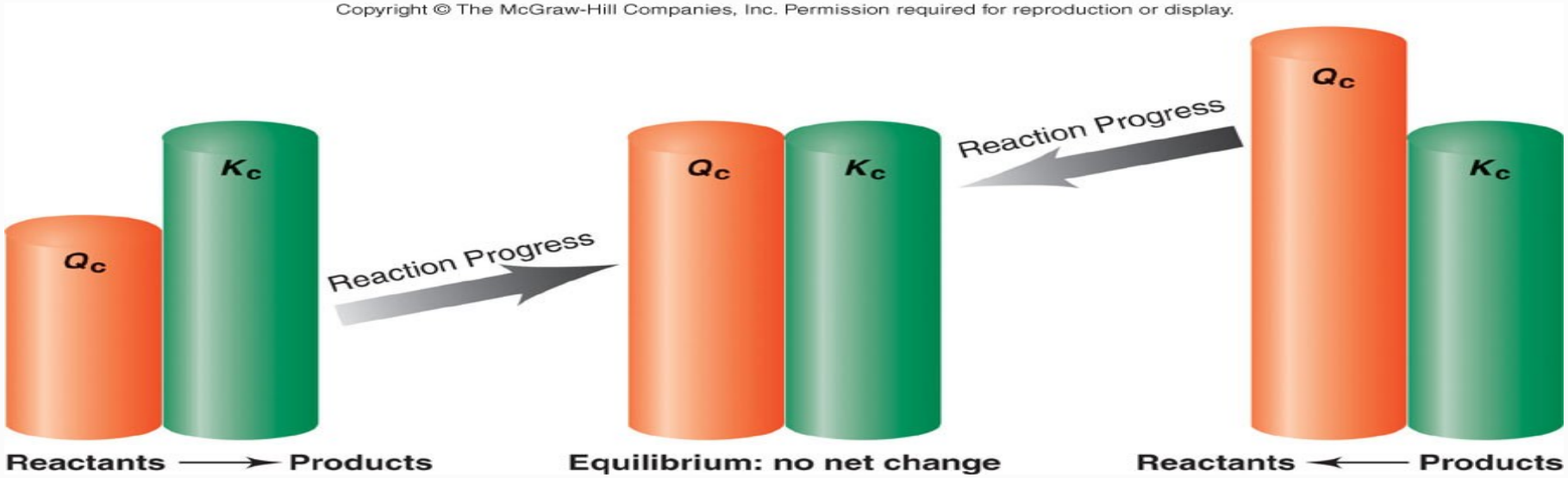
Predicting the Direction of Reaction

We define Q, the rxn quotient, for a rxn at conditions not at equil.

as

where [A], [B], [P], and [Q] are molarities at any time.

- $Q = K$ only at equilibrium.
- If Q > K then the reverse rxn must occur to reach equil. (go left)
- If $Q < K$ then the forward rxn must occur to reach equil. (go right)



If $Q < K_{eq}$, shift to right

If $Q > K_{eq}$, shift to left

Le Châtelier's Principle

- Le Châtelier's Principle: if you disturb an equilibrium, it will shift to undo the disturbance.
- Remember, in a system at equilibrium, come what may, the concs will always arrange themselves to multiply and divide in the Keq equation to give the same number (at constant temperature).
- Change in Reactant or Product Concentrations
- Adding a reactant or product shifts the equil. away from the increase.
- Removing a reactant or product shifts the equil. towards the decrease.
- To optimize the amount of product at equilibrium, we need to flood the rxn vessel with reactant and continuously remove product (Le Châtelier).
- We illustrate the concept with the industrial preparation of ammonia
- Consider the Haber process
- If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 (by Le Châtelier).

Le Châtelier's Principle

- That is, the system must consume the H_2 and produce products until a new equilibrium is established.
- Therefore, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.
- The unreacted nitrogen and hydrogen are recycled with the new N_2 and H_2 feed gas.
- The equilibrium amount of ammonia is optimized because the product NH_3 is continually removed and the reactants N_2 and H_2 are continually being added.

Effects of Volume and Pressure

- As volume is decreased pressure increases.
- Le Châtelier's Principle: if pressure is increased the system will shift to counteract the increase.

Consider the production of NH_3

As the pressure increases, the amount of ammonia present at equilibrium increases.

Le Châtelier's Principle

As the T^0 decreases, the amount of ammonia at equilibrium increases.

Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance**.**

In a study of the chemistry of glass etching, an inorganic chemist examines the rxn between sand (SiO_2) and HF at a temp above the bpt of H_2O: $SiO_2(s) + 4HF(g) \rightleftharpoons SiF_4(g) + 2H_2O(g)$

Predict the effect of [SiF_4] when (a) $H_2O(g)$ is removed; (b) some liquid H_2O is added ; (c) HF is removed ; (d) some sand is removed

Effects of Volume and Pressure

The system shifts to remove gases and decrease pressure.

An increase in pressure favors the direction that has fewer moles of gas.

In a reaction with the same number of product and reactant moles of gas, pressure has no effect.

Consider

An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4.

The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.

The system moves to reduce the number moles of gas (i.e. the forward reaction is favored).

A new equilibrium is established in which the mixture is lighter because colorless N_2O_4 is favored.

Reactions not affected by pressure changes

Consider the ff rxns: $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$;

$H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$;

- Rxns have same # of gas molecules in reactants and products.
- Reducing or increasing the volume will cause equal effect on both sides – no net rxn will occur.
- Equilibrium is not affected by change in pressure.

Effect of Temperature Changes

The equilibrium constant is temperature dependent.

For an endothermic rxn, ∴ $H > 0$ & heat can be considered as a reactant.

For an exothermic rxn, ∴ H < 0 & heat can be considered as a product.

Adding heat (i.e. heating the vessel) favors away from the increase:

- if ∴ $H > 0$, adding heat favors the forward reaction,
- if ∴ $H < 0$, adding heat favors the reverse reaction.

Removing heat (i.e. cooling the vessel), favors towards the decrease:

- if ∴ $H > 0$, cooling favors the reverse reaction,
- if ∴ $H < 0$, cooling favors the forward reaction.

- Consider

  for which $\Delta H > 0$. $Co(H_2O)_6^{2+}$ is pale pink and $CoCl_4^{2-}$ is blue.

Solubility Product Principle

- Another equilibrium situation is slightly soluble products
- K_{sp} is the solubility product constant
- K_{sp} can be found on a chart at a specific temperature
- Since the product is solid on the left side, only the products (ions) are involved in the K_{sp} expression

Solubility Product Principle

Solubility Product Constants

$AgBr$	5×10^{-13}	$CaSO_4$	3×10^{-5}	MnS	1×10^{-15}
Ag_2CO_3	1×10^{-11}	$CdCO_3$	5×10^{-12}	$NiCO_3$	1.4×10^{-7}
$AgC_2H_3O_2$	2×10^{-3}	$Cd(OH)_2$	2×10^{-14}	$Ni(OH)_2$	1×10^{-16}
$AgCl$	1.6×10^{-10}	CdS	1×10^{-26}	NiS	1×10^{-19}
Ag_2CrO_4	2×10^{-12}	$Co(OH)_2$	2×10^{-16}	$PbBr_2$	5×10^{-6}
AgI	1×10^{-16}	CoS	1×10^{-20}	$PbCO_3$	1×10^{-13}
Ag_3PO_4	1×10^{-15}	$Cr(OH)_3$	4×10^{-38}	$PbCl_2$	1.7×10^{-5}
Ag_2S	1×10^{-49}	$CuCO_3$	2×10^{-10}	$PbCrO_4$	1×10^{-16}
$Al(OH)_3$	5×10^{-33}	$Cu(OH)_2$	2×10^{-19}	PbF_2	4×10^{-8}
$BaCO_3$	2×10^{-9}	CuS	1×10^{-35}	PbI_2	1×10^{-8}
BaC_2O_4	1.5×10^{-8}	$Fe(OH)_2$	1×10^{-15}	$Pb(OH)_2$	4×10^{-15}
$BaCrO_4$	2×10^{-10}	$Fe(OH)_3$	5×10^{-38}	$Pb_3(PO_4)_2$	1×10^{-54}
BaF_2	2×10^{-6}	FeS	1×10^{-17}	PbS	1×10^{-27}
$BaSO_4$	1.4×10^{-9}	Hg_2Cl_2	1×10^{-18}	$PbSO_4$	1×10^{-8}
$CaCO_3$	5×10^{-9}	HgS	1×10^{-52}	$SrCO_3$	7×10^{-10}
CaC_2O_4	1.3×10^{-9}	$MgCO_3$	2×10^{-8}	$SrCrO_4$	4×10^{-5}
CaF_2	2×10^{-10}	MgC_2O_4	8.6×10^{-5}	$ZnCO_3$	2×10^{-10}
$Ca(OH)_2$	1.3×10^{-6}	$Mg(OH)_2$	1×10^{-11}	$Zn(OH)_2$	5×10^{-17}
$Ca_3(PO_4)_2$	1×10^{-33}	$Mn(OH)_2$	4×10^{-14}	ZnS	1×10^{-20}

Solubility Product Principle

- Example: Find the concentration of ions present in calcium fluoride (in water) and the molar solubility.

$CaF_2(s) \rightarrow Ca^{+2} + 2\ F^-$

$K_{sp} = [Ca^{+2}]\ [F^-]^2 = 2 \times 10^{-10}$

If $x = [Ca^{+2}]$, then $[F^-] = 2x$

$[x]\ [2x]^2 = 2 \times 10^{-10}$

$4x^3 = 2 \times 10^{-10}$

$x^3 = 5 \times 10^{-11}$

$x = 3.68 \times 10^{-4}$

$[Ca^{+2}] = x = 3.68 \times 10^{-4}$ $[F^-] = 2x = 7.37 \times 10^{-4}$

Solubility of $CaF_2 = 3.68 \times 10^{-4}$

CHAPTER EIGHT

INTRODUCTION TO ORGANIC CHEMISTRY

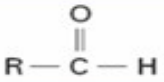
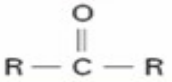
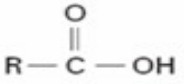
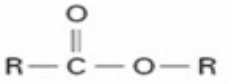
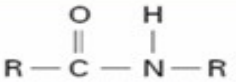
Hydrocarbons

- There are about 10 million substances that are organic compounds.
- The number of potential organic compounds has been estimated at 1060.
- The simplest organic compounds contain only the elements carbon and hydrogen, and are called hydrocarbons.
- There is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures.
- They differ in the types of carbon-carbon bonds present in their molecules.
- Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory.
- The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons.

Functional Group

- Specific arrangement of atoms in an organic compound that is capable of characteristic chemical reactions.
- Organic compounds can be classified according to their functional groups.

Organic Compounds Classified by Functional Group

Compound type	Compound structure	Functional group
Halocarbon	R—X (X = F, Cl, Br, or I)	Halogen
Alcohol	R—OH	Hydroxyl
Ether	R—O—R	Ether
Aldehyde		Carbonyl
Ketone		Carbonyl
Carboxylic acid		Carboxyl
Ester		Ester
Amine	R—NH_2	Amino
Amide		Amide

Alkanes

Is the most simplest organic compound that contain only C and H

Have the formula of C_nH_{2n+2}

They are common unreactive and found in many common substances:

- Natural gas
- Gasoline
- Plastic

Nomenclature:

- The suffix for the alkane family is –ane.
- **Prefix – root – suffix**

✓Prefix – where the substitutions are located

✓Root – how many carbons are in the molecules longest chain.

✓Suffix – family – type of functional group

No of carbons	Root
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pent-
6	Hex-
7	Hept-
8	Oct-
9	Non-
10	Dec-

Rules for naming alkanes

1. Find the longest chain of carbons, and use this number as parent name
2. Number the chain with the end nearest the first subsistent carbon #1.
3. Give the location of the alkyl subsistent by the number of the main-chain carbon that it is attached to.
4. Put the Constituents in alphabetical order (i.e. ethyl before methyl)

- Substitution Syntax:
  - Between numbers and words add a dash
  - Between each numbers add commas

Nomenclature.…contd.

Examples1:

- An alkane with 3 carbons is named as propane
- prop – for the 3 carbons
- ane – for the family alkane

Examples2:

- An alkane with 8 carbons and having methyl substituent is named as methyloctane.
- Methyl- prefix for substituent
- oct- for 8 carbons
- ane- for single bonded alkane family

Structural Formula

It is the condensed form to write the chemical structures of the compounds.

Chemical Formula:

- C_4H_{10}

Structural Formula:

- Condensed Structural Formula:

  $CH_3CH_2CH_2CH_3$

Line Structure:

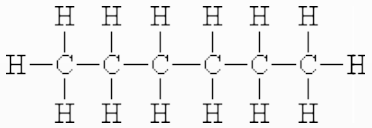
Isomers

Are compounds with:

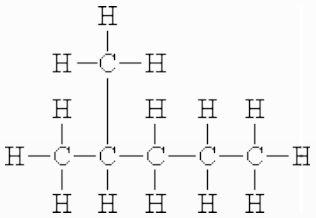
- Same molecular formula
- But different structure.
- Different properties for the molecule.
- The same chemical formula

The number of possible isomers increases rapidly as the length of the chain increases.

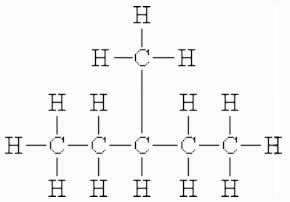
Example: C_6H_{14} have five different structural formulas.



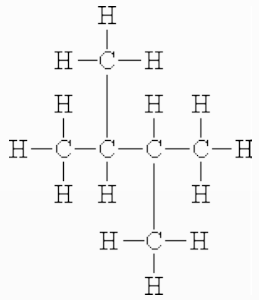
Hexane



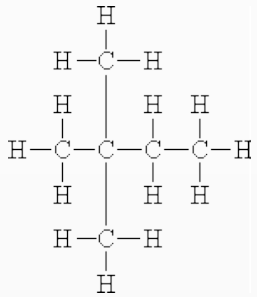
2-methyl pentane



3-methyl pentane



2,3-dimethyl butane



2,2-dimethyl butane

Cyclic Alkanes:

- The type of alkane that have the ring structure.
- They commonly form rings and have the general formula of C_nH_{2n} where n starts from 3 in case of a lkane.

Example: Cyclohexane (C_6H_{12})

Line Structure

Condensed Structural Formula

A hydrocarbon that contains at least one C=C bond and has general formula $C_nH_{2n.}$

Alkenes are considered unsaturated hydrocarbons because their carbon atoms are bonded to fewer than the maximum of four atoms each.

They differ from those of alkanes in two respects:

1. The main chain (root) must contain both C atoms of the double bond. The chain is numbered from the end closer to the C=C bonds.
2. The suffix for alkenes is –ene.

Cis –trans Isomerism

- The double bonded C atoms in alkenes are trigonal planar (≈ 120^0) and sp2 hybridization.
- The π bond of the C=C bond restricts rotation
- T his to another type of stereoisomerism also called cis-trans isomers.
- Cis- trans isomers have different orientations with in the similar structural feature.

Alkynes

- Hydrocarbons that contain at least one CC bond and have general formula C_nH_{2n-2}.

Because a carbon in a CC bond can bond to only one other atom, the geometry around each C atom is linear (180°): each C is sp hybridized.

They are named in the same way as alkenes, except that the suffix is -yne.

Because of their localized π electrons, CC and CC bonds are electron rich and act as functional groups. Due to this alkynes are more reactive than the corresponding alkanes and alkenes.

Alcohols and Ethers

‡ **Alcohols -** An alcohol is an organic compound with an — OH group.

‡ OH functional group in alcohols is called a **hydroxyl group**



Alcohol molecule

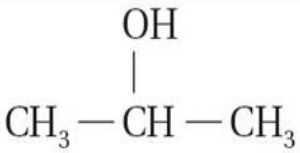
In order to name an alcohol, the position of the hydroxyl group is indicated by a number before the name. The hydrocarbon must be numbered so that the position of the OH group is the lowest possible number.

- When naming an alcohol, drop the -*e* ending of the parent hydrocarbon name and add the ending -*ol*.

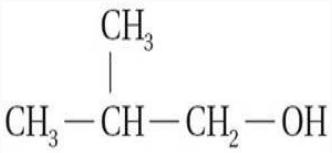
Examples:



Ethanol
(ethyl alcohol)



2-propanol
(isopropyl alcohol)



2-methyl-1-propanol
(isobutyl alcohol)

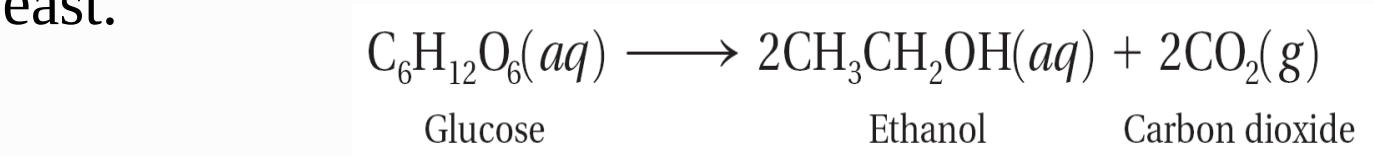
Properties of Alcohols

Physical properties

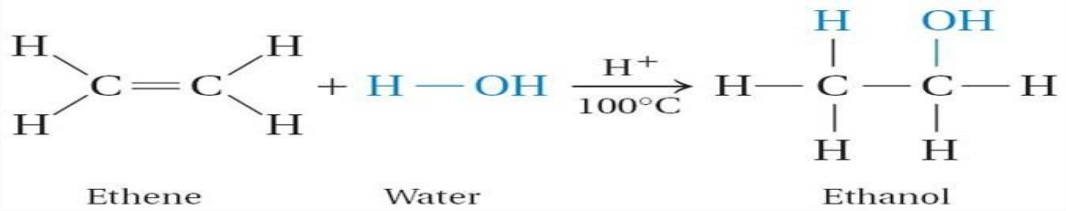
- Capable of hydrogen bonding because they contain the "OH" hydroxyl group.
- Have higher boiling points due to hydrogen bonding
- Alcohols of up to four carbons are soluble in water in all proportions.

Production of Alcohols

- Fermentation is the production of ethanol from sugars by the action of yeast.



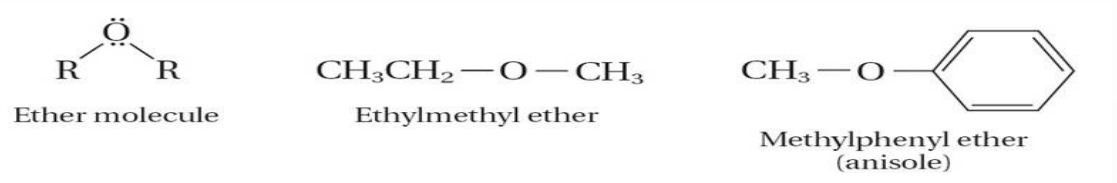
- Addition reactions of alkenes with water



Ethers

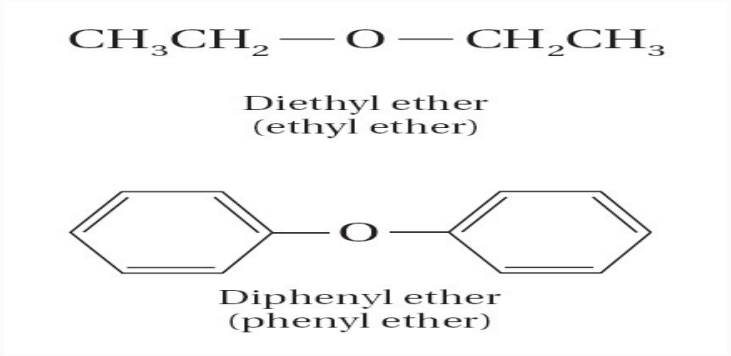
- A compound in which oxygen is bonded to two carbon groups
- Are typically volatile liquids.
- Have general structure of R—O—R'.
- The alkyl groups attached to the ether linkage are named in alphabetical order and are followed by the word *ether*.

Example



When the R group is the same on both sides, it is acceptable to drop the prefix *di*.

Example

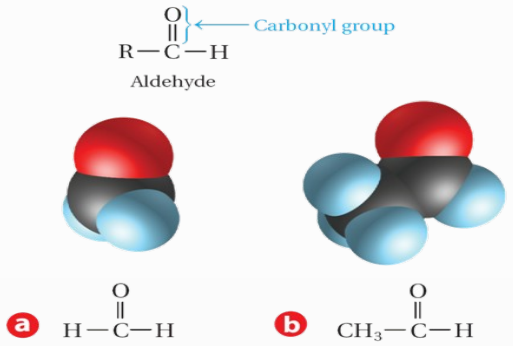


Ethers… contd.

- Ethers have lower boiling points than alcohols of comparable mass.
- Ethers are less soluble than alcohols, but more soluble than hydrocarbons and halocarbons (the O in the ether helps create some polarity).

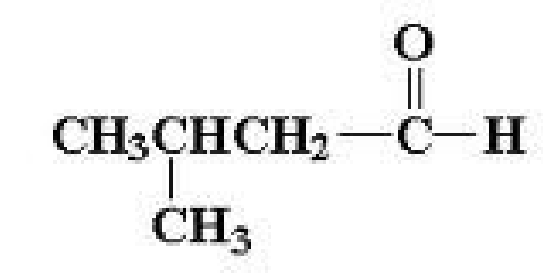
Carbonyl Compounds

- Is a functional group with the general structure C═O.
- Oxygen can be bonded to a single carbon atom by a double covalent bond.
- **Aldehyde** is an organic compound in which the carbon of the carbonyl group is always joined to at least one hydrogen**.**
- Example



Naming Aldehydes

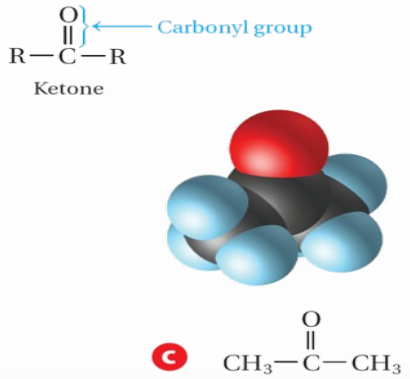
- Aldehydes are named by replacing the "*e*" at the end of the name of the hydrocarbon and adding "*al*".
- The carbon chain must be numbered so that the aldehyde functional group is at the lowest number.
- A number does not need to be given to indicate the position of the aldehyde functional group.
- Example



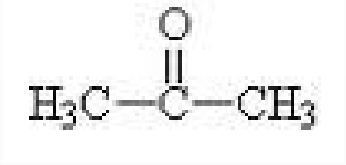
3-methylbutanal

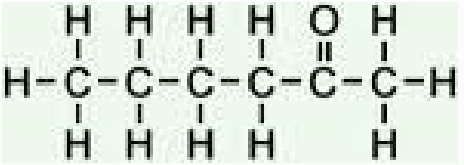
Ketones

- Carbon of the carbonyl group is joined to two other carbons.



- Named by changing the ending of the longest continuous carbon chain that contains the carbonyl group from "***e***" **to** "***one.***"



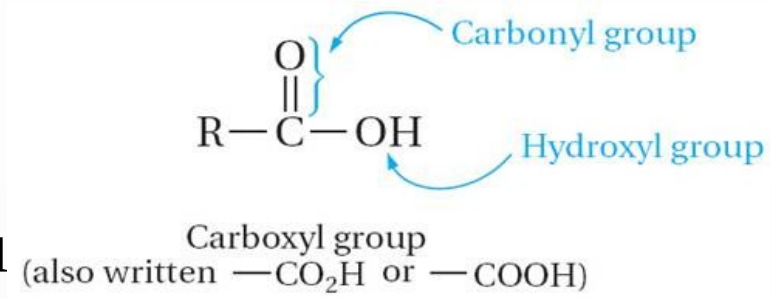


Uses of Aldehydes and Ketones

- They are isolated from plants and animals and have fragrant penetrating odors.
- Almonds contain benzaldehyde, vanillin, and cinnimon all have flavors due to aldehydes and ketones.
- 2-propanone is an excellent solvent used in nail polish remover.
- The simplest aldehyde methanal is used for preserving biological specimens and is in embalming fluid.

Carboxylic Acids

- ✓ Are called organic acids.
- ✓ They contain a carboxyl group.
- ✓ consists of a carbonyl group attached to a hydroxyl group



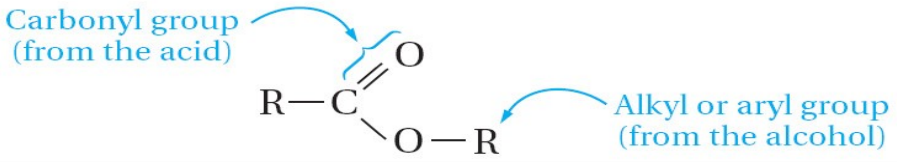
- A carboxyl grou e end of a hydrocarbon chain.
- Named by replacing the "*e*" from the end of the name of the hydrocarbon with "*oic*" followed by the word acid.

Properties of Carboxylic acids

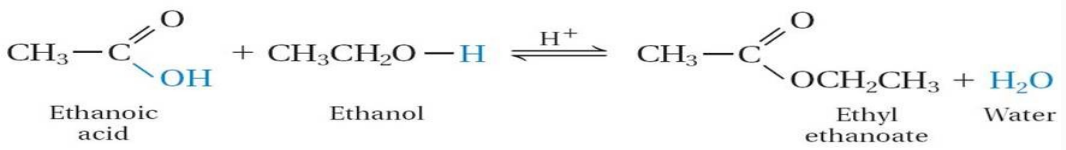
- Low mass CA are volatile and colorless with sharp, unpleasant odors.
- They are also soluble in water.
- That with high mass are waxy, odorless solids with low melting point.
- Have higher intermolecular force than the hydrogen bonding of water in turn leads to high boiling point.

Esters

- OH of the carboxyl group has been replaced by an —OR from an alcohol

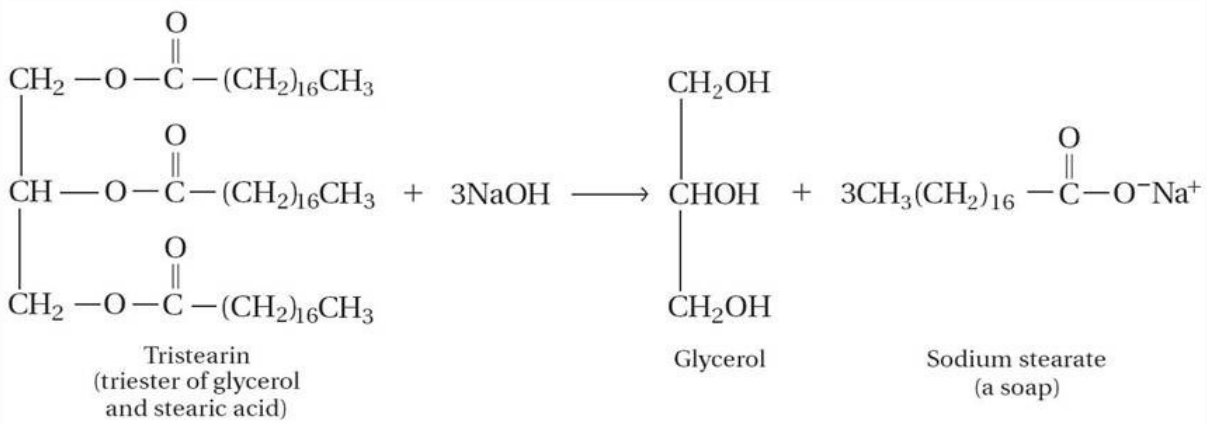


- Named by naming the alkyl group from the alcohol, followed by the name of the original organic acid, but the "*ic acid*" is replaced by "*ate*".
- Etherification: the process of adding carboxylic acid and alcohols to produce water and ester
- Example:



Ester …contd.

- **Saponification reactions -** Soap is prepared by the hydrolysis of triglycerides(animal fat) with a basic solution like NaOH .



THANK YOU