Grade 11 chemistry

Unit 1

Atomic Structure and the Periodic Table

Grade 11 chemistry
Unit 1 & Unit 2 full pdf

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Historical development of the atomic nature of substances

- The concept of an atom began in ancient Greek
- The idea of an atoms was believed to have originated with the Greek philosophers Leucippus and his student Democritus

Democritus

- proposed the first atomic theory
- atom is indivisible or uncuttble
- believed in particle theory that is discontinuous theory

Aristotle and Plato

- was the opponent of Democritus
- believed in particle theory that is continuous theory

Introduction

- The philosophers of ancient Greece wondered about the composition of matters: is matter continuously divisible into ever smaller and smaller pieces, or is there an ultimate limit?
- Although most philosophers, including Plato and Aristotle, believed that matter is continuous, Democritus disagreed.
- The Greek philosopher Democritus (460–370 BC) suggested that if you divided matter into smaller and smaller pieces, you would eventually end up with tiny, indestructible particles called atomos, or "atoms", meaning "indivisible".

- His ideas were based on philosophical speculation rather than experimental evidence.
- The ideas of Democritus were not widely accepted until 1808.
- After nearly 2000 years, John Dalton, developed an atomic theory that had gained broad acceptance.

Dalton's atomic theory and modern atomic theory

postulates of Dalton's atomic theory

- The laws that are the basis for Dalton's atomic theory are the law of conservation of mass and the law of definite proportions.

The Law of Conservation of Mass

- Mass is neither created nor destroyed in chemical reactions.
- In other words, the mass of any one element at the beginning of a reaction will equal the mass of that element at the end of the reaction.
- If we account for all reactants and products in a chemical reaction, the total mass will be the same at any point in time in any closed system.

The Law of Definite Proportions

- The law of definite proportions states that a given chemical compound always contains the same elements in the exact same proportions by mass.

Law of Multiple Proportions

- States that if two elements combine to form more than one compound, the ratio of the mass of the second element is a small, whole number of a fixed amount of the first element.

Example 1.1

1. What mass of hydrogen and oxygen can be obtained from

   a. 18.0 g of water

   b. 1.00 g of water

Solution

2. The following data were collected for several compounds of nitrogen and oxygen:

	Compound A	Compound B	Compound C
Mass of nitrogen that combines with 1 g of oxygen	1.750 g	0.8750 g	0.4375 g

Show how these data illustrate the law of multiple proportions.

Postulates of Dalton's atomic theory

- Elements are made of small particles called atoms.
- Atoms are indivisible
- Atoms can neither be created nor destroyed.
- All atoms of the same element are identical and have the same mass and size.
- Atoms of different elements have different masses and size.
- Atoms combine in small whole numbers to form compounds

Drawbacks of Dalton's Atomic Theory

- **The indivisibility of an atom** was proved wrong: an atom can be further subdivided into protons, neutrons, and electrons.
- **According to Dalton, the atoms of the same element are similar in all respects.** However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass numbers 35 and 37.

- **Atoms of different elements differ in mass.** This has been proven wrong in certain cases: argon and calcium atoms each have an atomic mass of 40 amu. These atoms are known as **isobars**.
- **According to Dalton, atoms of different elements combine in simple whole-number ratios to form compounds.** This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$) and protein molecules

Postulates of the modern atomic theory

- All matter is made up of tiny, indivisible particles called atoms
- Atoms cannot be created or destroyed during ordinary chemical reactions.
- All atoms of the same element have the same atomic number but may vary in mass number due to the presence of different isotopes.
- Atoms of different elements are different.
- Atoms combine in small whole numbers to form compounds.

Early experiments to characterize the atom

Discovery of electron

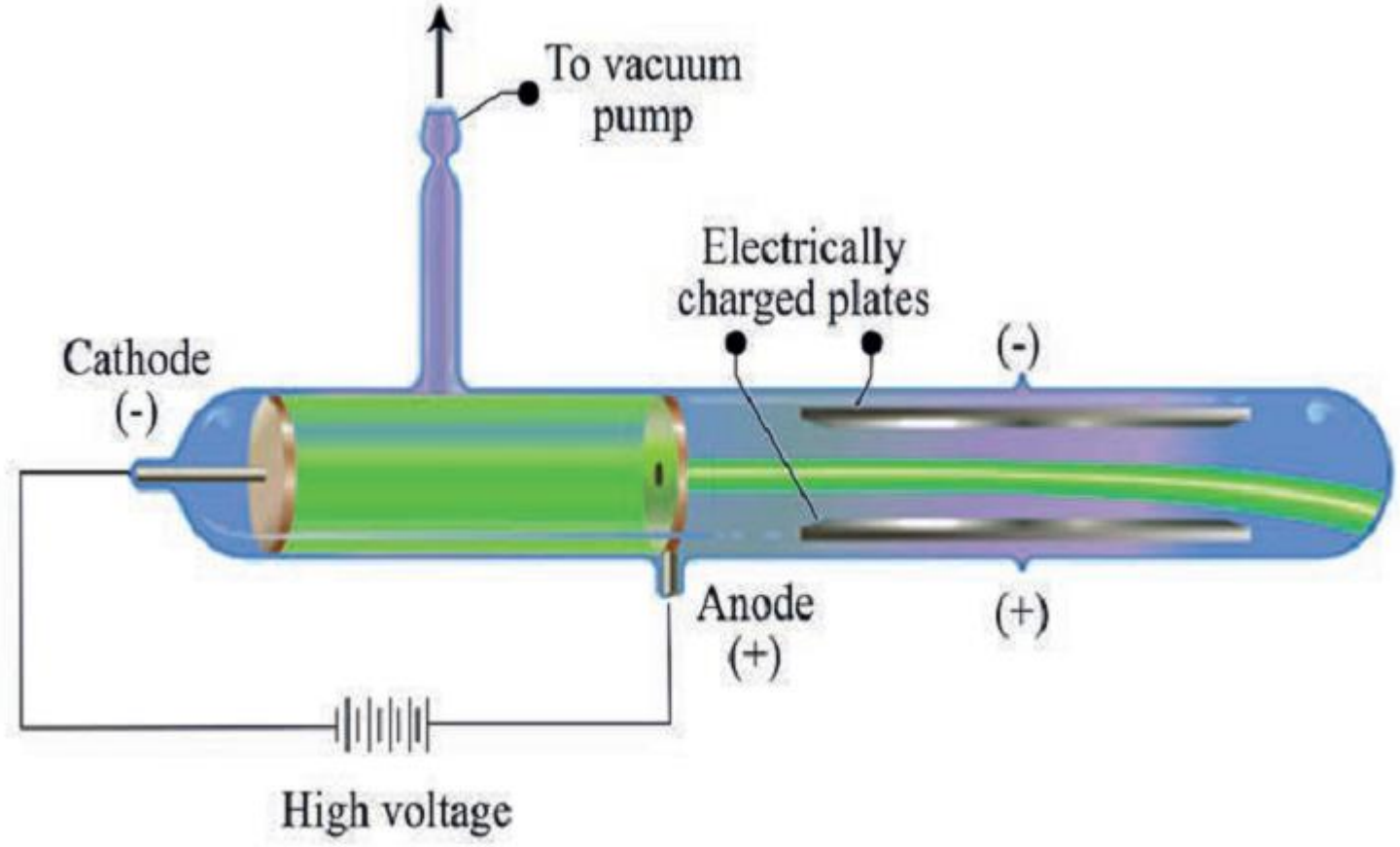


Figure 1.1: Formation of cathode rays

The Crooke's Discharge Tube or Cathode Ray Tube

- In 1855, the German inventor Heinrich Geissler developed the mercury pump and produced the first good vacuum tubes.
- These tubes, as modified by Sir William Crookes, became the first to produce cathode rays, leading eventually to the discovery of the electron.

- Sir William Crookes was the first scientist who designed the discharge tube which was called the Crooke's Discharge Tube or Cathode Ray Tube.
- The discharge tube consists of a glass tube from which most of the air has been evacuated having two metal plates sealed at both ends. These metal plates are called electrodes.
- These electrodes are connected to positive and negative terminals of a battery.
- The electrode connected to the positive terminal is known as anode and the electrode connected to the negative terminal is known as cathode.

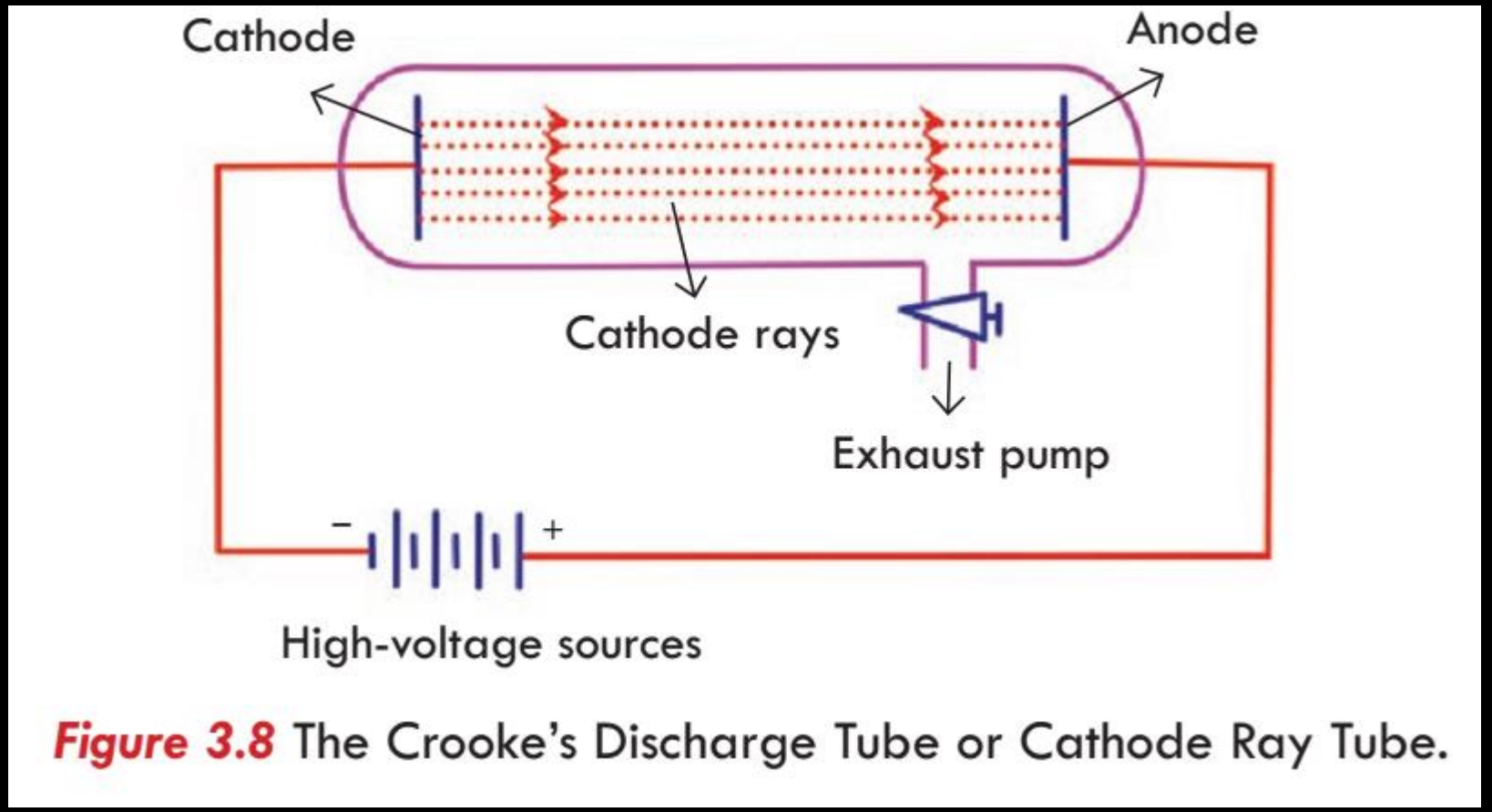
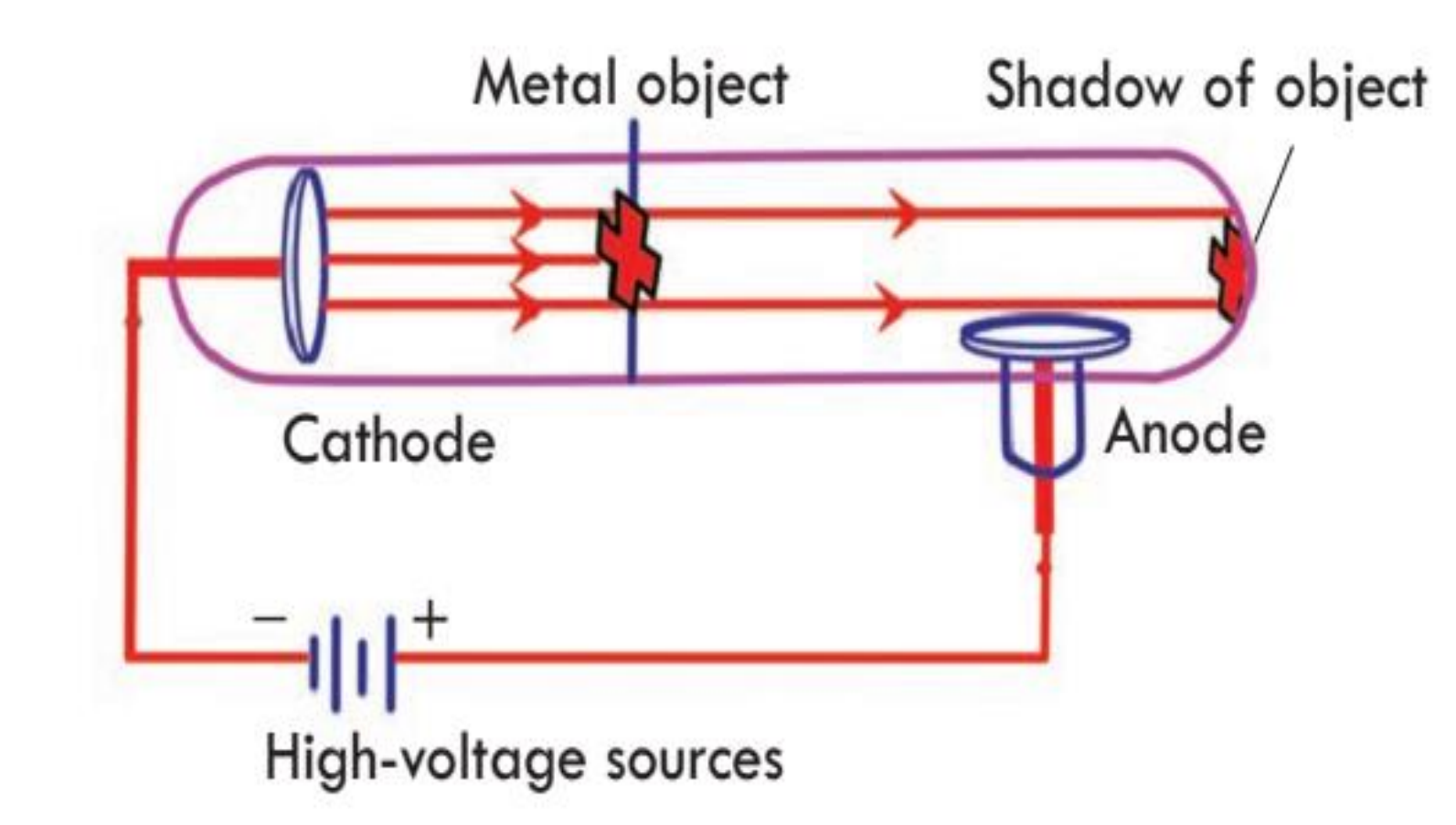


Figure 3.8 The Crooke's Discharge Tube or Cathode Ray Tube.

- When both electrodes are connected to high voltage, current starts flowing.
- a greenish glow was observed at anode.
- The rays are emitted from the direction of the cathode, and are called Cathode rays.

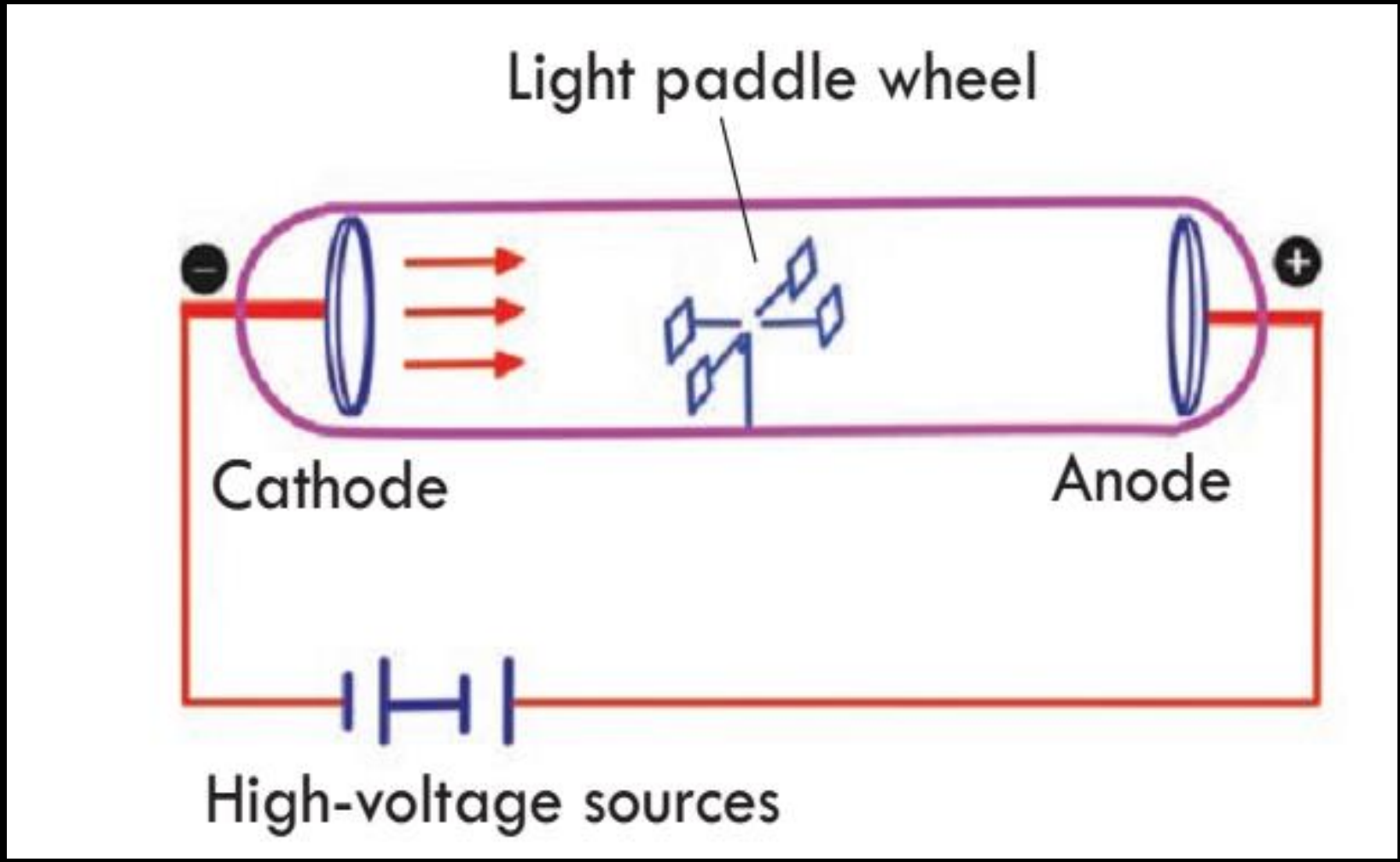
1.Thomson’s Experiment on the Path of Cathode Rays

- J. J. Thomson conducted some experiments with a discharge tube for studying the properties of cathode rays.
- The first experiment he has done is studying how cathode rays travel in the discharge tube by placing a small object between the cathode and the anode.
- The formation of a shadow of the object on the opposite side of the cathode revealed that the cathode rays travel in straight lines.


Metal object
Shadow of object
Cathode
Anode
−
+
High-voltage sources

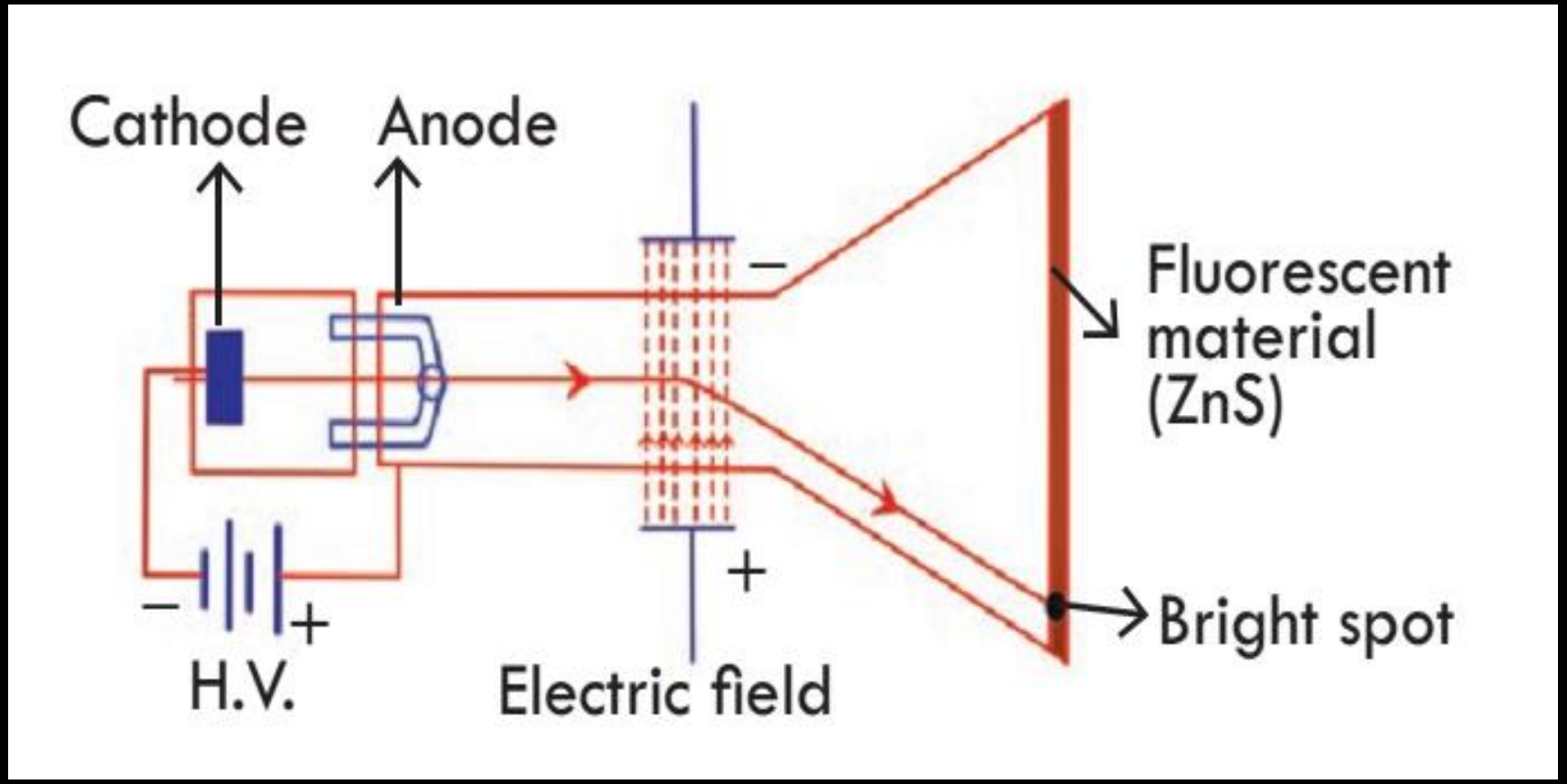
2.Thomson’s Experiment on the Particle Nature of the Cathode Rays

- J. J. Thomson’s second experiment was performed by placing a light paddle wheel between cathode and anode to study the particulate nature of the cathode rays .
- If they do so, then they have a particle nature. He observed the rotation of the light paddle wheel which revealed that the cathode rays are small particles having mass and kinetic energy.


Light paddle wheel
Cathode
Anode
High-voltage sources

Thomson's Experiment on the Charge of the Cathode Ray

- J. J. Thomson performed the third experiment to investigate the charge of the cathode ray by passing cathode rays through electric and magnetic fields.
- Upon passing through an electric field, the cathode rays bent towards the positive plate.
- This proved that cathode rays are negatively charged particles.
- Thomson concluded that the particles had a net negative charge; these particles are now called electrons.


Cathode
Anode
−
Fluorescent material (ZnS)
Bright spot
+
−
+
H.V.
Electric field

- By measuring the amount of deflection of a cathode ray beam in electric and magnetic fields of known strengths, Thomson was able to calculate the ratio of the mass of an electron, m_e, to its charge, e.
- The number he came up with is – $5.686 \times 10^{-12} kgC^{-1}$(kilograms per coulomb).
- However, he could not obtain either the mass or the charge separately.

- In 1909, Robert A. Millikan, an American physicist, measured the charge of the electron by measuring the effect of an electrical field on the rate at which charged oil drops fell under the influence of gravity.
- Based on careful experiments, Millikan established the charge on an electron as e = -1.602×10^{-19}C.
- He used this value and Thomson's mass/charge ratio to calculate an electron's mass to be 9.109×10^{-31}kg.

$$m_e = \frac{m_e}{e} \times e = -5.686 \times 10^{-12}\ \text{kg C}^{-1} \times -1.602 \times 10^{-19}\ \text{C}$$

$$= 9.109 \times 10^{-31}\ \text{kg}$$

Radioactivity and Discovery of Nucleus

Radioactivity

- Radioactivity or radioactive decay is the spontaneous emission of particles and/or radiation from the unstable nuclei of certain atoms such as uranium, radium, etc.
- Does radioactivity support Dalton's idea of atoms?
- Shortly after the discovery of radioactivity, three types of rays were identified in the emissions from radioactive substances.
- Two are deflected by oppositely charged metal plates .

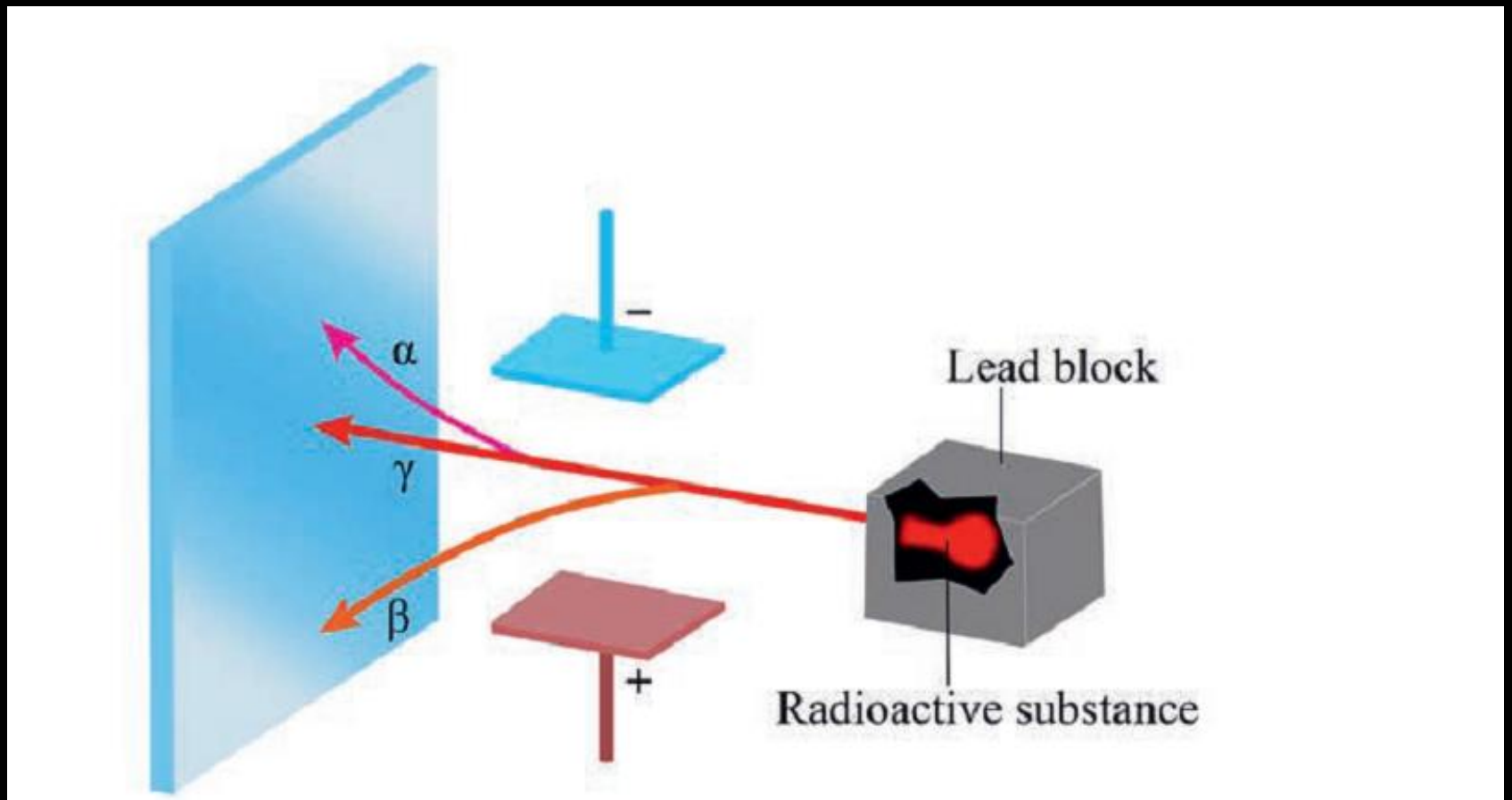


Figure 1.3: Three types of ray emitted by radioactive elements

Alpha(α)rays

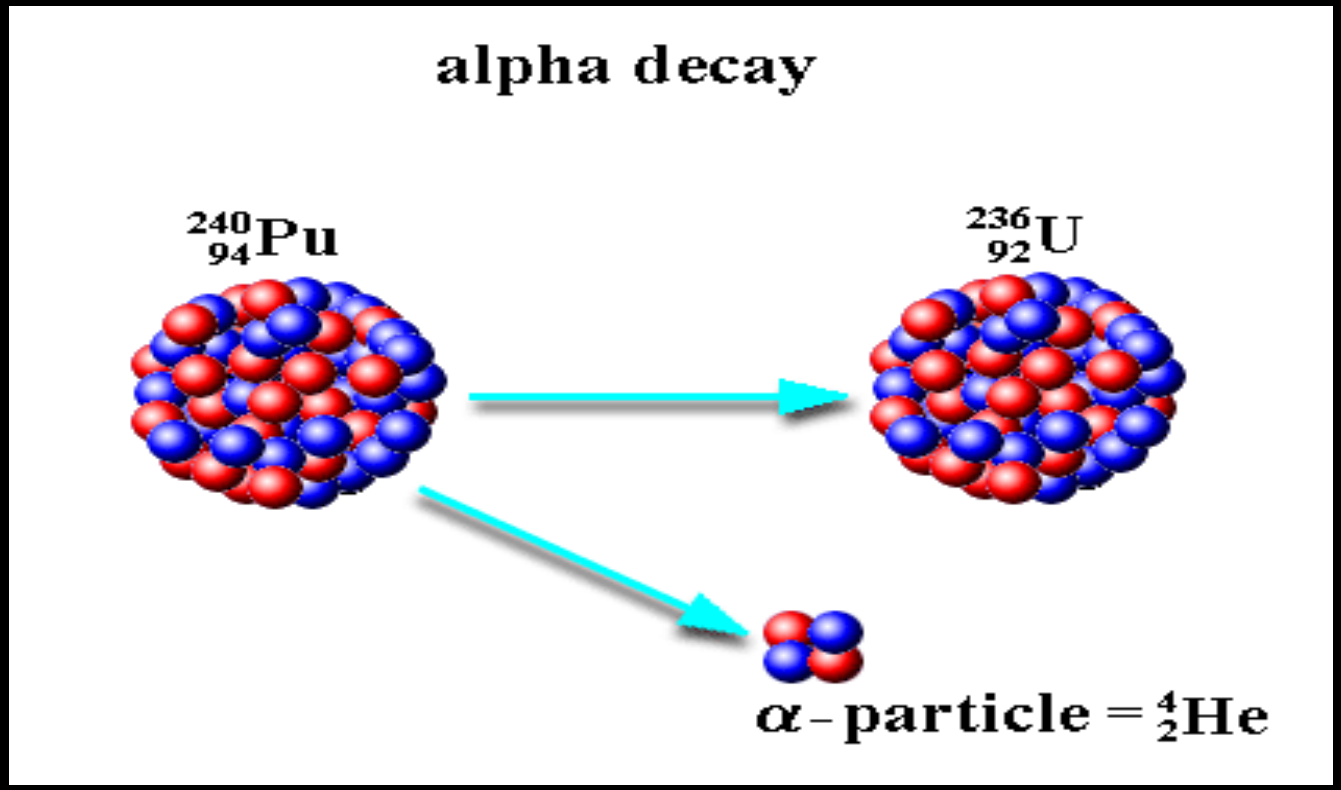
- Alpha(α)rays consist of positively charged particles
- They have a mass of about four times that of a hydrogen atom and a charge twice the magnitude of an electron; they are identical to helium nuclei.

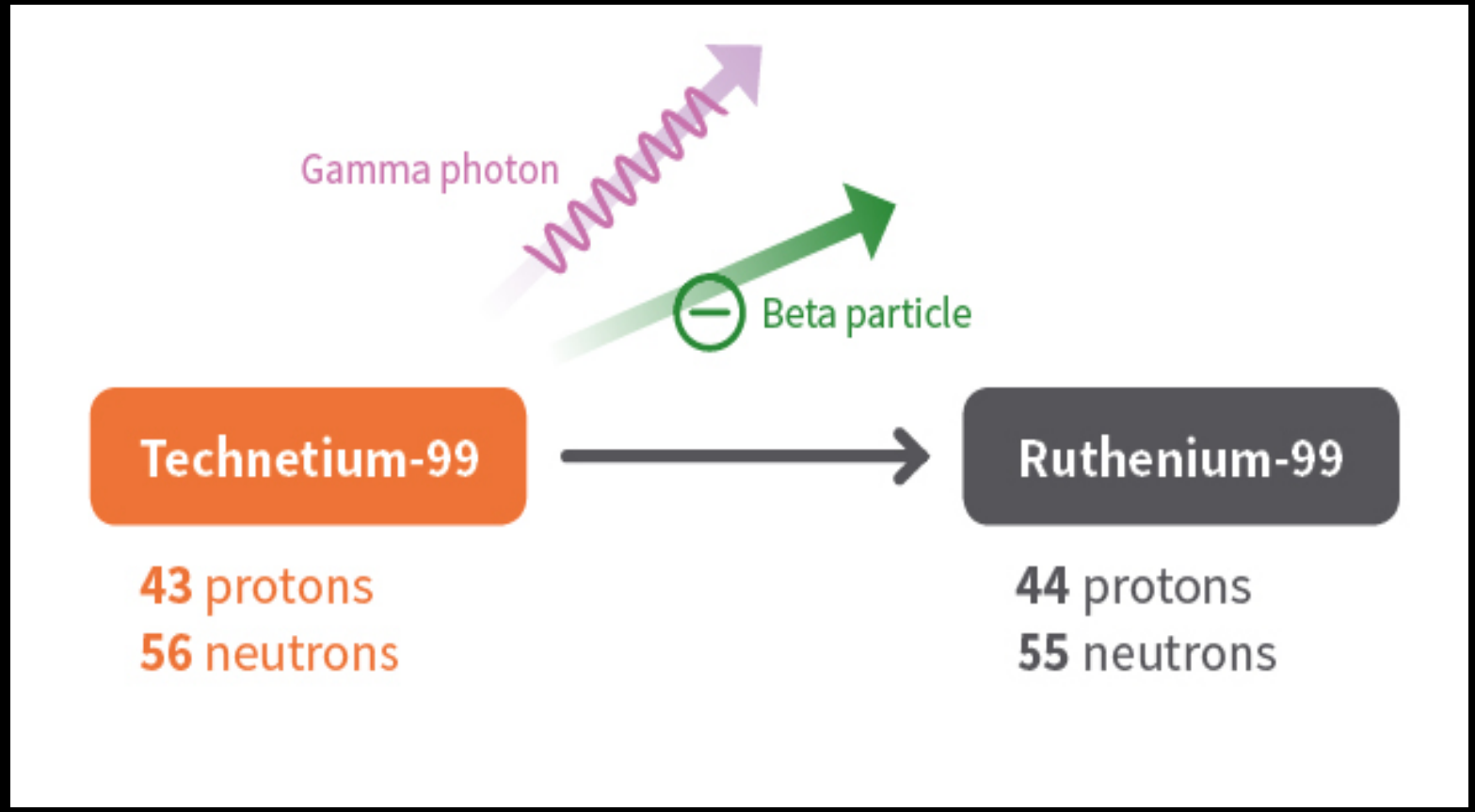
Beta (β) rays

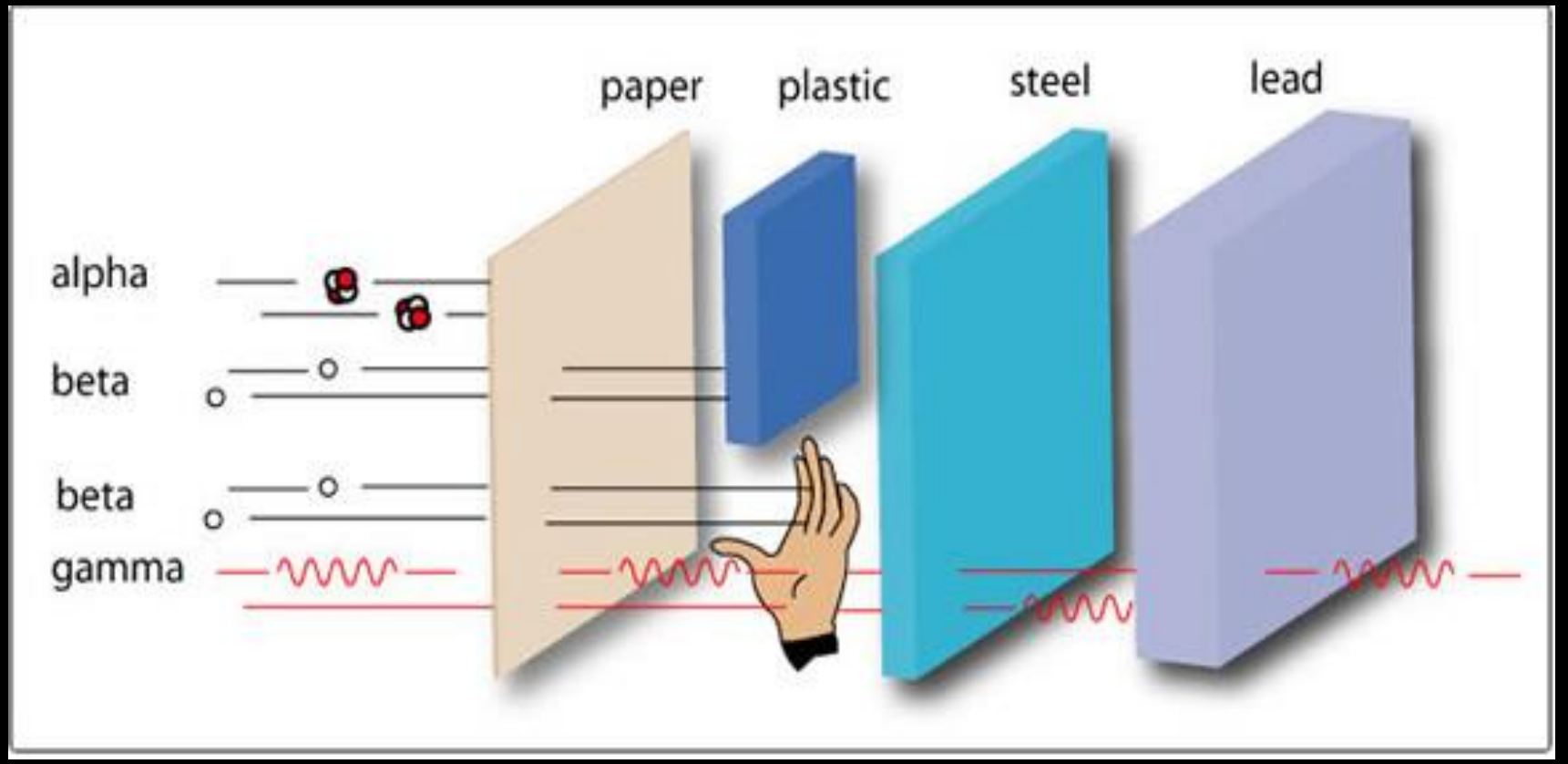
- Beta (β) rays, or β particles, are electrons coming from inside the nucleus and are deflected by the negatively charged plate.

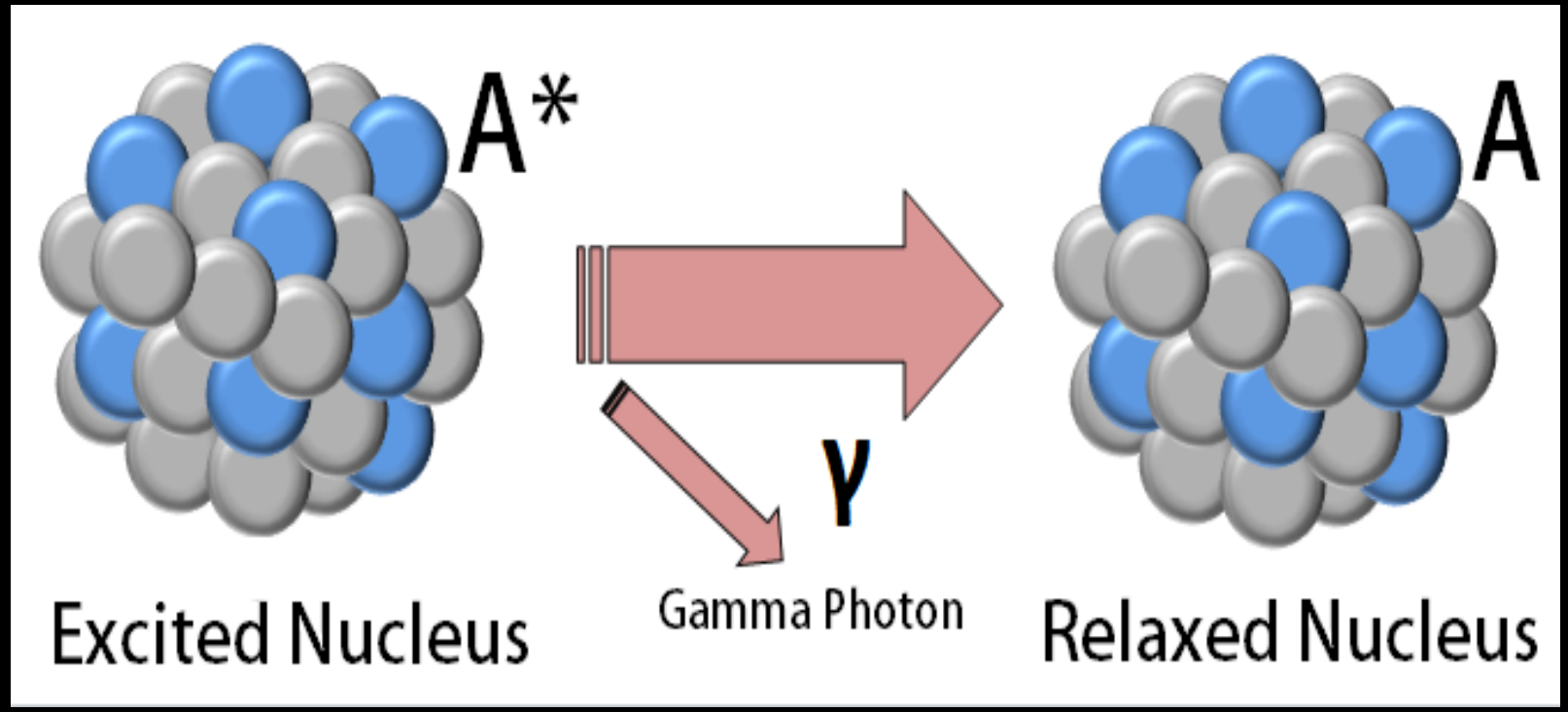
gamma(γ) rays.

- The third type of radioactive radiation consists of high-energy rays called gamma(γ) rays.
- They have no charge and are not affected by an external electric or magnetic field.


alpha decay
$^{240}_{94}$Pu
$^{236}_{92}$U
α – particle = $^{4}_{2}$He


Gamma photon
Beta particle
Technetium-99
Ruthenium-99
43 protons
56 neutrons
44 protons
55 neutrons


paper
plastic
steel
lead
alpha
beta
beta
gamma


A*
γ
A
Excited Nucleus
Gamma Photon
Relaxed Nucleus

The Discovery of the Nucleus

- Thomson proposed a “plum-pudding” model for the atom in which the electrons and protons were randomly distributed in a positively charged cloud like plums in a pudding.

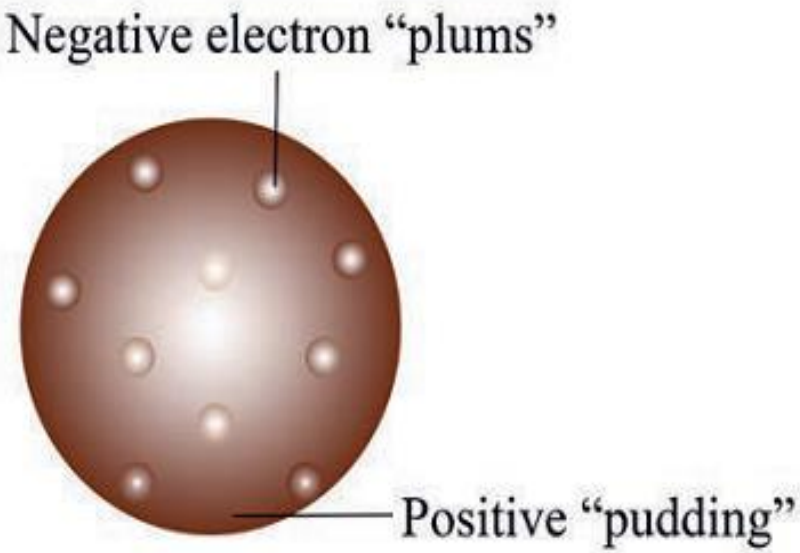


Figure 1.4: Thomson’s “plum-pudding” model of an atom

- In 1911, Ernest Rutherford worked with Thomson to test this model.
- In Rutherford's experiment, positively charged particles were aimed at a thin sheet of gold foil .
- If the Thomson model were correct, the particles would travel in straight paths through the gold foil.
- Rutherford was greatly surprised to find that some of the particles were deflected as they passed through the gold foil, and a few particles were deflected so much that they went back in the opposite direction.

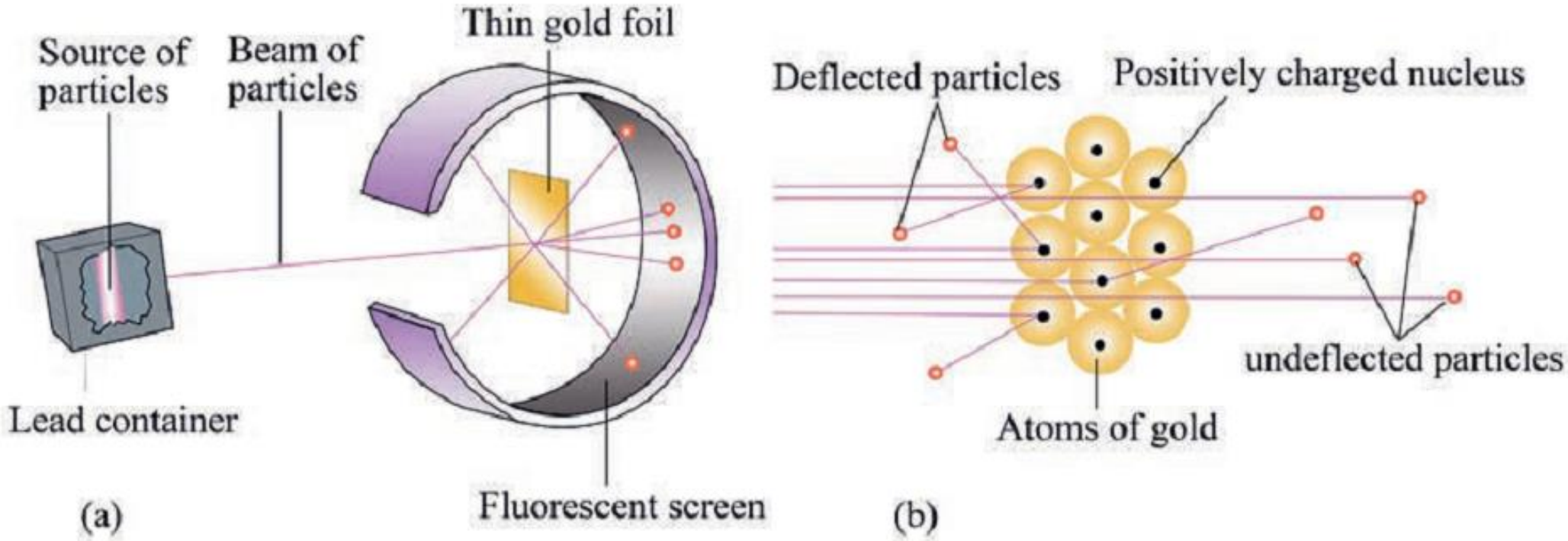


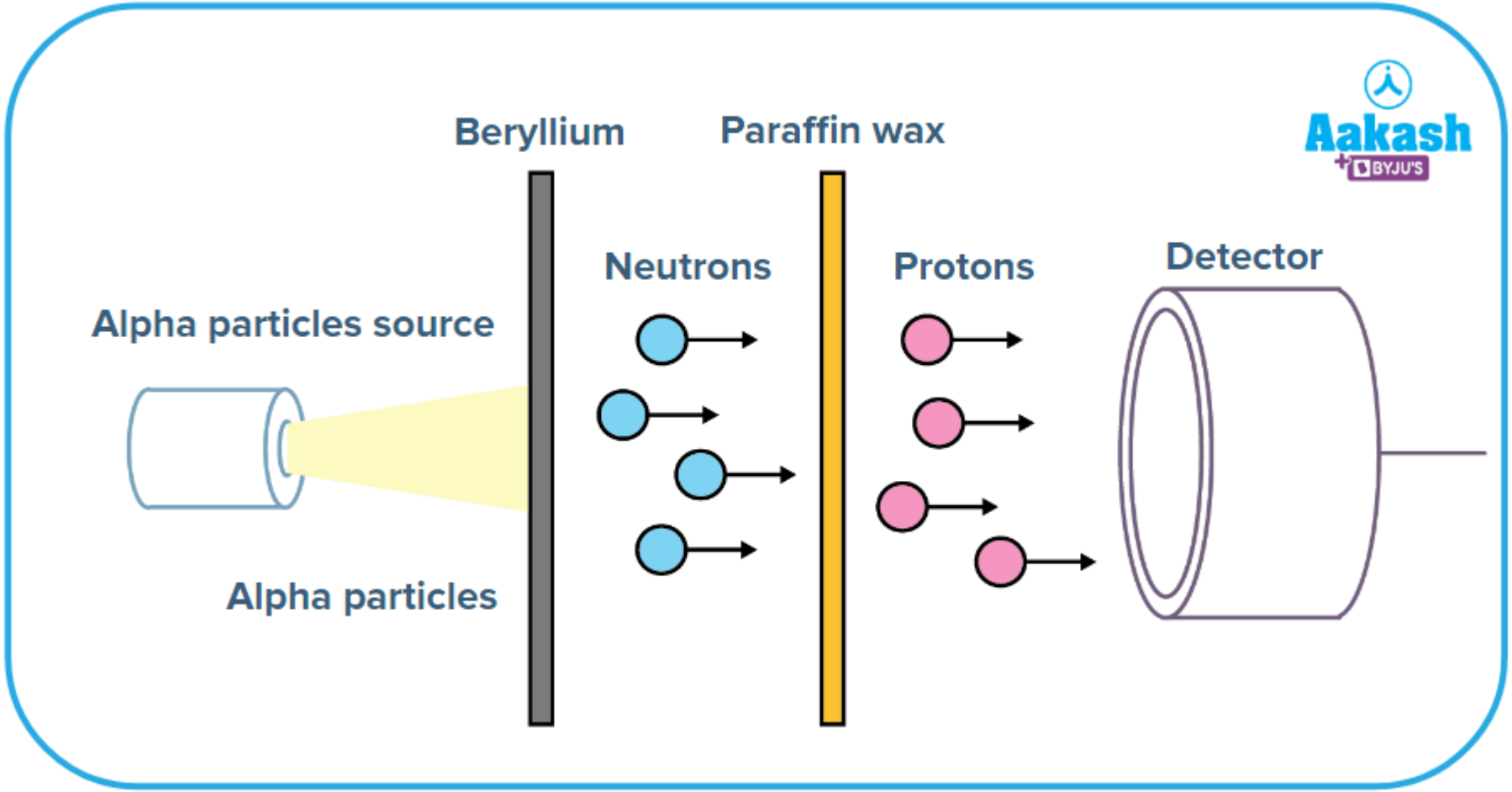
Figure 1.5: (a) α-particles aimed at a piece of gold foil, (b) Magnified view of α-particles passing through and being deflected by nuclei

Rutherford's experiments discovered the following aspects of the nucleus:

- **The nucleus of an atom is positively charged.**
- **Most of the mass of an atom is concentrated in the nucleus.**
- **There are large spaces within an atom.**

Discovery of neutron

- The neutron was also discovered by alpha-particle scattering experiments.
- When beryllium metal is irradiated with alpha rays, a strongly penetrating radiation is obtained from the metal.
- In 1932 the British physicist James Chadwick (1891–1974) showed that this penetrating radiation consists of neutral particles, called neutrons.
- The neutron is a nuclear particle having a mass almost identical to that of the proton but with no electric charge.
- The mass of a neutron, $m_n = 1.67493 \times 10^{-27}$ kg, which is about 1840 times the mass of an electron.



Experimentation of Neutron Discovery

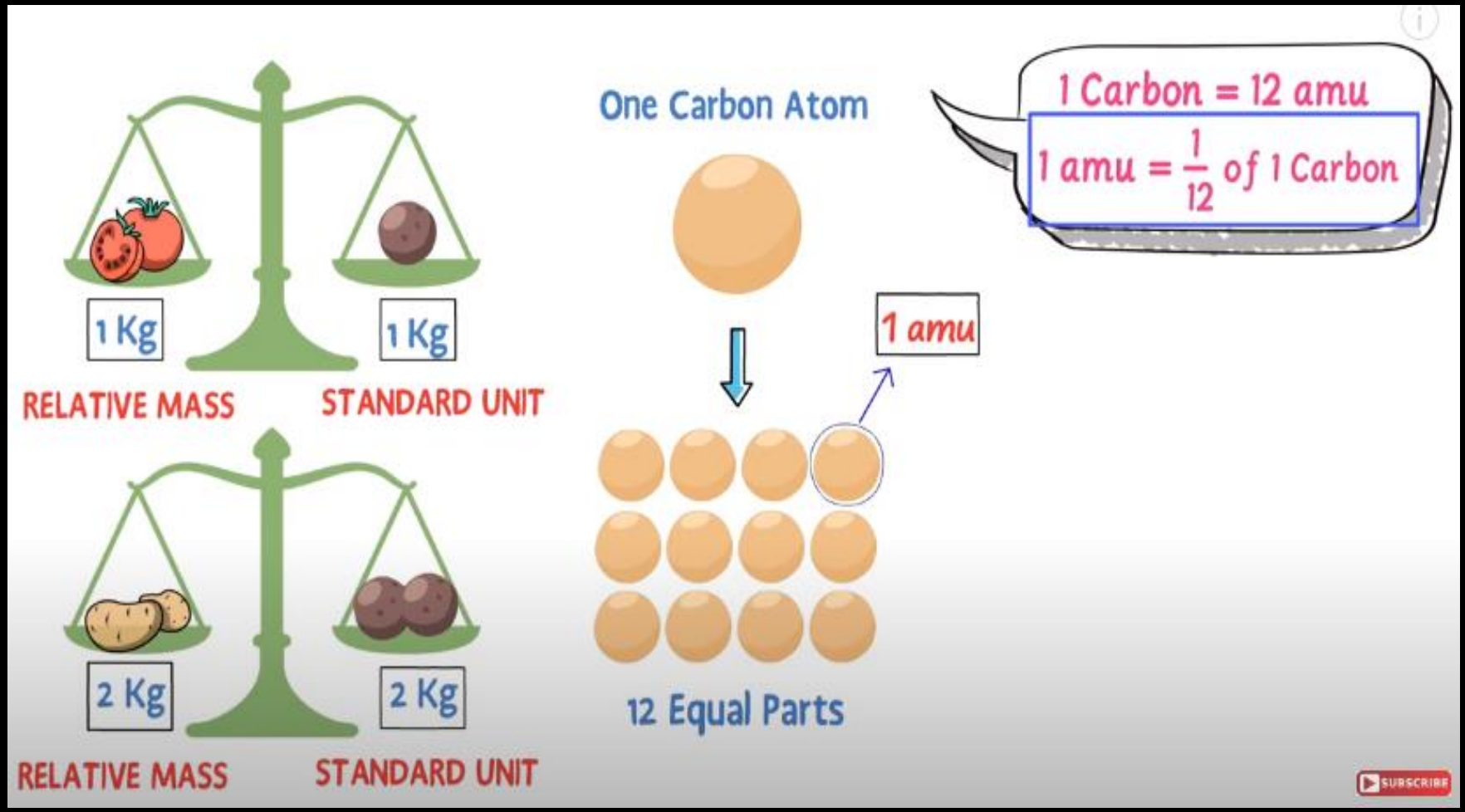
Make-up of the nucleus

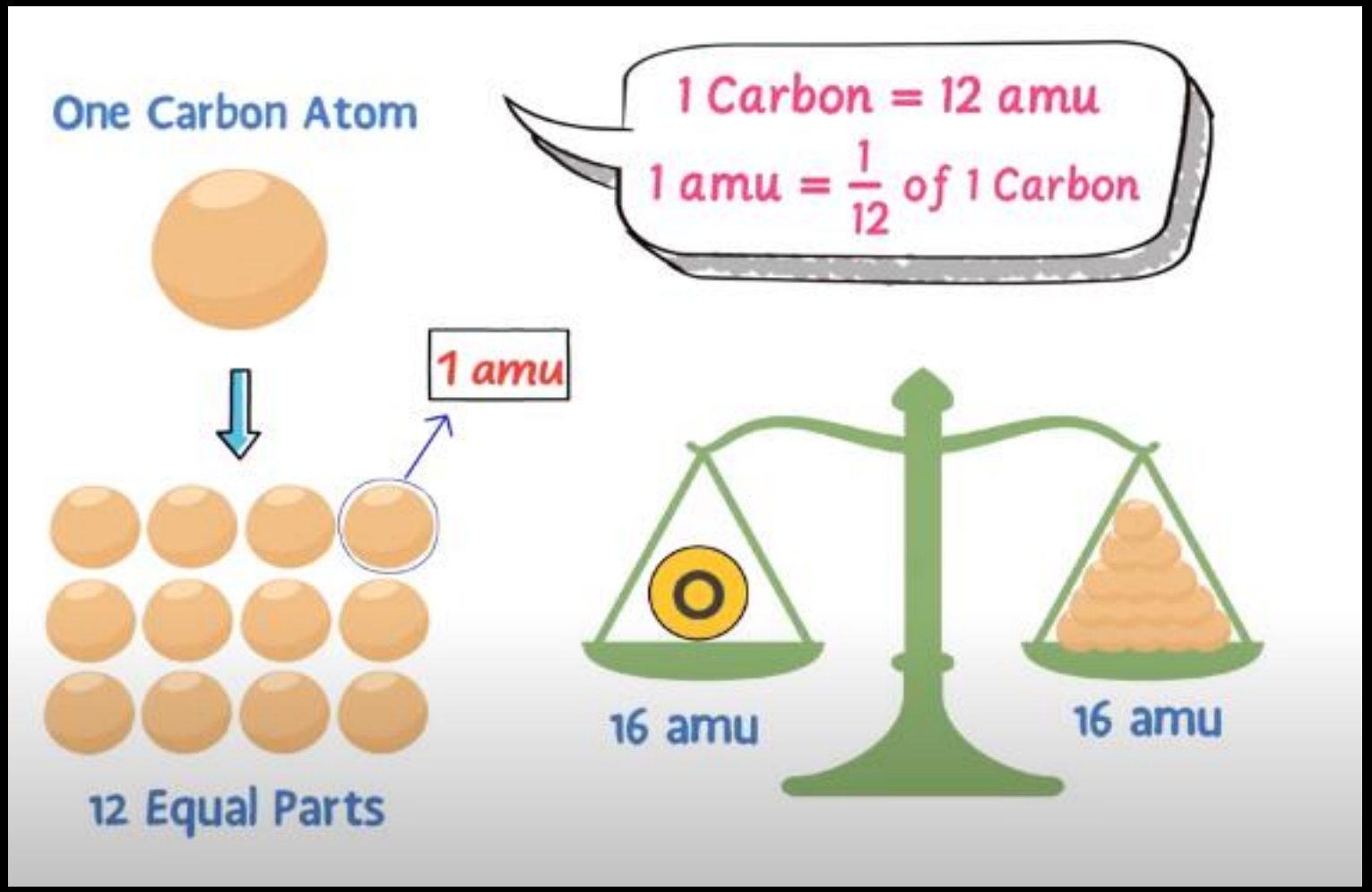
Sub-atomic particles

- A proton is a nuclear particle having a positive charge equal in magnitude to that of the electron.
- A proton has a mass of $m_p = 1.67262 \times 10^{-27}$kg, which is about 1840 times the mass of electrons.
- The protons in a nucleus give the nucleus its positive charge.

Table 1.1: Properties of subatomic particles

Particle	Actual mass (kg)	Relative mass (amu)	Actual charge (C)	Relative charge
Proton (p)	1.672622×10^{-27}	1.007276	1.602×10^{-19}	+1
Neutron (n)	1.674927×10^{-27}	1.008665	0	0
Electron (e^-)	9.109383×10^{-31}	5.485799×10^{-4}	-1.602×0^{-19}	-1


1 Kg
1 Kg
RELATIVE MASS
STANDARD UNIT
2 Kg
2 Kg
RELATIVE MASS
STANDARD UNIT
One Carbon Atom
1 amu
12 Equal Parts
1 Carbon = 12 amu
1 amu = 1/12 of 1 Carbon
SUBSCRIBE


One Carbon Atom
1 Carbon = 12 amu
1 amu = 1/12 of 1 Carbon
1 amu
12 Equal Parts
16 amu
16 amu

Atomic mass and Isotopes

- All atoms of an element are identical in atomic number but not in mass number.
- **Isotopes** of an element are atoms that have different numbers of neutrons and different mass numbers.
- **For example,** all carbon atoms have six protons in the nucleus (Z = 6) but only 98.89 % of naturally occurring carbon atoms have six neutrons in the nucleus (A = 12). A small percentage (1.11 %) have seven neutrons in the nucleus (A = 13), and even fewer (less than 0.01 %) have eight (A= 14). Hence, carbon has three naturally occurring isotopes:

- Most elements found in nature are mixtures of isotopes.
- The average mass for the atoms in an element is called the atomic mass of the element and can be obtained as averages over the relative masses of the isotopes of each element, weighted by their observed fractional abundances.
- If an element consists of n isotopes, of relative masses A1, A2…An and fractional abundances of f1,f2,…..fn
- Then the average relative atomic mass (A) of the element is:

$$A = A_1 f_1 + A_2 f_2 + \ldots + A_n f_n.$$

Example 1.2

There are two naturally occurring isotopes of silver. Isotope ^{107}Ag (106.90509 amu) accounts for 51.84% of the total abundance, and isotope ^{109}Ag (108.90476) accounts for the remaining 48.16%. Calculate the atomic mass of silver?

Exercise 1.3

1. How many protons and neutrons are in the nucleus of each of the following atoms?

   a. $^{27}_{13}Al$ b. $^{32}_{16}S$ c. $^{64}_{30}Zn$ d. $^{207}_{82}Pb$

2. Element X is toxic to humans in high concentration but essential to life at low concentrations. It has four naturally occurring isotopes that contain 24 protons. Identify element X and give the atomic symbol for the isotopes with 26, 28, 29, and 30 neutrons.
3. Naturally occurring boron consists of two isotopes, ^{10}B and ^{11}B, with the isotopic masses 10.013 amu and 11.009 amu, respectively. The observed atomic mass of boron is 10.811 amu. Calculate the abundance of each isotope
4. The two naturally occurring isotopes of lithium, lithium-6 and lithium-7, have masses of 6.01512 amu and 7.01600 amu, respectively. Which of these two occurs in greater abundance?

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4. The two naturally occurring isotopes of lithium, lithium-6 and lithium-7, have masses of 6.01512 amu and 7.01600 amu, respectively. Which of these two occurs in greater abundance?

5.Natural copper, cu is mixture of only two isotopes one of which has 29 proton,34 neutrons and a relative abundance of 69.17%.the relative atomic mass of natural copper is 63.6. how many neutrons must there in the second isotopes?

Electromagnetic radiation and Atomic spectra

Electromagnetic radiation

- In 1873, James Clerk Maxwell proposed that light consists of electromagnetic waves.
- According to his theory, an electromagnetic wave has an electric field and magnetic field components.
- These two components vibrate in two mutually perpendicular planes.
- EMR is the emission and transmission of energy in the form of electromagnetic waves.

Electromagnetic describe how current flowing through a wire generate magnetic field

Radiation refers to the emission or transmission of energy in the form of waves or particles through space or a material medium.

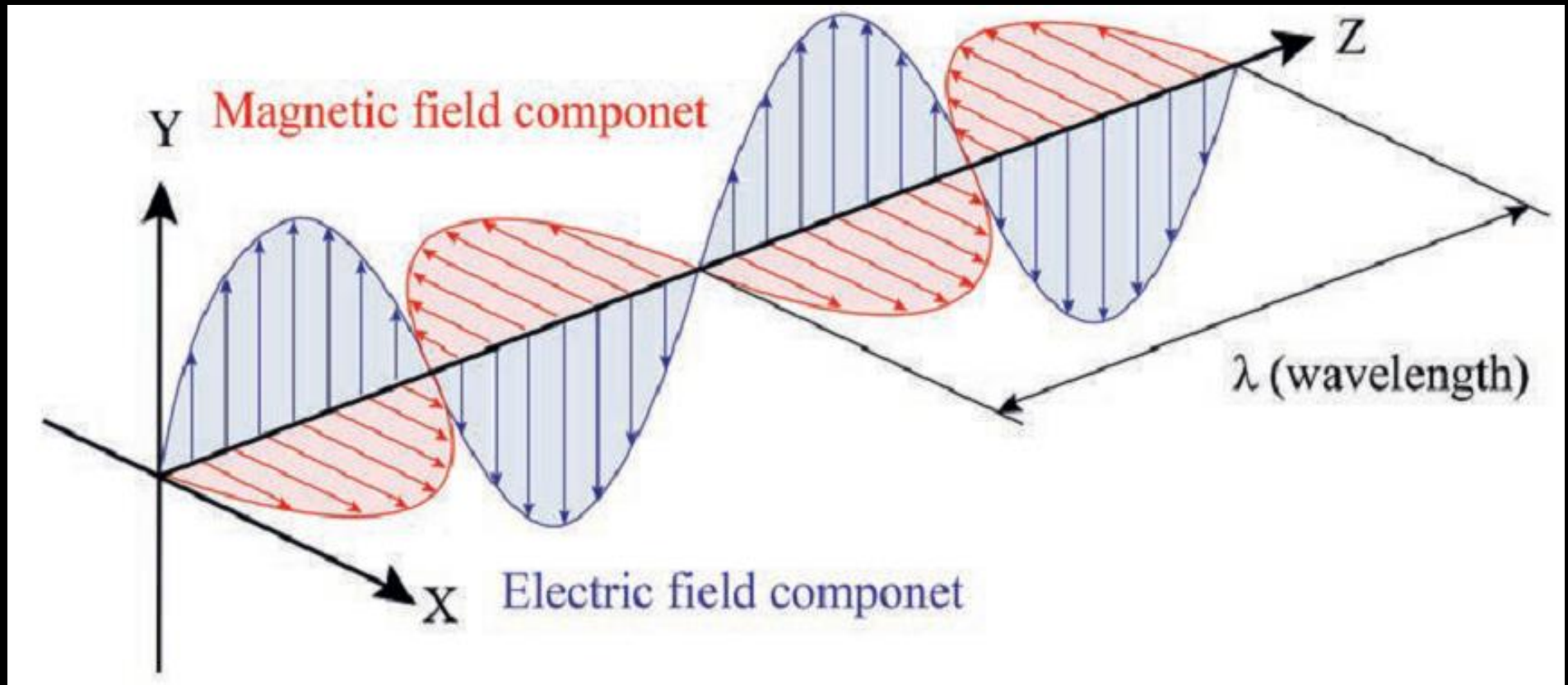
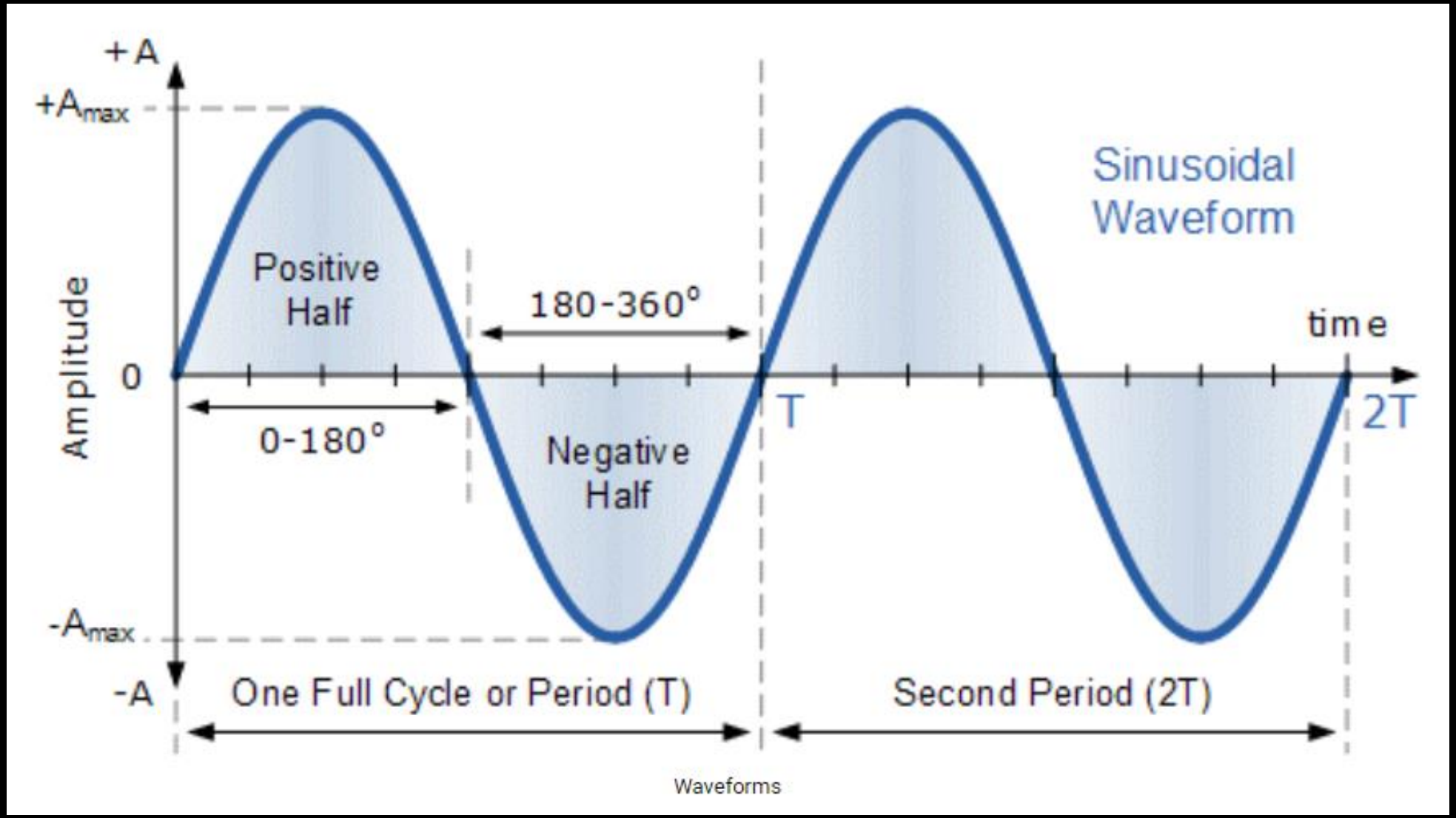


Figure 1.6: The electric field and magnetic field components of an electromagnetic waves

- Electromagnetic waves have three primary characteristics: wavelength, frequency and speed.
- Wavelength (λ, Greek lambda), is the distance the wave travels during one cycle.
- It is expressed in meters (m) and often, for very short wavelengths, in nanometers (nm), picometers (pm), or angstrom (Å).
- Frequency (v, Greek letter nu) is the number of cycles the wave undergoes per second and is expressed in units of l/second (1/s; also called hertz, Hz).


+A
+Amax
Amplitude
0
-Amax
-A
Positive Half
Negative Half
0-180°
180-360°
Sinusoidal Waveform
time
T
2T
One Full Cycle or Period (T)
Second Period (2T)

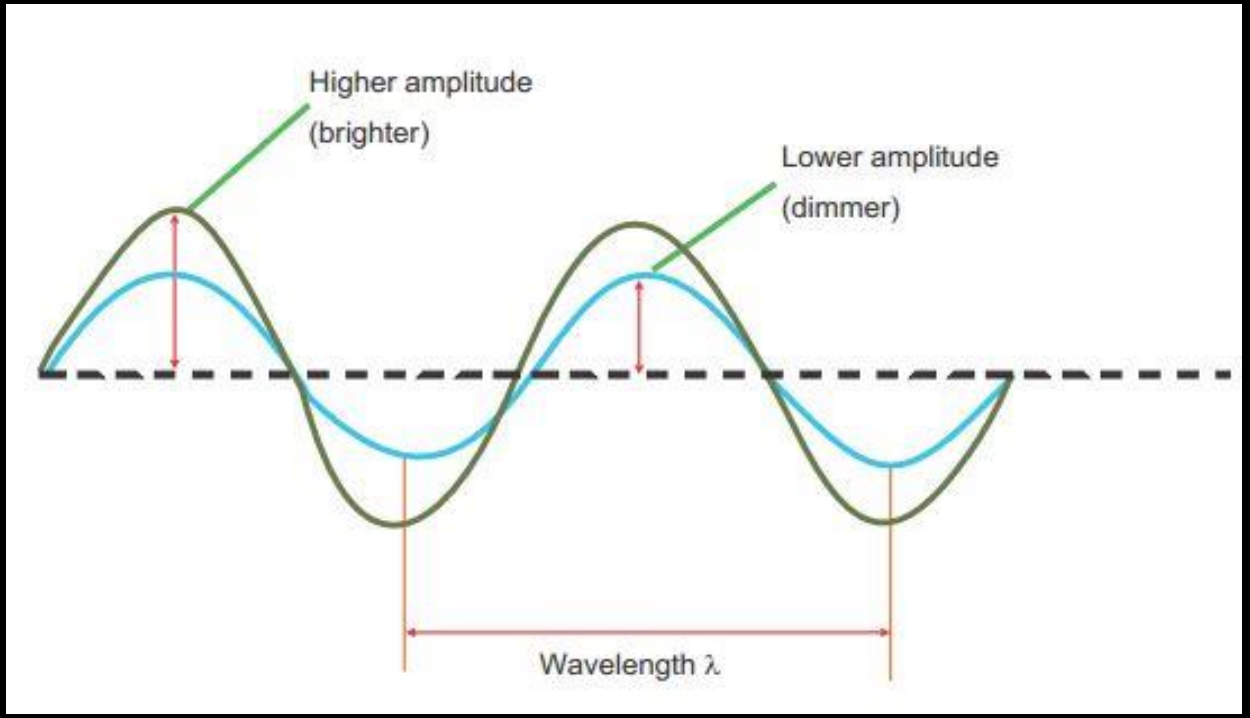
Waveforms

- Wave has a **speed** which depends on the type of wave and the nature of the medium through which it is traveling (for example, air, water, or a vacuum).
- The speed (c) of a wave is the product of its wavelength and its frequency:

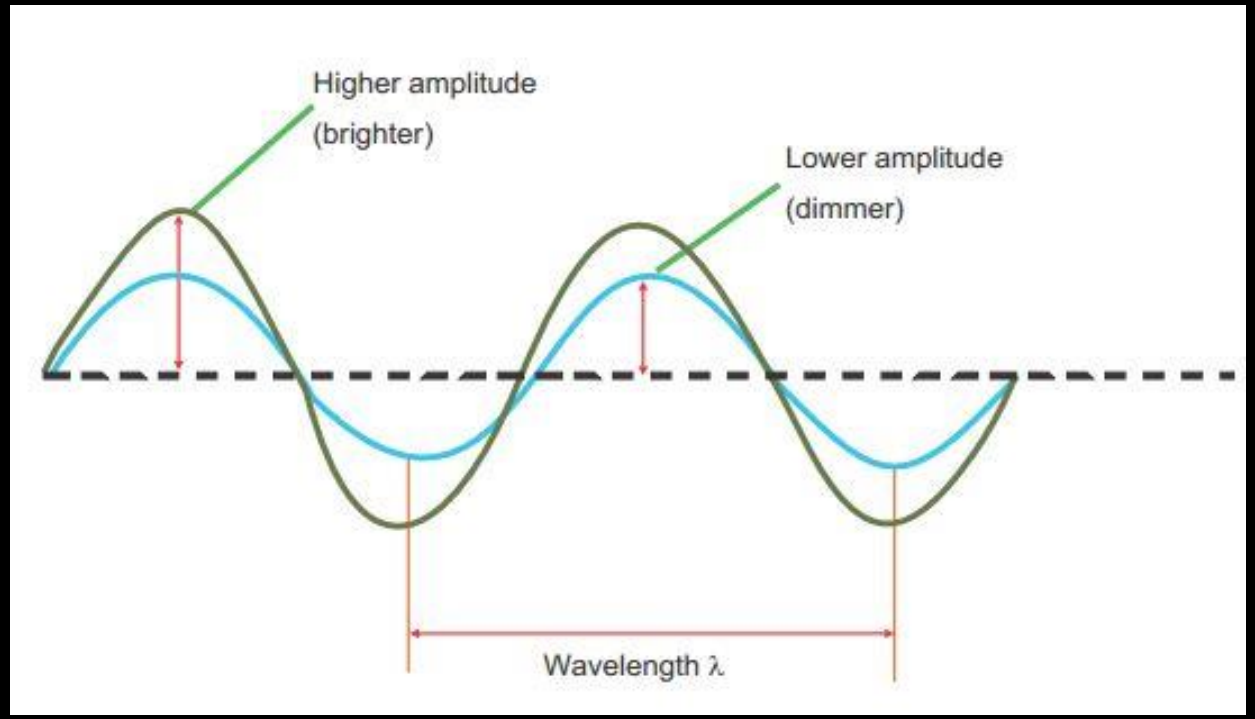
$$c_0 = \nu \times \lambda$$

- In vacuum, light travels at a speed of 3.0×10^8

- Electromagnetic radiation are also characterized by their amplitude or intensity.
- Amplitude is related to the intensity of the radiation, which we perceive as brightness in the case of visible light.
- The amplitude of an electromagnetic wave is a measure of the strength of its electric and magnetic fields.



- **The electromagnetic waves in the different spectral region travel at the same speed but differ in frequency and wavelength.**
- **Light of a particular shade of red, for instance, always has the same frequency and wavelength, but it can be dim (low amplitude) or bright (high amplitude).**



- EMR comes in a broad range of frequencies called the electromagnetic spectrum.
- A rainbow is an example of a continuous spectrum.
- Different wavelengths in visible light have different colors from red (λ = 750 nm) to violet (λ= 380 nm).

- **Electromagnetic Spectrum:** encompasses all the different types of electromagnetic waves, arranged according to their frequencies or wavelengths. This spectrum includes radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays

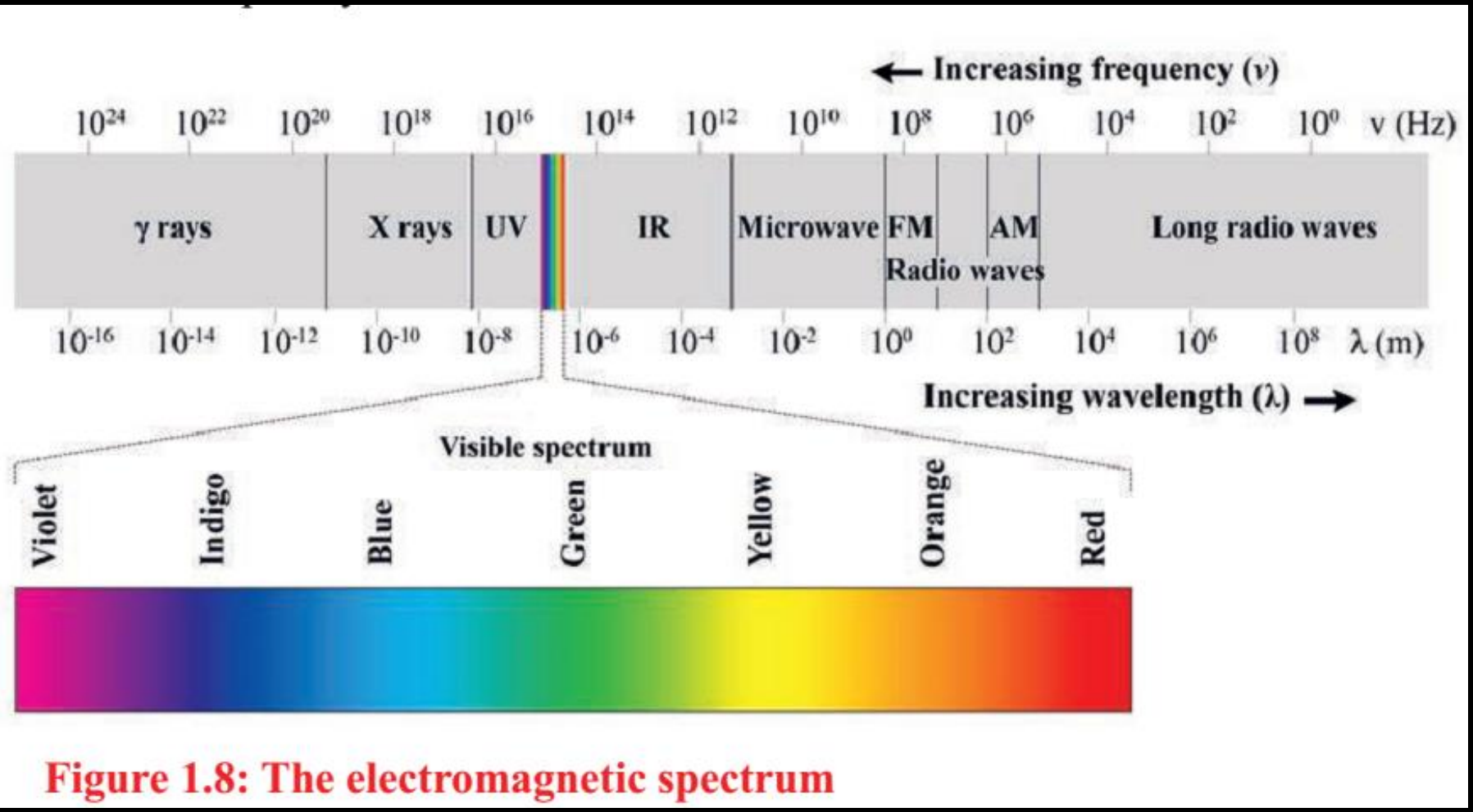


Figure 1.8: The electromagnetic spectrum

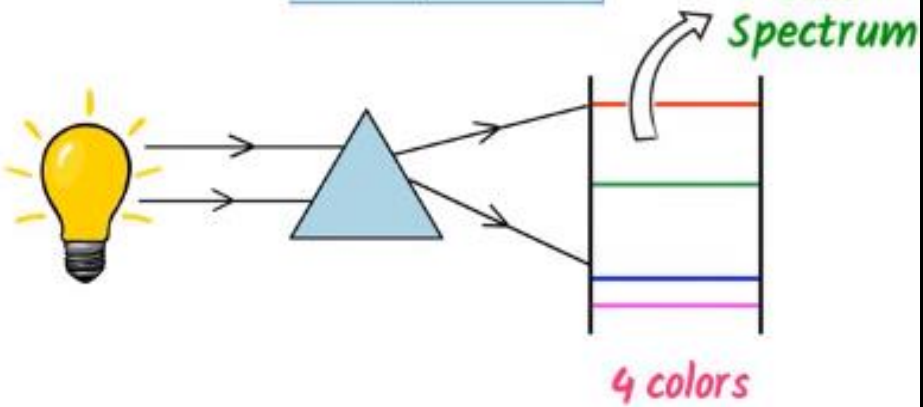
Types of Spectrum

Continuous Spectrum

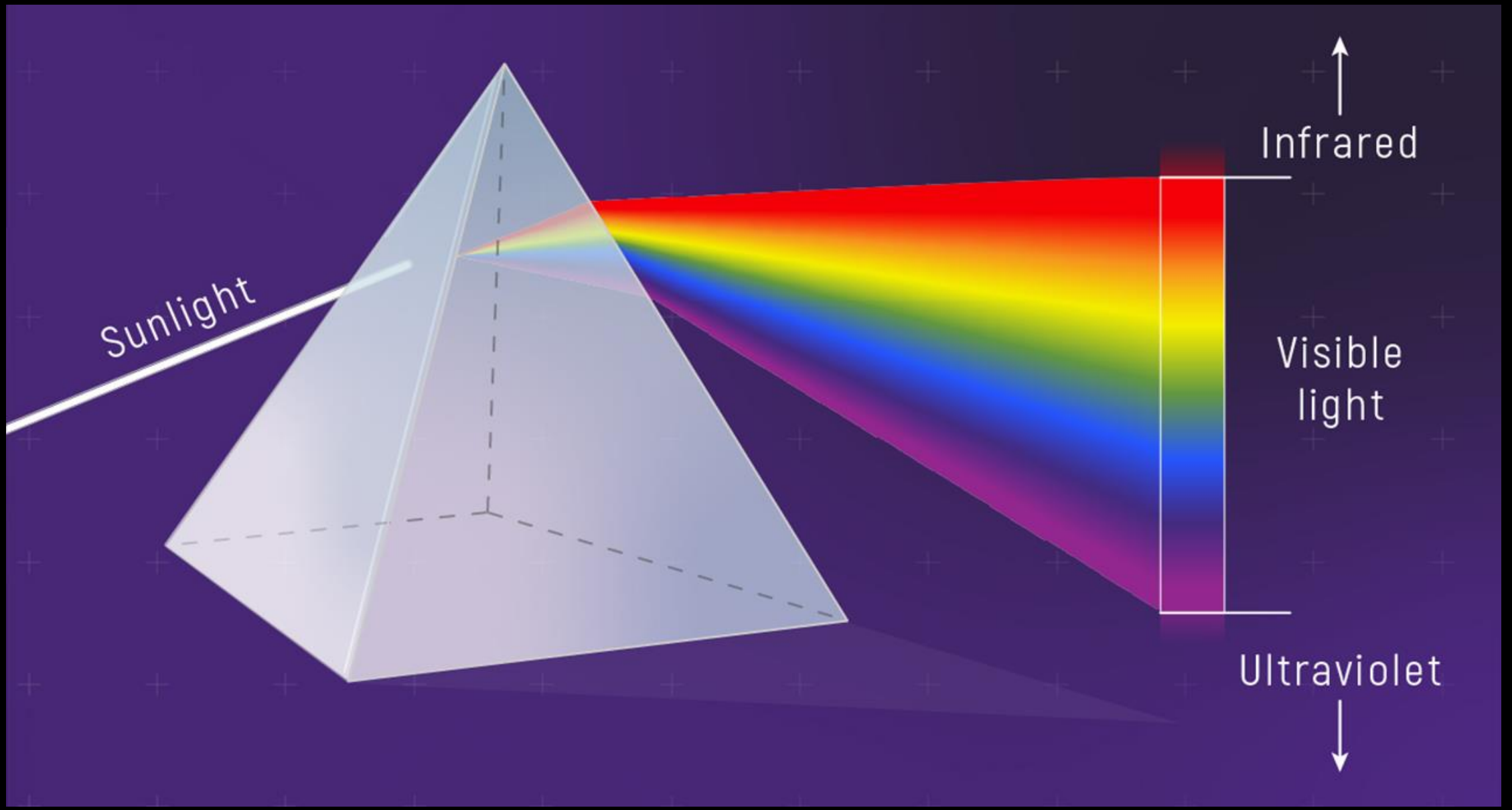


- No clear boundary line between colors.
- The colors partially overlap.
- The colors are not seperated by line.

Discontinuous Line Spectrum



- Clear boundary line between colors.
- The colors do not overlap.
- The colors are seperated by line.


Sunlight
Infrared
Visible light
Ultraviolet

- Radiation provides an important means of energy transfer.
- For instance, the energy from the Sun reaches the Earth mainly in the form of visible and ultraviolet radiation.
- The glowing coals of a fireplace transmit heat energy by infrared radiation.
- In microwave ovens, microwave radiation is used to heat water in foods, causing the food to cook quickly.


Zilan

Example 1.3

Ethiopian National Radio, Addis Ababa station broadcasts its AM signal at a frequency of 2400 kHz. What is the wavelength of the radio wave expressed in meters?

Exercise 1. 4

1. The most intense radiation emitted by the Earth has a wavelength of about 10.0 μm. What is the frequency of this radiation in hertz?
2. Addis Ababa Fana FM radio station, broadcasts electromagnetic radiation at a frequency of 98.1 MHz. What is the wavelength of the radio waves, expressed in meters?

Exercise 1. 4

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The Quantum theory and Photon

- In 1900, Max Planck, the German physicist, came to an entirely new view of matter and energy.
- He made a revolutionary proposal, energy like matter is discontinuous.

- According to Planck, atoms and molecules could emit or absorb energy only in discrete quantities, like small packages or bundles.
- Each of these small "packets" of energy is called a quantum.
- The energy of a quantum is proportional to the frequency of the radiation.
- The energy E of a single quantum is given by:

$$E = h\nu$$

Where h is called Planck's constant and ν is the frequency of radiation.

The value of Planck's constant is 6.63×10^{-34} J. s.

- The literal meaning of "discrete" is "individually separate and distinct."
- In the context of energy, when we say that energy is discrete, we are emphasizing that it exists in distinct, separate units or quantities. These discrete units cannot be further divided, and they represent specific and separate amounts of energy.
- When we say that energy is quantized, it means that energy can only exist in specific, discrete amounts or "quanta."

- Since ν = c/λ, E can also be expressed as:

$$E = \frac{hc}{\lambda}$$

- According to quantum theory, energy is always emitted or absorbed in integral multiples of hν; for example, hν, 2hν, 3hν,etc.

Example 1.4

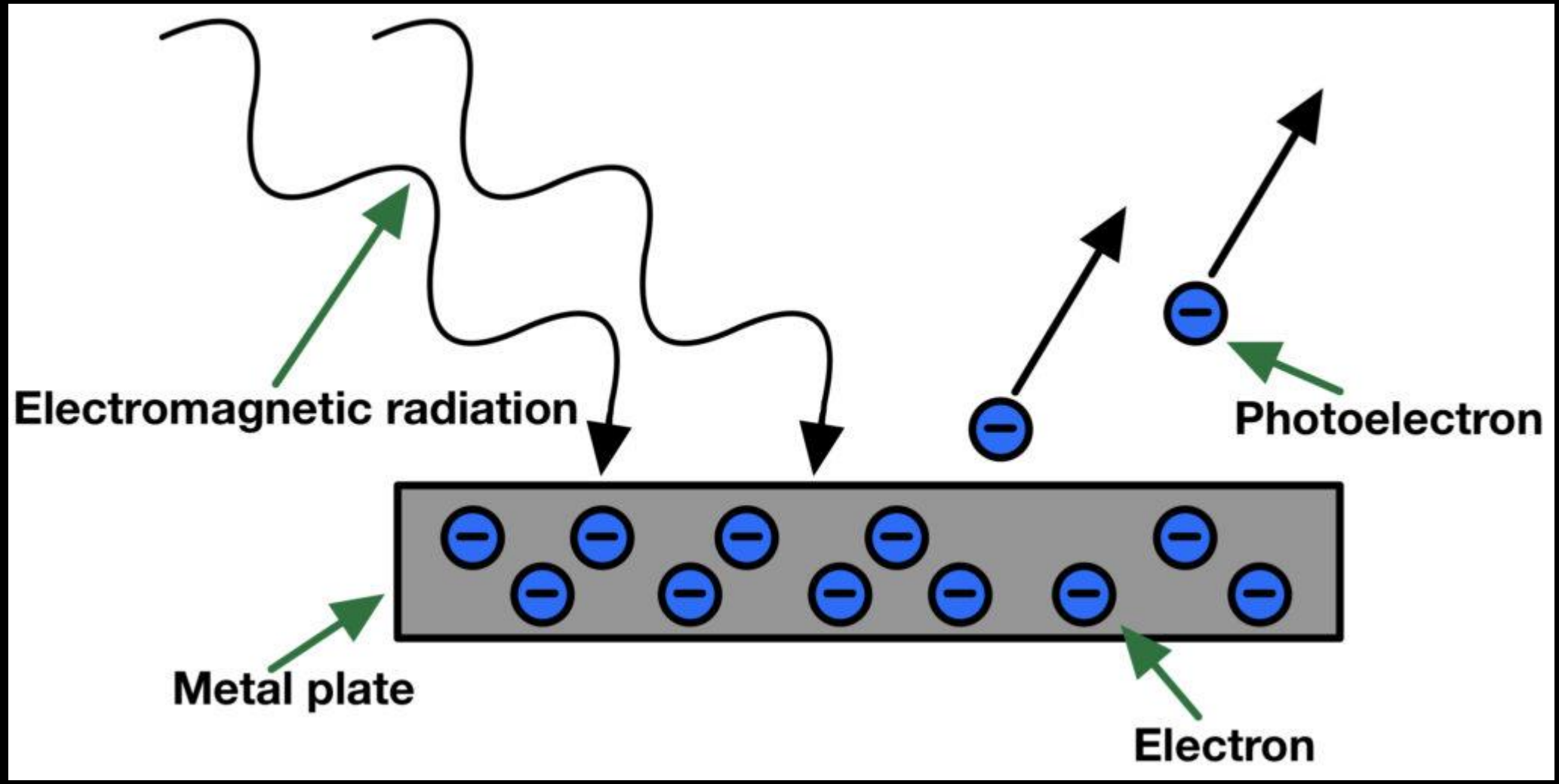
The blue color in fireworks is often achieved by heating copper (I) chloride (CuCl) to about 1200 °C. Then the compound emits blue light having a wavelength of 600 nm. What is the increment of energy (the quantum) that is emitted at 600 nm by CuCl?

The Photoelectric Effect

- In 1905, Albert Einstein used the quantum theory to explain the photoelectric effect.
- Light shining on a clean metallic surface can cause the surface to emit electrons. This phenomenon is known as the photoelectric effect.
- The minimum amount of energy required to remove an electron from the metal surface is called work function(Φ).

$$\Phi = hv_o$$

- v_o-The minimum frequency required to remove an electron from the metal surface .it is also called threshold frequency.


Electromagnetic radiation
Photoelectron
Metal plate
Electron

- **Photons** are particles of light or energy packet.
- A photon with energy less than E_o($\nu < \nu o$) can not remove an electron, or a light with a frequency less than the ν_o produces no electrons.
- On the other hand, if a light has $\nu > \nu_o$, the energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

$$KE_e = \tfrac{1}{2} m v^2 = h\nu - h\nu_o$$

- Where KE_e is the kinetic energy of an electron, m is mass of an electron, v is the velocity of an electron, $h\nu$, is the energy of an incident photon, and $h\nu_o$ is the energy required to remove an electron from the metal's surface.

- **Intensity of light** is a measure of the number of photons present in a given part of the beam:
- Now consider two beams of light having the same frequency (which is greater than the threshold frequency) but different intensities.
- The more intense beam of light consists of a larger number of photons. Consequently, it ejects more electrons from the metal's surface than the weaker beam of light.
- Thus, the more intense the light the greater the number of electrons emitted by the target metal.
- The higher the frequency of the light, the greater will be the kinetic energy of the emitted electrons

- **In his theory of relativity in 1905, Einstein derived the famous equation:**

$$E = mc^2$$

Rearranging this equation, we have

$$m = \frac{E}{c^2}$$

Where E is energy, m is mass, and c is speed of light.

- The main significance of that Equation is that energy has mass.
- Using this equation, we can calculate the mass associated with a given quantity of energy or the apparent mass of a photon.
- For electromagnetic radiation of wavelength, λ, the energy of each photon is given by the expression:

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Then, the apparent mass of a photon of light with wavelength is given by:

$$m = \frac{E}{c^2} = \frac{\left(hc/\lambda\right)}{c^2} = \frac{h}{c\lambda} \tag{1.9}$$

- We can summarize the important conclusions from the work of Planck and Einstein as follows:
- Energy is quantized. It can occur only in discrete units called photon or quanta.
- EMR, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well.
- This phenomenon is sometimes referred to as the dual nature of light

Example 1.5

1. Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.00×10^{7} m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

2. The maximum kinetic energy of the photoelectrons emitted from a give metal is 1.5×10^{-20} J when a light that has a 750 nm wavelength shines on the surface. Determine the threshold frequency, v_o, for this metal. Calculate the corresponding wavelength, λ_o.

Exercise 1.5

1. The following are representative wavelengths in the infrared, ultraviolet, and X-ray regions of the electromagnetic spectrum, respectively: 1.0×10^{-6} m, 1.0×10^{-8} m, and 1.0×10^{-10} m.
   a. What is the energy of a photon of each radiation?
   b. Which has the greatest amount of energy per photon?
   c. Which has the least?
2. A clean metal surface is irradiated with light of three different wavelengths λ_1, λ_2, and λ_3. The kinetic energies of the ejected electrons are as follows: λ_1: 7.2×10^{-20} J; λ_2: approximately zero; λ_3: 5.8×10^{-19} J. Which light has the shortest wavelength and which has the longest wavelength? Determine the threshold frequency, ν_o, for this metal.
3. The minimum energy required to cause the photoelectric effect in potassium metal is 3.69×10^{-19} J. Will photoelectrons be produced when visible light, 520 nm and 620 nm, shines on the surface of potassium? What is or are the velocities of the ejected electron/s?

1. The following are representative wavelengths in the infrared, ultraviolet, and X-ray regions of the electromagnetic spectrum, respectively: 1.0×10^{-6} m, 1.0×10^{-8} m, and 1.0×10^{-10} m.

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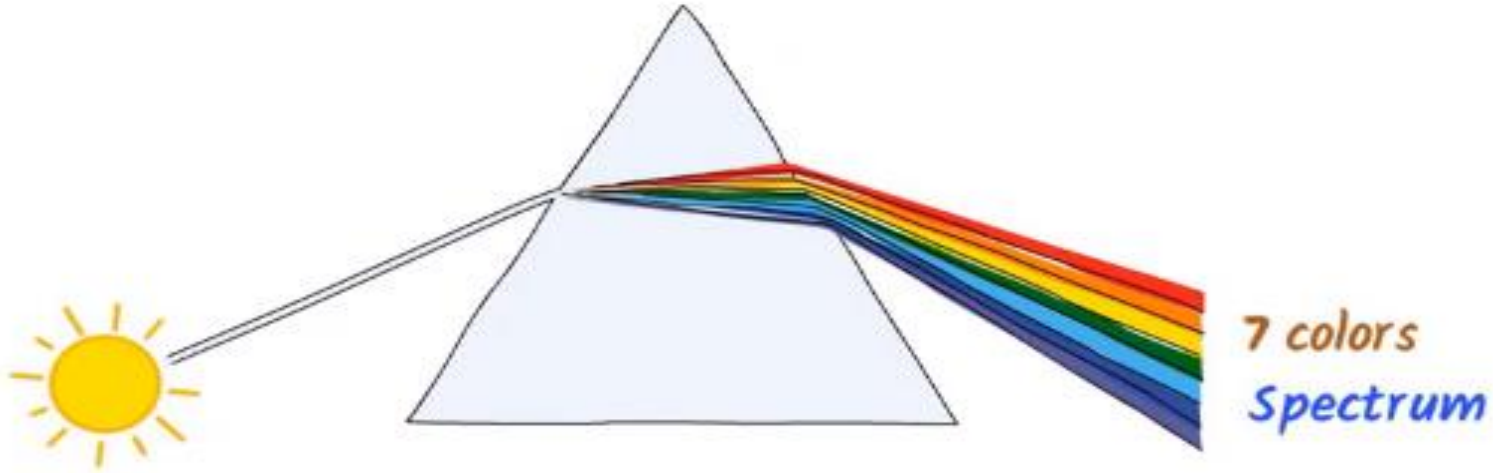
Atomic or line spectra

- Atomic or line spectra are produced from the emission of photons of electromagnetic radiation (light).
- Different kinds of spectrum are observed when an electric discharge, or spark, passes through a gas such as hydrogen.
- The electric discharge is an electric current that excites, or energizes, the atoms of the gas

- More specifically, the electric current transfers energy to the electrons in the atoms raising them to excited states.
- The atoms then emit the absorbed energy in the form of light as the electrons return to lower energy states
- When a narrow beam of this light is passed through a prism, we do not see a continuous spectrum, or rainbow, as sunlight does.
- Rather, only a few colors are observed, displayed as a series of individual lines. This series of lines is called the element's **atomic spectrum or emission spectrum.**

Spectrum

"The group of radiations when light passes through the prism and splits into seven colors..."



7 colors = 7 different radiations

They have different wavelengths.

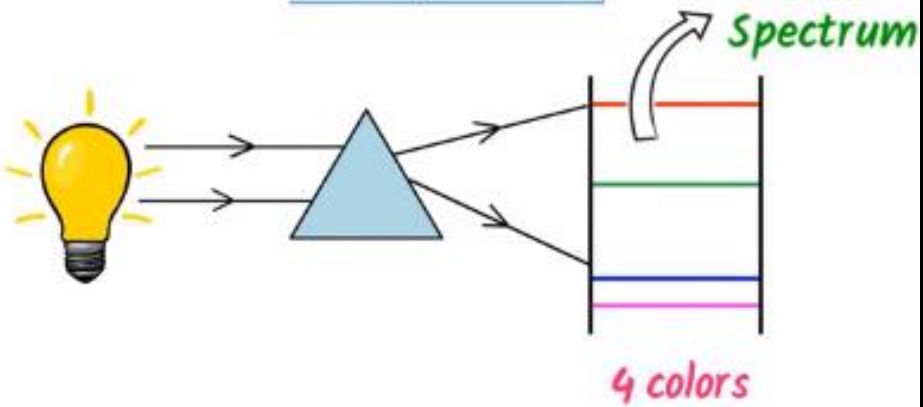
Types of Spectrum

Continuous Spectrum



- No clear boundary line between colors.
- The colors partially overlap.
- The colors are not seperated by line.

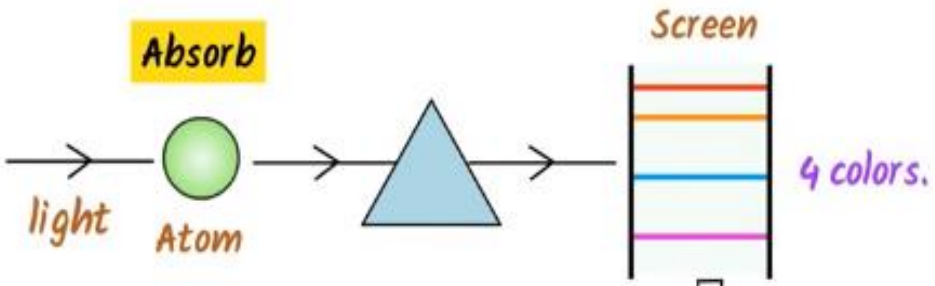
Discontinuous Line Spectrum



- Clear boundary line between colors.
- The colors do not overlap.
- The colors are seperated by line.

Types of Line Spectrum

Absorption Spectrum



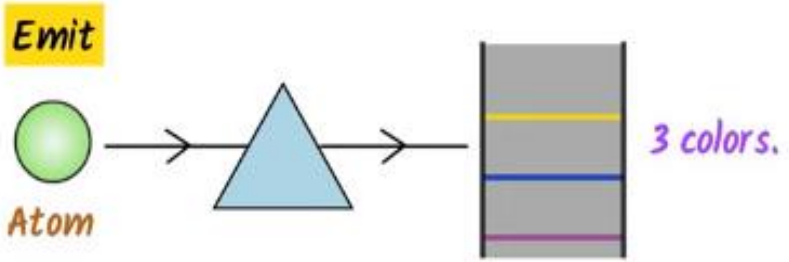
Why 3 colors are missing ?

- Abosrb 3 colors fom white light.

Absorption Spectrum

Absorption Spectrum = Absorb Specific wavelengths

Emission Spectrum

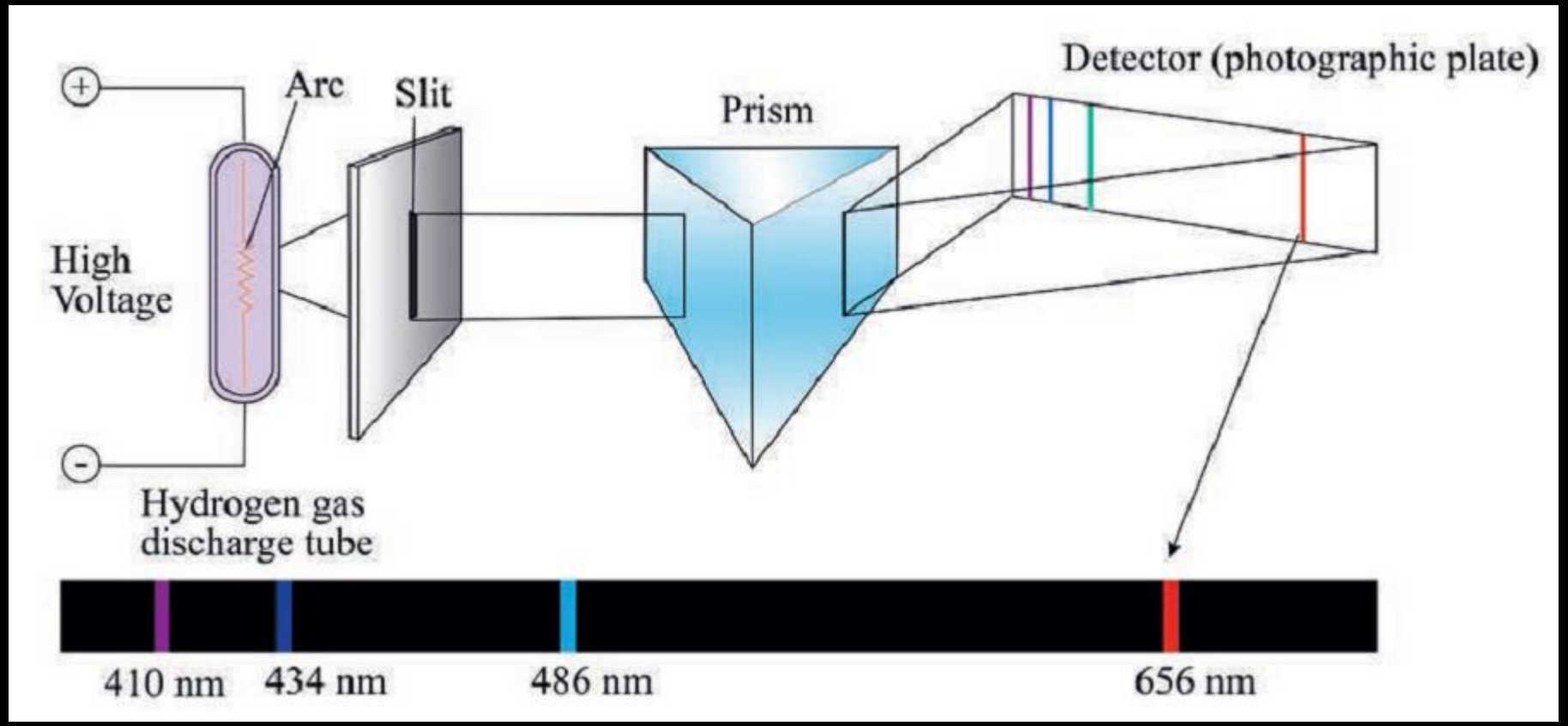


Emission Spectrum

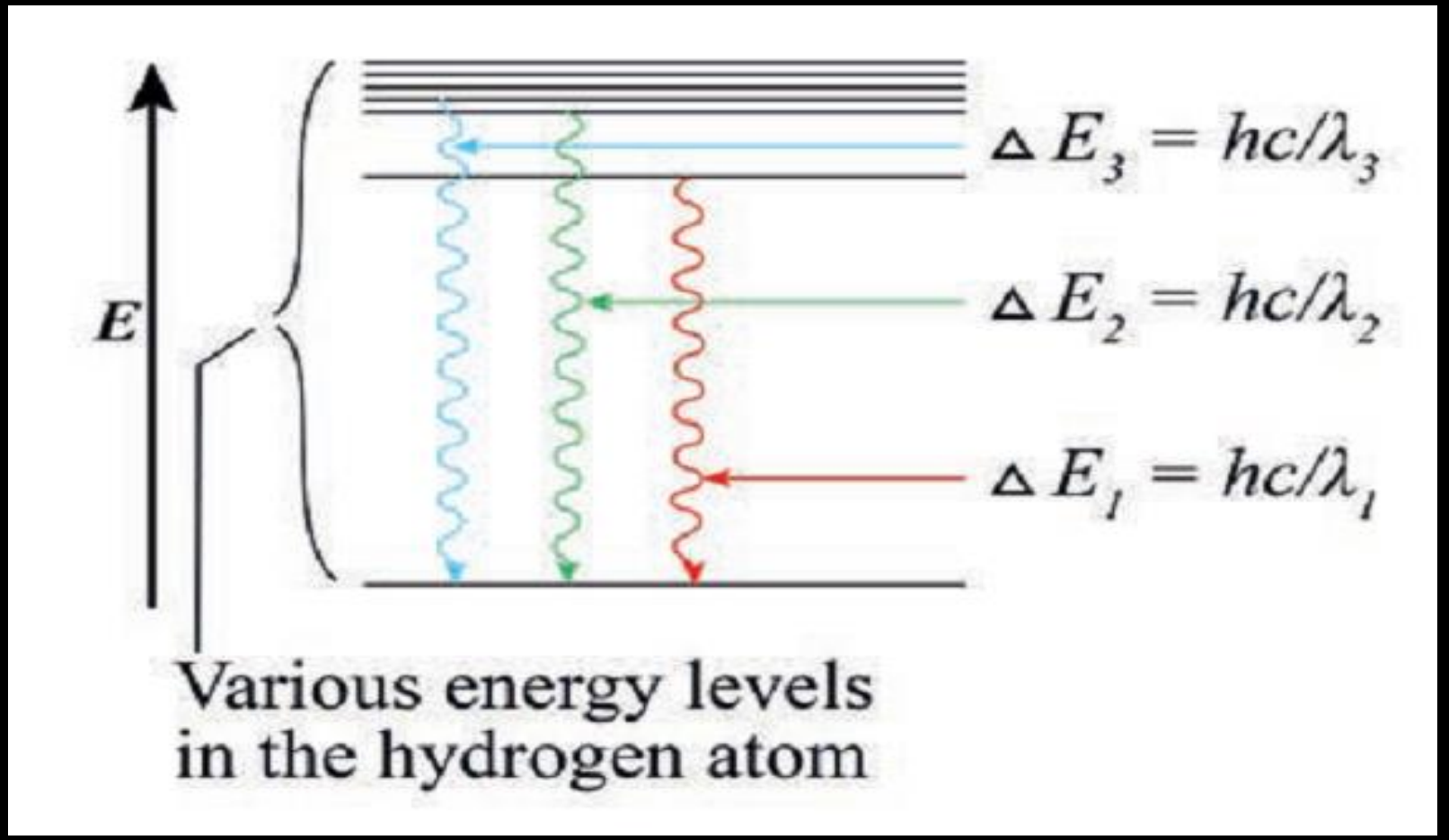
Emission Spectrum = Emitt Specific wavelengths

SUBSCRIBE

- **For example, the emission (line) spectrum of hydrogen atom is show**



- Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light
- For example, a given change in energy from a high to a lower level would give a wavelength of light which can be expressed using Planck's equation: $\Delta E = h\nu = hc/\lambda$



Various energy levels in the hydrogen atom

Atomic Spectrum of Hydrogen

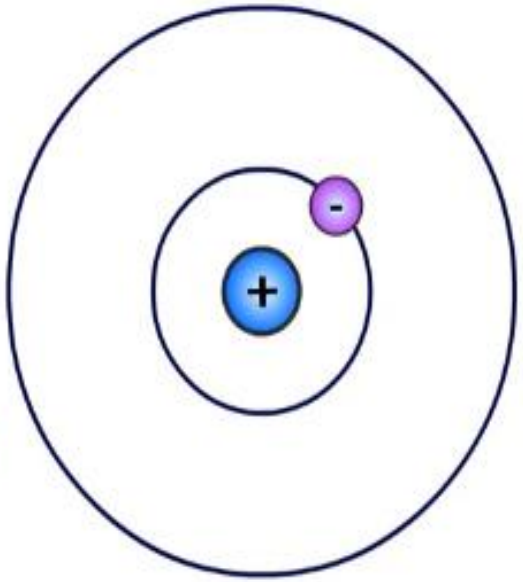
Energy

Radiation

How much energy it loses ?

Energy

According to Bohr, electron jumps to higher energy level.



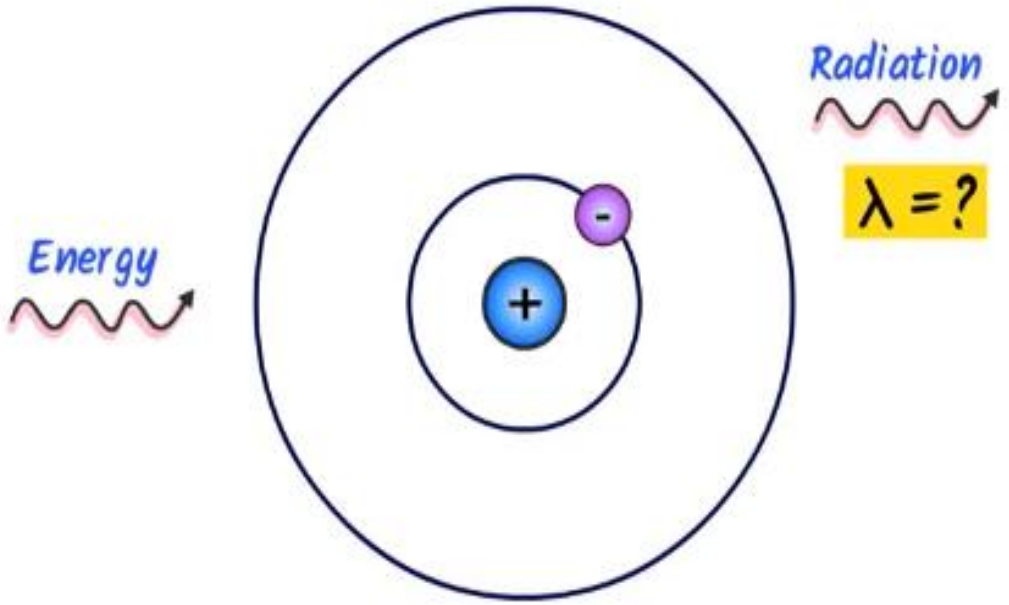
Energy emitted by electron = Energy difference between shells

$$\Delta E = E_2 - E_1$$



Bohr

Find the wavelength of emitted radiation ?



The Bohr model of Hydrogen Model

- In 1913, Niels Bohr (a Danish physicist) explained why the orbiting electron does not radiate energy as it moves around the nucleus.
- He introduced the fundamental idea that the absorption and emission of light by hydrogen atoms was due to energy changes of the electrons within the atoms.
- The fact that only certain frequencies are absorbed or emitted by an atom tells us that only certain energy changes are possible.
- Thus, energy changes in an atom are quantized.

- **Bohr used Planck's and Einstein's ideas about quantized energy and proposed the following assumptions:**

1. The electron in an hydrogen atom travels around the nucleus in a circular orbit.

2. The energy of the electron in an atom is proportional to its distance from the nucleus. The further an electron is from the nucleus, the more energy it has.

3. Only limited number of orbits with certain energies are allowed. This means, the orbits are quantized.

4. The only orbits that are allowed are those for which the angular momentum of the electron is an integral multiple of $h/2\pi$.

5. As long as an electron stays in a given orbital, it neither gains or losses energy.

That means, the atom does not change its energy while the electron moves within an orbit.

6. The electron moves to a higher energy orbit only by absorbing energy in the form of light, and emitting light when it falls to a lower energy orbit.

The energy (photon) of the light absorbed or emitted is exactly equal to the difference between the energies of the two orbits

- Furthermore, Bohr showed that the radii, r, of the permitted orbits or energy levels for an atom of hydrogen atom are related to Planck's constant, h, the electron's charge, e, and its mass, m.
- Consider hydrogen atom with an electron with constant speed, v, circulating the nucleus in an orbit of radius, r.
- The total energy of the electron is the sum of the kinetic energy (energy of movement) and the potential energy (energy of position):

$$E = \frac{1}{2}mv^2 + \frac{e^2}{r}$$

$$E = \frac{1}{2}mv^2 + \frac{e^2}{r}$$

- Bohr showed that the energies that an electron in hydrogen atom can occupy are given by:

$$E_n = -\frac{R_H}{n^2}$$

- Where RH, the Rydberg constant for the hydrogen atom and has the value 2.18×10^{-18}J. Thus,

$$E_n = -\frac{2.18 \times 10^{-18}\ \text{J}}{n^2}$$

- The negative sign in Equation is an arbitrary convention, signifying that the energy of the electron in the atom is lower than the energy of a free electron, which is an electron that is infinitely far from the nucleus.
- The energy of a free electron is given a value of zero.

- As the electron gets closer to the nucleus (as n decreases),n becomes larger in absolute value, but also more negative.
- The most negative value, then, is reached when n = 1, which corresponds to the most stable energy state.
- We call this the ground state or ground level, which refers to the lowest energy state of an atom.

- The stability of the hydrogen electron diminishes for n= 2, 3.... Each of these levels is called an excited state, or excited level, which is higher in energy than the ground state.
- A hydrogen electron for which n is greater than 1 is said to be in an excited state.
- Using Bohr's Equation, relating the energy (En)and energy level (n) for an electron it is possible to calculate the energy of a single electron in a ground state or excited state, or the energy change when an electron moves between two energy levels.

Example 1.6

Consider the $n = 5$ state of hydrogen atom. Using the Bohr model, calculate the radius of the electron orbit, the velocity and the energy of the electron.

- Bohr’s model also quantitatively explained the line spectra of hydrogen atom.
- He proposed that the absorptions and emissions in line spectra correspond to the transfer of the electron from one orbit to another.
- Energy must be absorbed for the electron to move from one orbit to another one having a bigger radius.
- Whereas, energy is emitted when an electron moves from the higher orbital energy level, ni,to the lower orbital, nf, energy level.
- Thus, the change in energy, E, is the difference in the energy between the final and the initial state electron:

$$\Delta E = E_f - E_i$$

This equation is similar to:

$$\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- **Notice that when nf > ni, ΔE is positive, indicating that the system has absorbed energy. But, ni > nf, ΔE is negative and this corresponds to emission of energy.**

Example 1.7

Calculate the energy emitted when an electron moves from the $n = 3$ to the $n = 2$ energy level. Determine the wavelength of the emitted energy.

Exercise 1.6

1. What is the wavelength of a photon (in nanometers) emitted during a transition from the $n = 5$ state to the $n = 2$ state in the hydrogen atom?
2. Calculate the frequency of the green line arising from the electron moving from $n = 4$ to $n = 20$ in the visible spectrum of the hydrogen atom using Bohr's theory.

- Each spectral line in the emission spectrum corresponds to a particular transition in a hydrogen atom
- line spectra of a hydrogen atom when its electron moves from n= 4 to n= 1; n= 3 to n= 1 and n= 2 to n= 1.

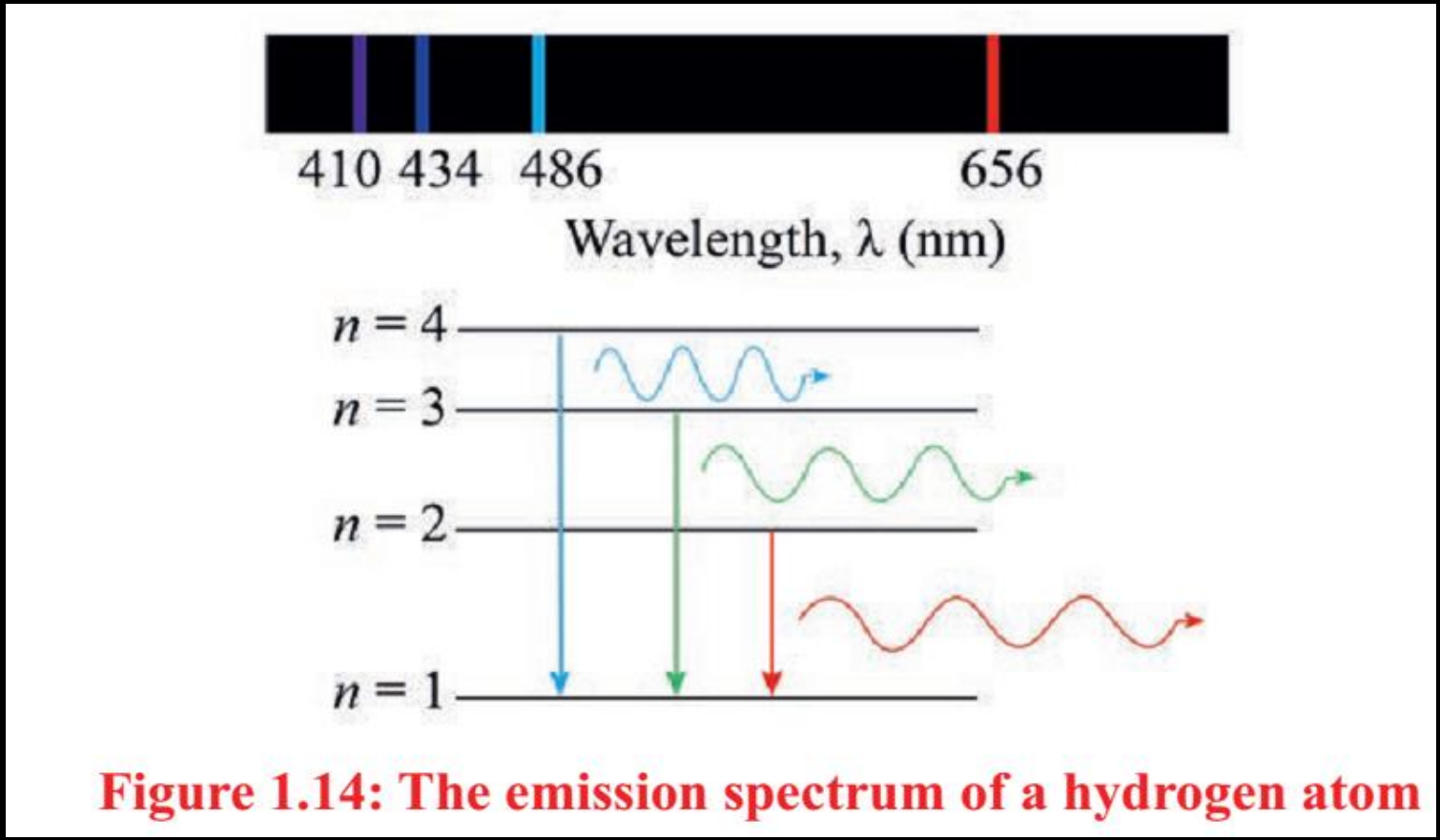


Figure 1.14: The emission spectrum of a hydrogen atom

- The emission spectrum of hydrogen includes a wide range of wavelengths from the infrared to the ultraviolet.
- The Balmer series was particularly easy to study because some its lines fall in the visible range.

Table 1.2: The various series in atomic hydrogen emission spectrum

Series	n_f	n_i	Spectrum region
Lyman	1	2, 3, 4, …	Ultraviolet
Balmer	2	3, 4, 5, …	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

- **For a larger orbit radius (i.e. a higher atomic energy level), the further the electron drops, the greater is the energy (higher ν, shorter λ) of the emitted photon.**

Exercise 1.7

1. Calculate the energies of the states of the hydrogen atom with $n = 2$ and $n = 3$, and calculate the wavelength of the photon emitted by the atom when an electron makes a transition between these two states.
2. What is the wavelength of a photon emitted during a transition from the $n_i = 10$ state to the $n_f = 2$ state in the hydrogen atom?

Limitations of Bohr Model

The model explains atoms and ions containing only one electron such as H, He+ and Li2+.

- It doesn't explain the atomic spectra of more complicated atoms and ions, even that of helium, the next simplest element.
- It doesn't explain about further splitting of spectral lines in the hydrogen spectra on application of a magnetic field.
- It considers electrons to have both known radius and orbit, which is impossible according to Heisenberg's uncertainly principle

The wave-particle duality of matter and energy

Bohr's model assumed that an atom has only certain allowable energy levels in order to explain the observed line spectrum.

However, his assumption had no basis in physical theory. In 1924, Louis de Broglie, the French physicist, proposed a surprising reason for fixed energy levels: if energy is particle-like, perhaps matter is wavelike.

De Broglie reasoned that if electrons have wavelike motion and are restricted to orbits of fixed radii that would explain why they have only certain possible frequencies and energies.

- By combining Einstein's equation for the quantity of energy equivalent to a given amount of mass (E= mc2) with Planck's equation for the energy of a photon (E = hv = hc/λ), de Broglie derived an equation for the wavelength of any particle of mass, m, whether a planet, ball, or electron-moving at speed, v.

$$\lambda = \frac{h}{mv}$$

- According to this Equation 1.20,matter and energy show both wave and particulate properties.
- The distinction between a particle and a wave is only meaningful in the macroscopic world, it disappears at the atomic level. This dual character of matter and energy is known as the **wave-particle duality**.

Example 1.8

Calculate the de Broglie wavelength of an electron that has a velocity of 1.00×10^6 m/s. (electron mass, $m_e = 9.11 \times 10^{-31}$ kg; $h = 6.63 \times 10^{-34}$ J.s).

Exercise 1.8

1. What is the characteristic wavelength of an electron (in nm) that has a velocity of 5.97×10^{6} m/s ($m_e = 9.11 \times 10^{-31}$ kg)?
2. Calculate the wavelength (in nanometers) of an H atom (mass = 1.67×10^{-27} kg) moving at 7.00×10^{2} cm/s.
3. Calculate the wavelength (in nm) of a photon emitted when a hydrogen atom undergoes a transition from $n = 5$ to $n = 2$.

The quantum mechanical model of the atom

- The Bohr model of an electron orbiting around the nucleus, looking like a planet around the Sun, doesn't explain properties of atoms.
- The planetary view of one charged particle orbiting another particle of opposite charge does not match some of the best-known laws of classical physics.

- Scientists have developed quantum mechanics,which presents a different view of how electrons are arranged about the nucleus in the atom.
- This view depends on two central concepts: the wave behavior of matter and the uncertainty principle.
- The combination of these two ideas leads to a mathematical description of electronic structure.

Quantum Numbers

- The quantum mechanical description of the atom is based on the assumption that there
- are waves associated with both matter and radiations. The mathematical description of such wave provides information about the energy of electrons and their position.

- **Erwin Schrödinger (1927),**suggested that an electron or any other particle exhibiting wavelike properties can be described by a mathematical equation called a wave function (denoted Greek latter psi, ψ).
- The equation is very complex. However, it leads to series of solutions that describe the allowed energy states of electrons.
- The square of a wave function, ψ^2, gives the probability of finding an electron in a certain region of a space.

- The results of a quantum mechanics indicate that the electron may be visualized as being in a rapid motion within a given region of space around the nucleus.
- Although we cannot determine the precise position of an electron, the probability of the electron being at a definite location can be calculated.
- The region in which an electron is most likely found is called an **orbital**.

- **The electron may occupy anywhere within an orbital at any instant in time.**
- **So, an electron can be considered as a particle that can rapidly move from place to place, behaving like an "electron cloud" whose density varies within the orbital.**

- In quantum mechanics, each electron in an atom is descried by four quantum numbers.
- Three of the quantum numbers specify the wave function that gives the probability of finding an electron at various place in spaces.
- The fourth one is used to describe the spin (magnetic property) of the electrons that occupy the orbitals.
- **The four quantum numbers are:**

  The principal quantum number (n)

  The angular momentum quantum number (ℓ)

  The magnetic quantum number (mℓ)

  The electron spin quantum number (ms)

1. The principal quantum number (n)

- describes the main energy level, or shell, an electron occupies.
- It may be any positive integer, n= 1, 2, 3, 4,etc. It describes
- The size and energy of the shell in which the orbital resides and it is analogous to the energy levels in Bohr's model.

2.The angular momentum quantum number (ℓ)

- Designates the shape of the atomic orbitals.
- Within a shell different sublevels or subshells are possible, each with a characteristic shape.
- It takes values from 0 to n-1.
- Orbitals of the same n, but different ℓ are said to belong to different subshells.
- It is also called azimuthal quantum number or subsidiary quantum number .

- A given energy level, n, has n^2 total number of orbitals.
- For example, in n = 4, ℓ has values of 0, 1, 2, and 3. Each
- value of ℓ corresponds to an orbital label and an orbital shape.

- **The following letters are usually used to denote the values of ℓ:**

Value of ℓ	Corresponding subshell
0	s
1	p
2	d
3	f

Example 1.9

What do "4" and "*d*" represent in 4d?

Solution:

The number 4 gives the principal quantum number ($n = 4$) and the letter d gives the type of orbital ($\ell = 2$).

3. The magnetic quantum number (mℓ)

- is also called the orbital-orientation quantum number .
- It has integral values between -ℓ and ℓ,including 0.
- The value of mℓ is related to the orientation of the orbital in space relative to the other orbitals in the atom.
- The number of possible mℓ values or orbitals for a given ℓ value is 2ℓ + 1.

4.The electron spin quantum number (ms)

- refers to the spin of an electron and the orientation of the magnetic field produced by this spin.
- For every set of n, ℓ, and mℓ values, ms can take the value +½ or -½.
- Each atomic orbital cannot accommodate more than two electrons, one with ms = +½ and another with ms = -½.

Exercise 1.9

1. What are the values of n and ℓ for the following subshells?

   a. 1s c. 4s e. 4f

   b. 3p d. 3d

2. Write the subshell notations that correspond to

   a. $n = 3$ and $\ell = 0$ c. $n = 7$ and $\ell = 0$

   b. $n = 3$ and $\ell = 1$ d. $n = 3$ and $\ell = 2$

Example 1.10

1. What are the allowed values of the quantum numbers through $n = 2$?

2. What values of the angular momentum quantum number (ℓ) and magnetic quantum number (m_ℓ) are allowed for a principal quantum number, $n = 3$? How many orbitals are allowed for $n = 3$?

Exercise 1.10

1. What are the allowed values of the quantum numbers through $n = 4$?
2. Write an orbital designation corresponding to the quantum numbers:
   a. $n = 4, \ell = 2, m_\ell = 0$
   b. $n = 3, \ell = 1, m_\ell = 1$
   c. $n = 5, \ell = 1, m_\ell = -1$
   d. $n = 4, l = 3, m_\ell = -3$
3. What values ℓ and m_ℓ are allowed for a principal quantum number (n) of 3? How many orbitals are allowed for $n = 3$?
4. Can an orbital have the quantum number $n = 2, \ell = 2, m_\ell = 2$
5. For an orbital with $n = 3$ and $m_\ell = 1$, what is (are) the possible value(s) ℓ?
6. Which of the following orbitals do not exist: 1p, 2s, 2d, 3p, 3d, and 3f?

1. What are the allowed values of the quantum numbers through $n = 4$?

2. Write an orbital designation corresponding to the quantum numbers:

a. $n = 4, \ell = 2, m_\ell = 0$

b. $n = 3, \ell = 1, m_\ell = 1$

c. $n = 5, \ell = 1, m_\ell = -1$

d. $n = 4, l = 3, m_\ell = -3$

3. What values ℓ and m_ℓ are allowed for a principal quantum number (n) of 3? How many orbitals are allowed for $n = 3$?

4. Can an orbital have the quantum number $n = 2$, $\ell = 2$, $m_\ell = 2$

5. For an orbital with $n = 3$ and $m_\ell = 1$, what is (are) the possible value(s) ℓ?

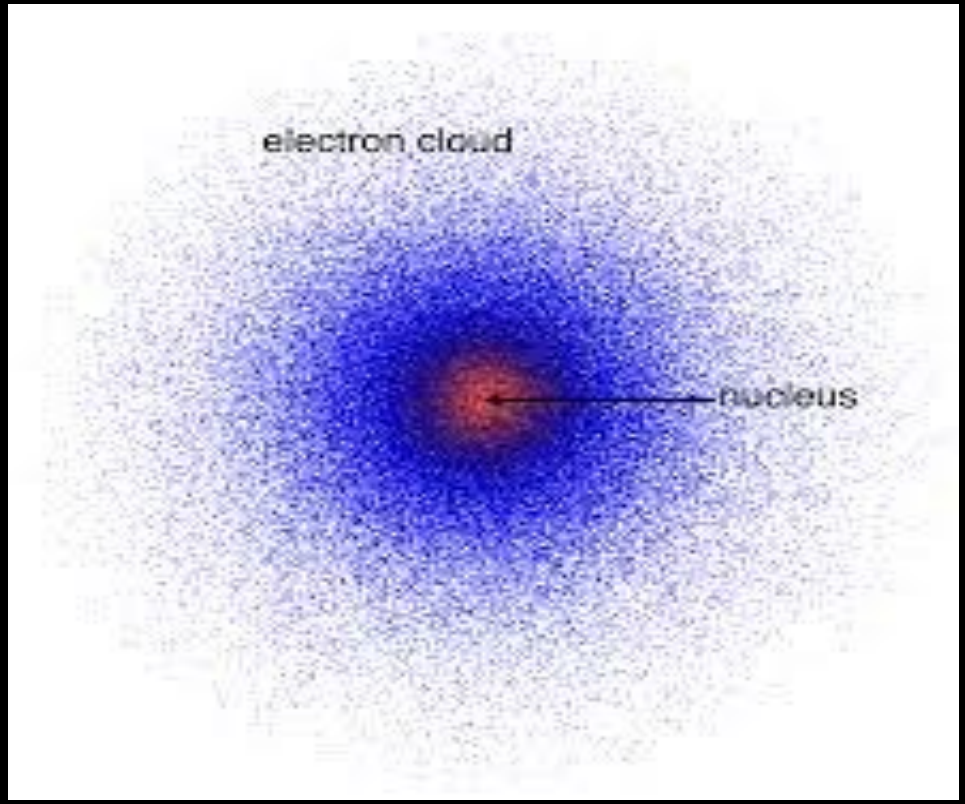
6. Which of the following orbitals do not exist: 1p, 2s, 2d, 3p, 3d, and 3f?

Periodic Properties

- The electron configurations of the atoms display a periodic variation with increasing atomic number (nuclear charge).
- As a result, the elements show periodic variations of physical and chemical behavior.
- In this section you will examine some periodic atomic properties like atomic radii, ionization energies, electron affinities, electronegativity, and metallic character.

Atomic size(Atomic radii)

- Exact size of an isolated atom cannot be measured because the electron cloud surrounding the atom does not have a sharp boundary.
- However, an estimate of the atomic size can be made by measuring the distance between the nuclei of two adjacent atoms. This property is called the **atomic radius.**
- One of the most common methods to determine the atomic radius is to assume that atoms are spheres touching each other when they are bonded together (Figure 1.19).


electron cloud
nucleus

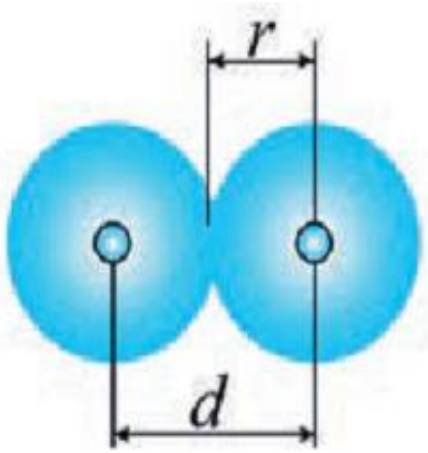


Figure 1.19: Atomic radius for a diatomic molecule.

$$r = \frac{d}{2}$$

- Atomic size varies within both a group and a period of the main-group elements.
- These variations in atomic size are the result of two opposing influences: changes in the principal quantum number (n) and changes in the effective nuclear charge (Zeff)the nuclear charge an electron actually experiences.
- The net effect of these depends on the shielding of the increasing nuclear charge by the inner electrons.

- **Atomic radius generally increases in a group from top to bottom but it decreases in a period from left to right.**
- **These trends hold well for the main-group elements but not as for the transition elements (electrons enter an inner electron shell, not the valence shell).**

- As we move from left to right, size shrinks through the first two or three transition elements because of the increasing nuclear charge.
- But, from then on, the size remains relatively constant because shielding by the inner d electrons cancels out the usual increase in Zeff.
- For instance, vanadium (V; Z=23), the third Period 4 transition metal, has the same atomic radius as zinc (Zn; Z= 30), the last Period 4 transition metal.

Exercise 1.12

1. What are the factors affecting the size of an atom of an element? Explain your answer using examples.
2. Using the periodic table, rank each set of main-group elements in order of decreasing atomic size:

   a. Ca, Mg, Sr b. K, Ga, Ca c. Br, Rb, Kr d. Sr, Ca, Rb
3. Why is the difference in atomic radius between the elements $Z = 11$ (Na; 186 pm) and $Z = 12$ (Mg; 160 pm) so large, whereas between $Z = 24$ (Cr; 125 pm) and $Z = 25$ (Mn; 124 pm) the difference is very small. (Note that "pm" is picometers.).

Ionization energy (IE)

- The ionization energy (IE)is the energy (in kJ) required for the complete removal of 1 mol of electrons from 1 mol of gaseous atoms or ions.
- Multi-electron atoms can lose more than one electron, so the ionization energies required to remove each electron are numbered in sequence from the ground-state atom.

- For instance, boron atom has five electrons, two in an inner core (1s2) and three valence electrons (2s22p1).
- The five ionization steps and their ionization energies, IE1 through IE5, are:

$B\ (g)$	$\rightarrow$	B^{+}	$(g) + e^{-}$	IE_1	$= 801\ kJ\ mol^{-1}$
$B^{+}\ (g)$	$\rightarrow$	B^{2+}	$(g) + e^{-}$	IE_2	$= 2427\ kJ\ mol^{-1}$
$B^{2+}\ (g)$	$\rightarrow$	B^{3+}	$(g) + e^{-}$	IE_3	$= 3660\ kJ\ mol^{-1}$
$B^{3+}\ (g)$	$\rightarrow$	B^{4+}	$(g) + e^{-}$	IE_4	$= 25{,}025\ kJ\ mol^{-1}$
$B^{4+}\ (g)$	$\rightarrow$	B^{5+}	$(g) + e^{-}$	IE_5	$= 32{,}822\ kJ\ mol^{-1}$

- **The first ionization energy (IE1) of an atom is the minimum energy needed to remove the first electron from the outermost shell of a gaseous atom to produce a gaseous ion.**

$$\text{Atom (g)} \rightarrow \text{Ion}^{+}\text{(g)} + e^{-} \quad \Delta E = IE_1 > 0$$

- **The second ionization energy (IE2) removes the second electron. Since the electron is being pulled away from a positively charged ion, IE2 is always larger than IE1:**

$$Ion^{+}(g) \rightarrow Ion^{2+}(g) + e^{-} \qquad \Delta E = IE_2 \text{ (always} > IE_1)$$

- **The first ionization energy** is a key factor in an element's chemical reactivity because, atoms with a low IE1 tend to form cations during reactions, whereas those with a high IE1, (except the noble gases) often form anions.

- Ionization energies display a periodic variation when plotted against atomic number, as Figure 1.20 shows.
- Within any period, values tend to increase with atomic number.
- Thus, the lowest values in a period are found for the Group IA elements (alkali metals).
- It is characteristic of reactive metals such as these to lose electrons easily.
- The largest ionization energies in any period occur for the noble-gas elements.

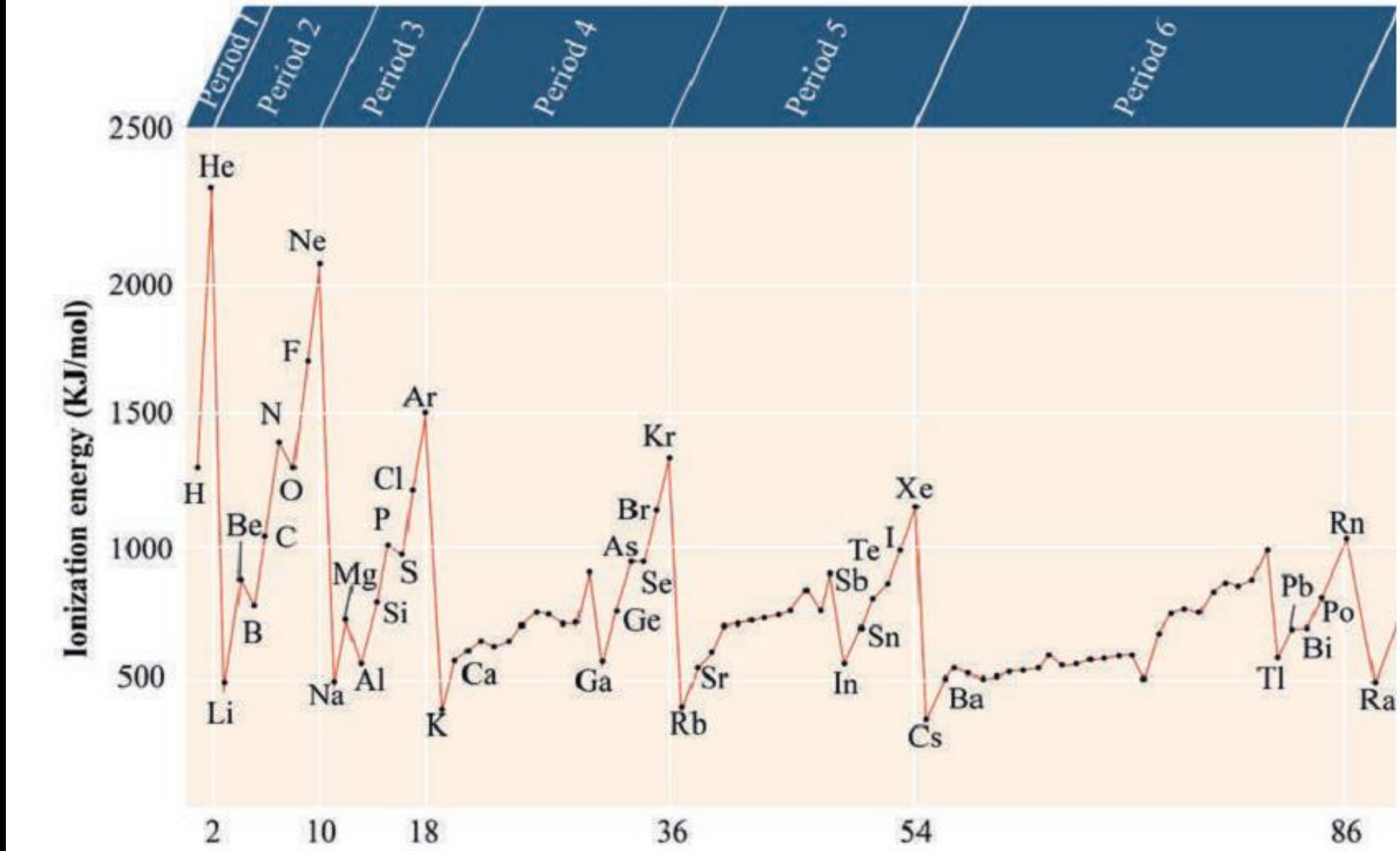
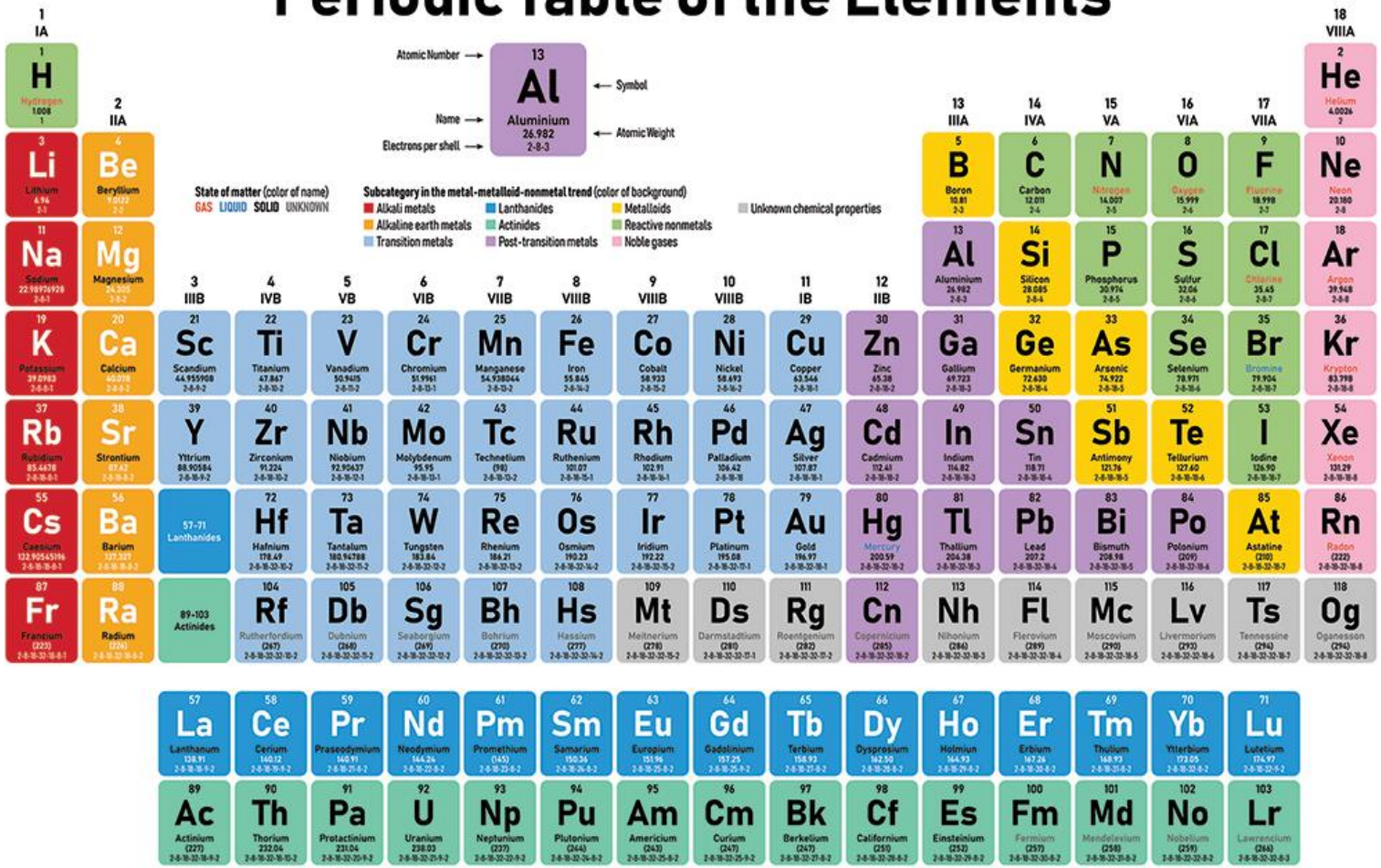


Figure 1.20: Ionization energy versus atomic number

- This general trend increasing ionization energy with atomic number in a given period is due to the fact that as we move across a period, Zeff generally increases so atomic radii become smaller.
- As a result, the attraction between the nucleus and the outer electrons increases, so an electron becomes more difficult to remove.

Periodic Table of the Elements



- Small deviations from this general trend occur. A Group IIIA element (ns^2np^1) has a smaller ionization energy than the preceding Group IIA element (ns^2).
- Apparently, the np electron of the Group IIIA element is more easily removed than one of the ns electrons of the preceding Group IIA element.

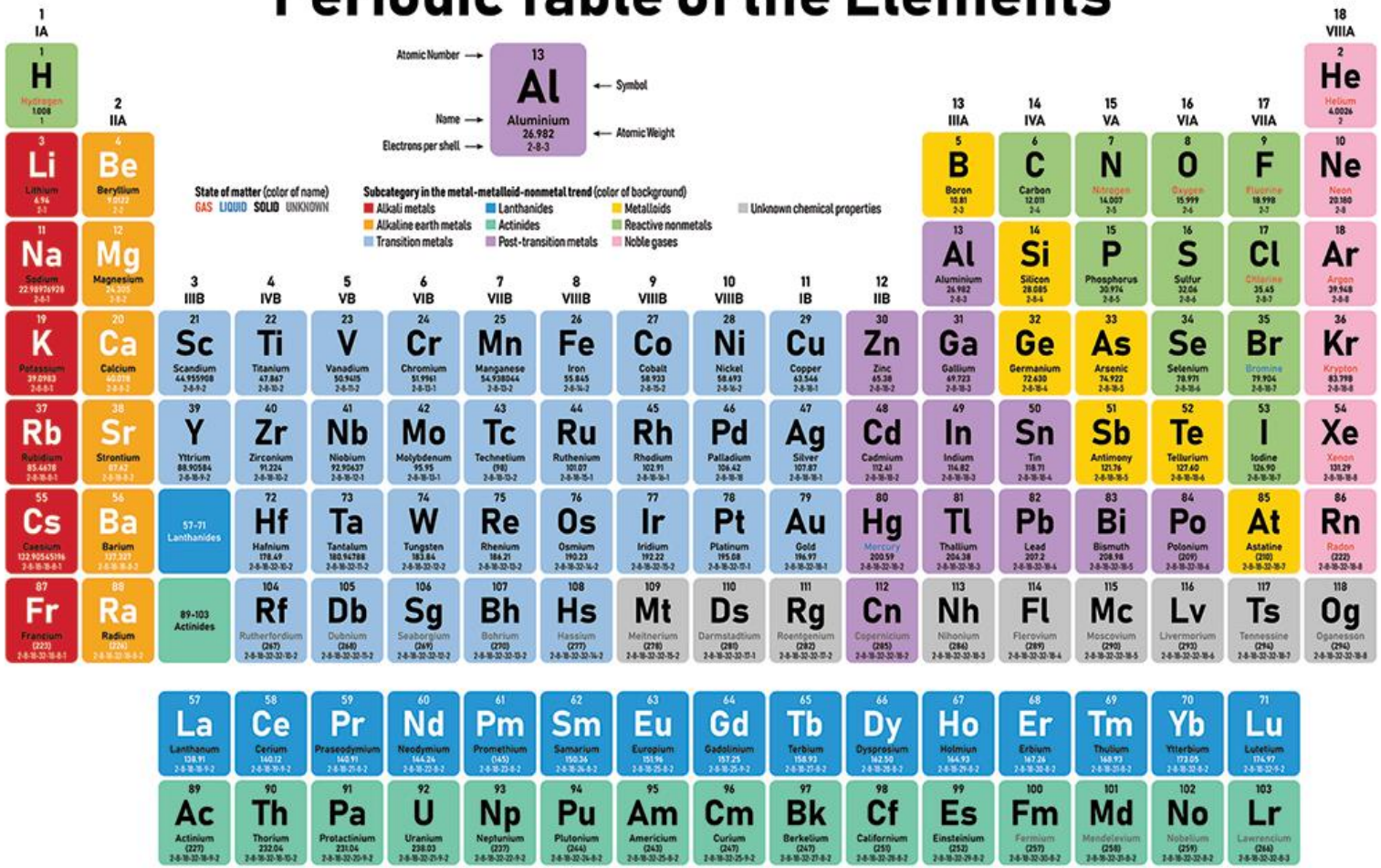
- Also note that a Group VIA element (ns2np4) has a smaller ionization energy than the preceding Group VA element.
- As a result of electron repulsion, it is easier to remove an electron from the doubly occupied np orbital of the Group VIA element than from a singly occupied orbital of the preceding Group VA element.

Exercise 1.13

1. Choose the element with the higher ionization energy from each pair:
   a. As or Bi b. As or Br c. Al or In d. K or Ge
2. The first and second ionization energies of potassium, K, are 419 kJ mol^{-1} and 3052 kJ mol^{-1} and those of calcium, Ca, are 590 kJ mol^{-1} and 1145 kJ mol^{-1}, respectively. Compare their values and comment on the differences.
3. Based on their positions in the periodic table, predict which atom of the following pairs will have the larger first ionization energy:
   a. Ga or Ge b. Br or Sb c. K or Cr d. Mg or Sr e. O or Ne
4. Name the period 3 element with the following ionization energies (in kJ/mol), and write its electron configuration:

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
1012	1903	2910	4956	6278	22,330

Periodic Table of the Elements



Electron Affinity (EA)

- The electron affinity is the energy change for the process of adding an electron to a neutral atom in the gaseous state to form a negative ion:

$$\text{Atom (g)} + e^- \longrightarrow \text{Ion}^- \text{(g)} \qquad \Delta E = EA_1$$

- An electron approaching a neutral atom experiences an attraction for the positively charged nucleus.
- Repulsion of the incoming electron by electrons already present in the atom tends to offset this attraction.
- Still, in many cases the incoming electron is absorbed by the atom and energy is evolved in the process.

- Thus, **first electron affinity (EA1)** is usually negative.
- The **second electron affinity (EA2)** , however, is always positive because energy must be absorbed to overcome electrostatic repulsions and add another electron to a negative ion.
- For example, the EA1 and EA2 of an oxygen atom can be written as:

$$O(g) + e^- \rightarrow O^-(g) \qquad EA_1 = -141 \text{ kJ mol}^{-1}$$

$$O^-(g) + 1e^- \rightarrow O^{2-}(g) \qquad EA_2 = +744 \text{ kJ mol}^{-1}$$

IA (1)	IIA (2)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
H -72.8							He (0.0)
Li -59.6	Be ≤0	B -26.7	C -122	N +7	O -144	F -328	Ne (+29)
Na -52.9	Mg ≤0	Al -42.5	Si -134	P -72	S -200	Cl -349	Ar (+35)
K -48.4	Ca -2.37	Ga -28.9	Ge -119	As -78.2	Se -195	Br -325	Kr (+39)
Rb -46.9	Sr -5.03	In -28.9	Sn -107	Sb -103	Te -190	I -295	Xe (+41)
Cs -45.5	Ba -13.95	Ti -19.3	Pb -35.1	Bi -91.3	Po -183	At -270	Rn (+41)

Figure 1. 21: Electron affinities of the main-group elements (in kJ/mol)

- **Electron affinities, EA, have a periodic variation, just as atomic radii and ionization energies do.**
- **Broadly speaking, the general trend is toward more negative electron affinities from left to right in any period.**

- **Note that the Group VIA and Group VIIA elements have the largest negative electron affinities of any of the main-group elements.**
- **The trend in going across a period is rather clear but there is no simple trend in going down a column of elements.**

- In most cases, the added electron goes into an energy sublevel that is already partly filled.
- For Group IIA and VIIIA atoms, however, the added electron would be required to enter a significantly higher energy level, the np level for the Group IIA atoms and the s level for the next principal level for the Group VIIIA atoms. In these cases, a stable anion does not form.

Electronegativity

- Electronegativity indicates the extent of attraction by which the electrons of the bond pair are attracted by an atom linked by this bond.
- Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. This is known as the **Pauling scale.**

Table 1.4: (a) Electronegativity values (on Pauling scale) across the periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 1.4: (b) Electronegativity values (on Pauling scale) down a group

Atom (Group IA)	Electronegativity value	Atom (Group VIIA)	Electronegativity value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

- Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decreases down a group (say from fluorine to astatine) in the periodic table.
- The attraction between the valence electrons and the nucleus increases as the atomic radius decreases in a period.
- The electronegativity also increases.
- On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization energy.

Metallic Character

- Metallic character refers to the chemical properties associated with elements classified as metals.
- These properties arise from the elements, ability to lose electrons.
- Metallic character decreases as you move across a period in the periodic table from left to right.
- This occurs as atoms more readily accept electrons to fill a valence shell than lose them to remove the unfilled shell.

- **Metallic character increases as you move down an element group in the periodic table.**
- **This is because electrons become easier to lose as the atomic radius increases, where there is less attraction between the nucleus and the valence electrons because of the increased distance between them.**

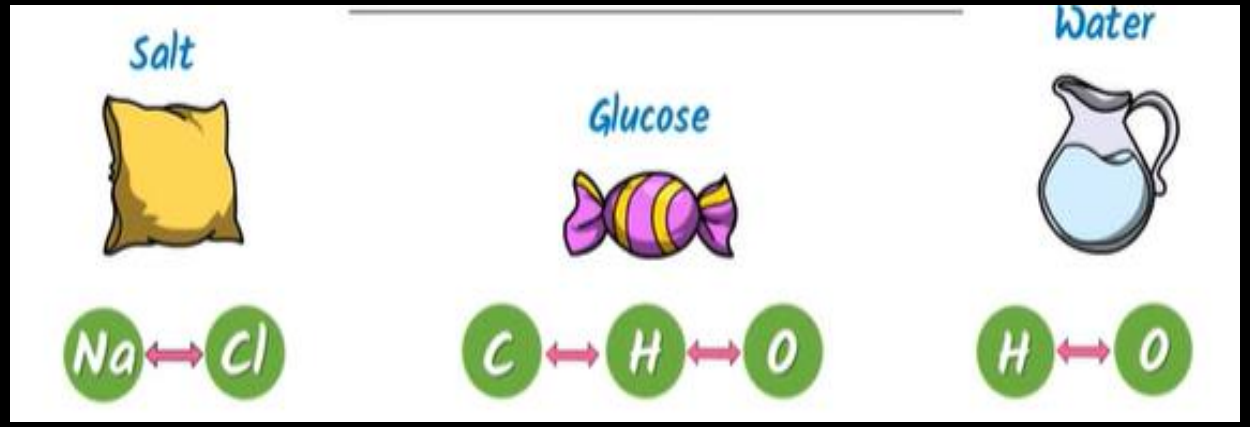
Advantage of Periodic Classification of the element

- The classification of elements is based on the atomic number, which is a fundamental property of an element.
- Isotopes are averaged in one place, as the classification is on the basis of atomic number (For example, chlorine (atomic number 17) is given the atomic mass 35.5.)
- It explains the periodicity of the properties of the elements and relates them to their electronic configurations.

- **The position of the elements that were misfits on the basis of mass number (anomalous pairs like argon and potassium) could be justified on the basis of atomic number.**
- **The lanthanides and actinides are placed separately at the bottom of the periodic table.**
- **The table is a simple, systematic and an easy way of remembering the properties of various elements, as it is based on the electronic configuration.**

Unit 2
Chemical Bonding

- **Chemical bond** is the attractive force which holds atoms, ions, and molecules together
- Since these forces of attraction are intramolecular forces, they have an effect on the chemical properties as well as the physical properties of the chemical.

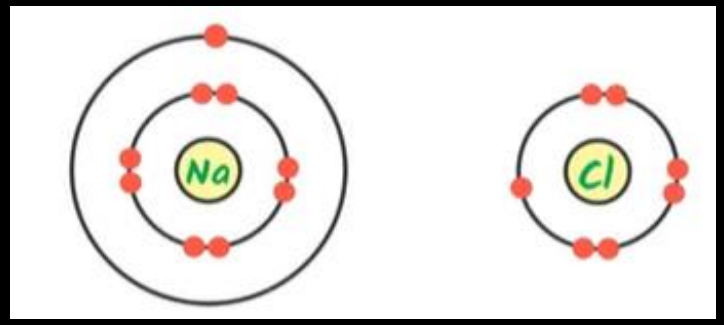


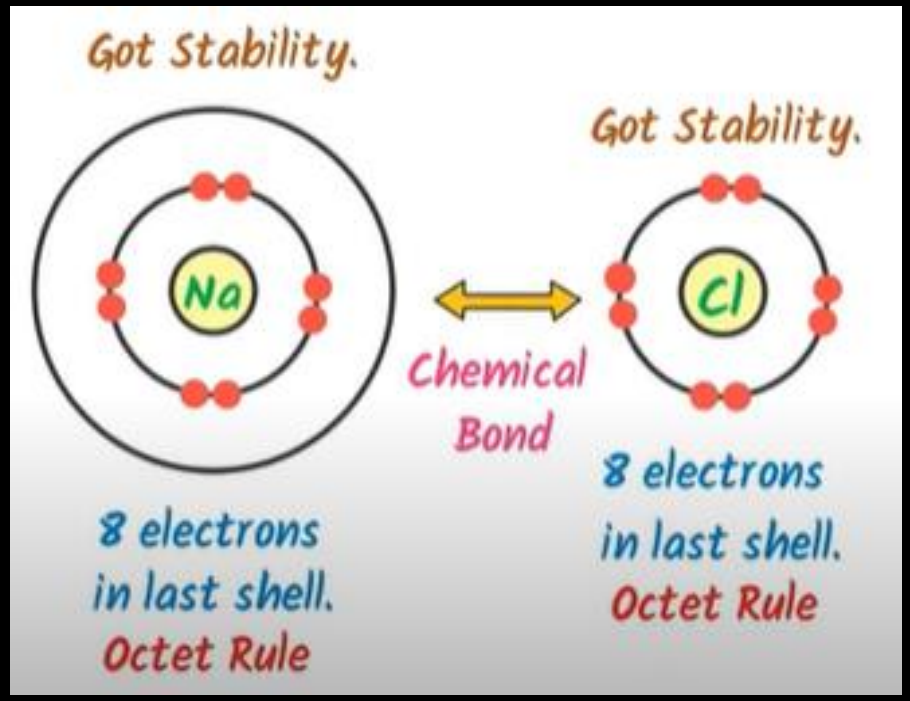
Why atoms form chemical bonds?

- atoms combine in order to achieve / get stability

How can we measure the stability of atom?

- Atoms containing less than eight electrons in their outermost shell are unstable.
- To attain stability, atoms tend to have eight electrons in their valence shells. This rule is called **Octet rule**





Octet rule

Octet rule the rule states that Atoms tend to gain or lose electrons or share electrons until they have achieved an outer shell that contains an octet of electrons (eight electrons).

- All noble gases except helium (1s2) have ns^2np^6 electron configurations (where n indicates the highest occupied shell).
- The noble gases are quite unreactive because they have very stable electron configurations, as reflected by their high ionization energies and low electron affinities.
- Do you know any compound whose central atom does not obey the octet rule?

Type of chemical bonding

- In general, there is a gradual change from metallic to non-metallic character as you move from left to right across a period and from bottom to top within most groups in the periodic table.
- Accordingly, atoms can combine to form three types of bond:

  Metal with non-metal (ionic bond),

  Non-metal with non-metal (covalent bond), and

  Metal with metal (metallic bond).

Ionic bond

- An ionic bond is formed by the electrostatic attraction between positive and negative ions.
- The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other.
- The atom that loses electrons becomes a cation (positive ion), and the atom that gains electrons becomes an anion(negative ion).

Example 2.1

The formation of NaCl from sodium and chlorine can be explained as:

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

$$[Ne]3s^{1} \qquad [Ne]$$

$$Cl + e^{-} \rightarrow Cl^{-}$$

$$[Ne]3s^{2}3p^{5} \qquad [Ne]3s^{2}3p^{6} \text{ or } [Ar]$$

$$Na^{+} + Cl^{-} \rightarrow NaCl \text{ or } Na^{+}Cl^{-}$$

- The bond formed, as a result of the electrostatic attraction between the positive and negative ions is called the **electrovalent bond or ionic bond**.
- Note: Ionic compounds are usually formed when **metal cations bond** with **non-metal anions**.

What about an ionic compound containing an ammonium ion?

Exercise 2.1

1. Explain the formation of bonds in the following pairs of elements:
   a. potassium and chlorine
   b. magnesium and oxygen
   c. sodium and oxygen
2. Which of the following elements will form an ionic bond with chlorine, why?
   a. calcium b. carbon c. oxygen d. silicon
3. Identify the species found in the following ionic compounds: $CaCl_2$, MgO, and Al_2O_3. From this what can you conclude about the formation of these compounds?
4. Why do elements located on the opposite sides of the periodic table tend to form ionic bonds?

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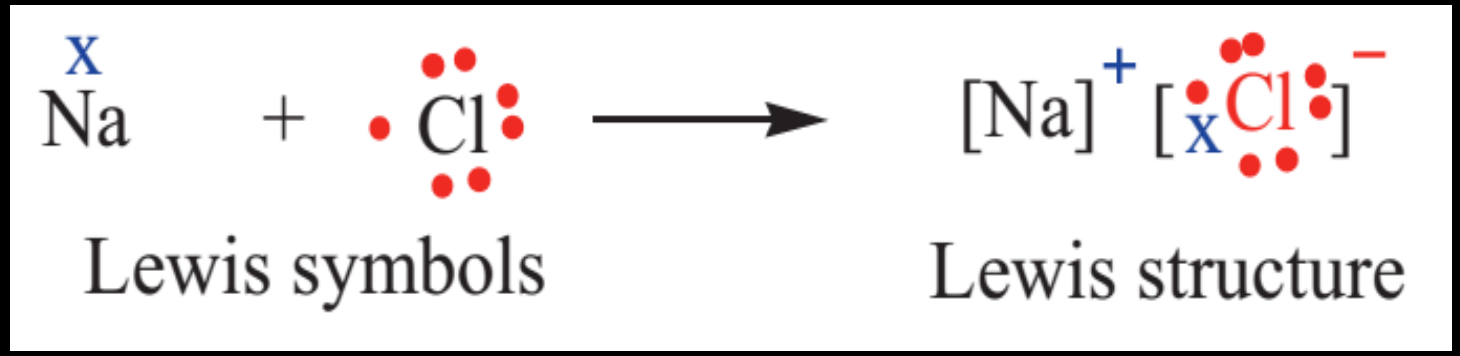
4. Why do elements located on the opposite sides of the periodic table tend to form ionic bonds?

Lewis electron dot symbol

- The American Chemist Gilbert N. Lewis (1875–1946) developed a special set of symbols for his theory.
- A Lewis symbol consists of a chemical symbol to represent the nucleus and core (inner-shell) electrons of an atom, together with dots placed around the symbol to represent the valence (outer-shell) electrons.



- A Lewis structure is a combination of Lewis symbols that represents either the transfer or the sharing of electrons in a chemical bond.
- For example, the formation of sodium chloride from sodium and chlorine atoms can be represented as:



Exercise 2.2

1. Use Lewis electron-dot symbols to depict the formation of lithium and fluoride ions from the atoms and determine the formula of the compound.
2. Apply the Lewis formula to illustrate the formation of calcium chloride from calcium and chlorine atoms.
3. Write Lewis structures for the following compounds:

   a. BaO b. potassium oxide c. aluminum oxide
4. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions:

   a. K and S b. Ca and O c. Al and N

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Formation of Ionic Compound

- You may be surprised to learn that the electron-transfer process actually absorbs energy!
- So why does it occur? As you will see, the reason ionic substances exist at all is because of the enormous release of energy when the ions come together and form a solid.

- **Consider just the electron-transfer process for the formation of lithium fluoride, which involves two steps:**

1. A gaseous Li atom loses an electron (IE_1):

$$Li(g) \rightarrow Li^+(g) + e^- \qquad IE_1 = +520\ kJ$$

2. A gaseous F atom gains an electron lost by Li atom (EA):

$$F(g) + e- \rightarrow F^-(g) \qquad EA = -328\ kJ$$

Note that the two-step electron-transfer process by itself requires energy:

$$Li(g) + F(g) \rightarrow Li^+(g) + F^-(g) \qquad IE_1 + EA = +192\ kJ$$

- The total energy needed for ion formation is even greater than this because metallic lithium and diatomic fluorine must first be converted to separate gaseous atoms, which also requires energy.
- Despite this, the standard heat of formation (ΔH_f°) of solid LiF is –617 kJ/mol; that is, 617 kJ is released when 1 mol of LiF(s) forms from its elements.

- **That is, there must be some exothermic energy component large enough to overcome the endothermic steps. These are:**

- When 1 mol of $Li^+(g)$ and 1 mol of $F^-(g)$ form 1 mol of LiF (g):

  $Li^+(g) + F^-(g) \rightarrow LiF(g) \qquad \Delta H° = -755\ kJ$

- When the gaseous ions coalesce into a crystalline solid. That occurs because each ion attracts others of opposite charge:

  $Li^+(g) + F^-(g) \rightarrow LiF(s) \qquad \Delta H° = -1050\ kJ$

- When 1 mol of $Li^+(g)$ and 1 mol of $F^-(g)$ form 1 mol of LiF (g):

$$Li^+(g) + F^-(g) \rightarrow LiF(g) \qquad \Delta H° = -755 \text{ kJ}$$

- When the gaseous ions coalesce into a crystalline solid. That occurs because each ion attracts others of opposite charge:

$$Li^+(g) + F^-(g) \rightarrow LiF(s) \qquad \Delta H° = -1050 \text{ kJ}$$

- **The negative of this value, 1050 kJ, is the lattice energy of LiF.**
- **The lattice energy (U) is the enthalpy change that occurs when 1 mol of ionic solid separates into gaseous ions.**
- **It indicates the strength of ionic interactions, which influence melting point, hardness, solubility, and other properties.**

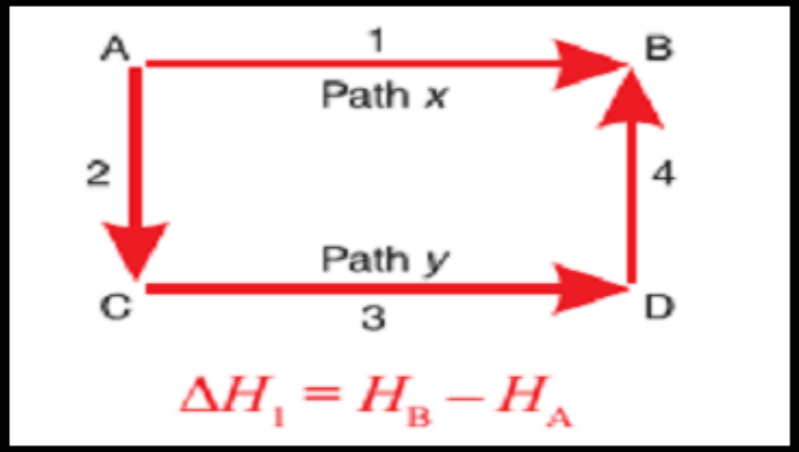
Lattice Energies from the Born–Haber Cycle

- Finding the lattice energy of an ionic solid by experiment is difficult.
- However, this quantity can be found indirectly using the Born–Haber cycle.
- The reasoning is based on Hess's law, which states that an overall reaction's enthalpy change is the sum of the enthalpy changes for the individual reactions that make it up:

$$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

Hess's Law

Hess's law states that if different processes are used to bring about the same change the enthalpy changes during these processes are the same.



- Consider the Born-Haber cycle for the formation of NaCl.
- In one route, NaCl(s) is formed directly from Na(s) and ½Cl2(g); ΔH_f° –411 kJ mol^{-1}

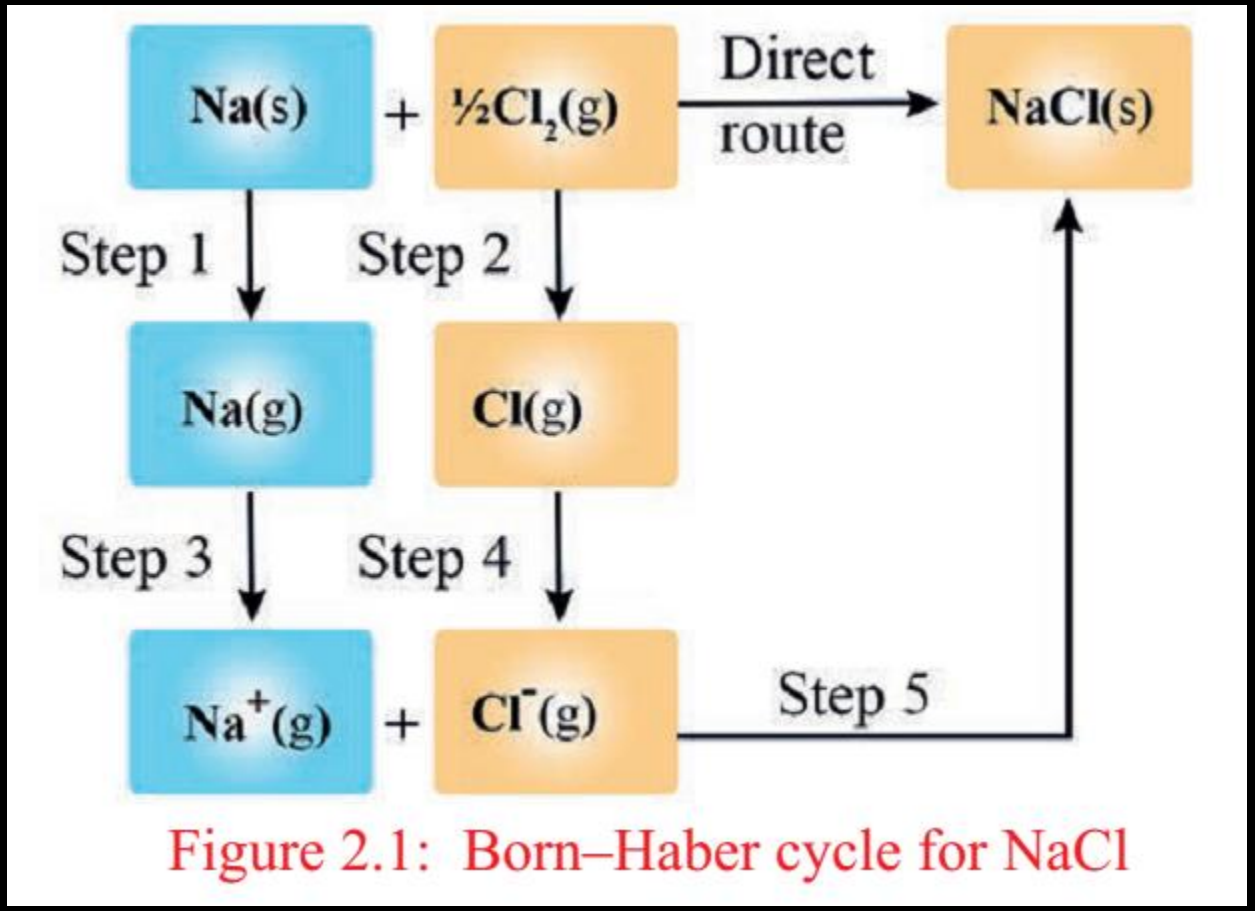


Figure 2.1: Born–Haber cycle for NaCl

- **The second route consists of the following five steps, along with the enthalpy change for each.**

Step1: Metallic sodium is vaporized to a gas of sodium atom:

$$Na\ (s) \rightarrow Na\ (g) \qquad \Delta H^\circ_{step1} = +\ 108\ kJ\ mol^{-1}$$

Step 2: Chlorine molecules are dissociated to atoms:

$$\tfrac{1}{2}Cl_2\ (g) \rightarrow Cl\ (g) \qquad \Delta H^\circ_{step2} = \tfrac{1}{2}\text{ bond energy of } Cl_2$$

$$= \tfrac{1}{2}\ (240\ KJ) = +\ 120\ kJ\ mol^{-1}$$

Step 3: Sodium atoms are ionized to Na^+ ions:

$$Na\ (g) \rightarrow Na^+\ (g) + e^- \qquad \Delta H^\circ_{step3} = IE_1 = +\ 496\ kJ\ mol^{-1}$$

Step 4: Formation of chloride ion:

$$Cl\ (g) + e^- \rightarrow Cl^-\ (g) \qquad \Delta H^\circ_{step4} = EA = -349\ kJ\ mol^{-1}$$

- **Step 5: Formation of NaCl(s) from ions. The ions Na^+ and Cl^- combine to give solid sodium chloride whose enthalpy changes (the lattice energy) is unknown:**

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^\circ_{step5} = U \text{ (lattice energy)} = ?$$

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^\circ_{step5} = U \text{ (lattice energy)} = ?$$

We know the enthalpy formation ($\Delta_f H^\circ$) of NaCl (Direct route) and equals −411 kJ mol^{-1}. Therefore, we can calculate the lattice energy using *Hess's low*: Solving for U_{NaCl} gives:

$$U_{NaCl} = \Delta_f H^{\circ -} (\Delta H^\circ_{step1} + \Delta H^\circ_{step2}\, \Delta H^\circ_{step3} + \Delta H^\circ_{step4})$$

$$= -411 \text{ kJ mol}^{-1} - [108 \text{ kJ mol}^{-1} + 120 \text{ kJ mol}^{-1} + 496 \text{ kJ mol}^{-1} + (-349 \text{ kJ mol}^{-1})]$$

$$= -786 \text{ kJ mol}^{-1}$$

Note: *Ionic solids exist only because the lattice energy exceeds the energy required for the electron transfer.*

Exercise 2.3

1. Draw a Lewis electron-dot symbol for each atom:

   a. Rb b. As c. I

2. Give the group number and general electron configuration of an element with each electron-dot symbol:

   a.  b. 

3. How does the lattice energy of an ionic compound depend on the charges and sizes of the ions?

4. Use condensed electron configurations and Lewis electron dot symbols to depict the monatomic ions formed from each of the following atoms, and predict the formula of the compound the ions produce.

a. Ba and Cl b. Sr and O c. Al and F d. Rb and O

5. Identify the main group to which X belongs to in each ionic compound formula:

a. X_2O_3 b. XCO_3 c. Na_2X

6. For each pair, choose the compound with the lower lattice energy, and explain your choice:

a. CaS or BaS b. NaF or MgO c. LiCl or CsCl d. BaS or CsCl

Factors Affecting the Formation of Ionic Bonds

- Ionization energy (IE)
- Electron affinity (EA)
- Lattice energy

1.Ionization energy (IE):

- The lesser the ionization energy, the greater is the ease of the formation of a cation.
- Thus, low ionization energy of metallic elements such as alkali and alkaline earth metals favours the formation of an ionic bond.

2.Electron affinity (EA):

- A higher electron affinity favours the formation of an anion.
- Generally, the elements having higher electron affinity such as halogens favour the formation of an ionic bond.
- Thus, low ionization energy of a metal atom and high electron affinity of a non-metal atom facilitate the formation of an ionic bond between them.

3.Lattice energy

- When a cation and an anion come closer, they get attracted to each other due to the electrostatic (coulombic) force of attraction.
- The electrostatic force of attraction between oppositely-charged ions release a certain amount of energy and an ionic bond is formed.
- If the coulombic attraction forces are stronger, then more energy gets released and a more stable or a stronger ionic bond is formed.

- Larger lattice energy would favour the formation of an ionic bond.
- Lattice energy thus is a measure of coulombic attractive force between the combining ions.
- The lattice energy (U) of an ionic compound depends directly on the product of the ionic charges (q1× q2), and inversely on the distance (r) between them:

$$U \propto \frac{q_1 \times q_2}{r}$$

$$U \propto \frac{q_1 \times q_2}{r}$$

- Where q_1 and q_2 are the charges on +ve and –ve ions respectively, and r is the distance between the charges q_1 and q_2 .
- Thus, small ions having a higher ionic charge will have a larger lattice energy.
- If the total energy released is more than that which is absorbed, then the formation of an ionic compound is favoured

Exceptions to the octet rule in ionic compound

- Why does the octet rule work well only for the representative metals (Groups IA, IIA) and the non-metals, but not for the transition elements?

Less than Octet (Central Atom is Deficient of Electrons)

- Ions of some elements which are near to helium in the periodic table do not obey the octet rule.
- The tendency of these atoms (H, Li, Be and B) is to attain an arrangement of two electrons like the noble gas He, which is also a stable configuration.
- The hydride ion (H^-), lithium ion (Li^+), beryllium ion (Be^{2+}) and boron ion (B^{3+}) are isoelectronic with He.

Can you give some compounds that contain less than eight electrons around the central atom?

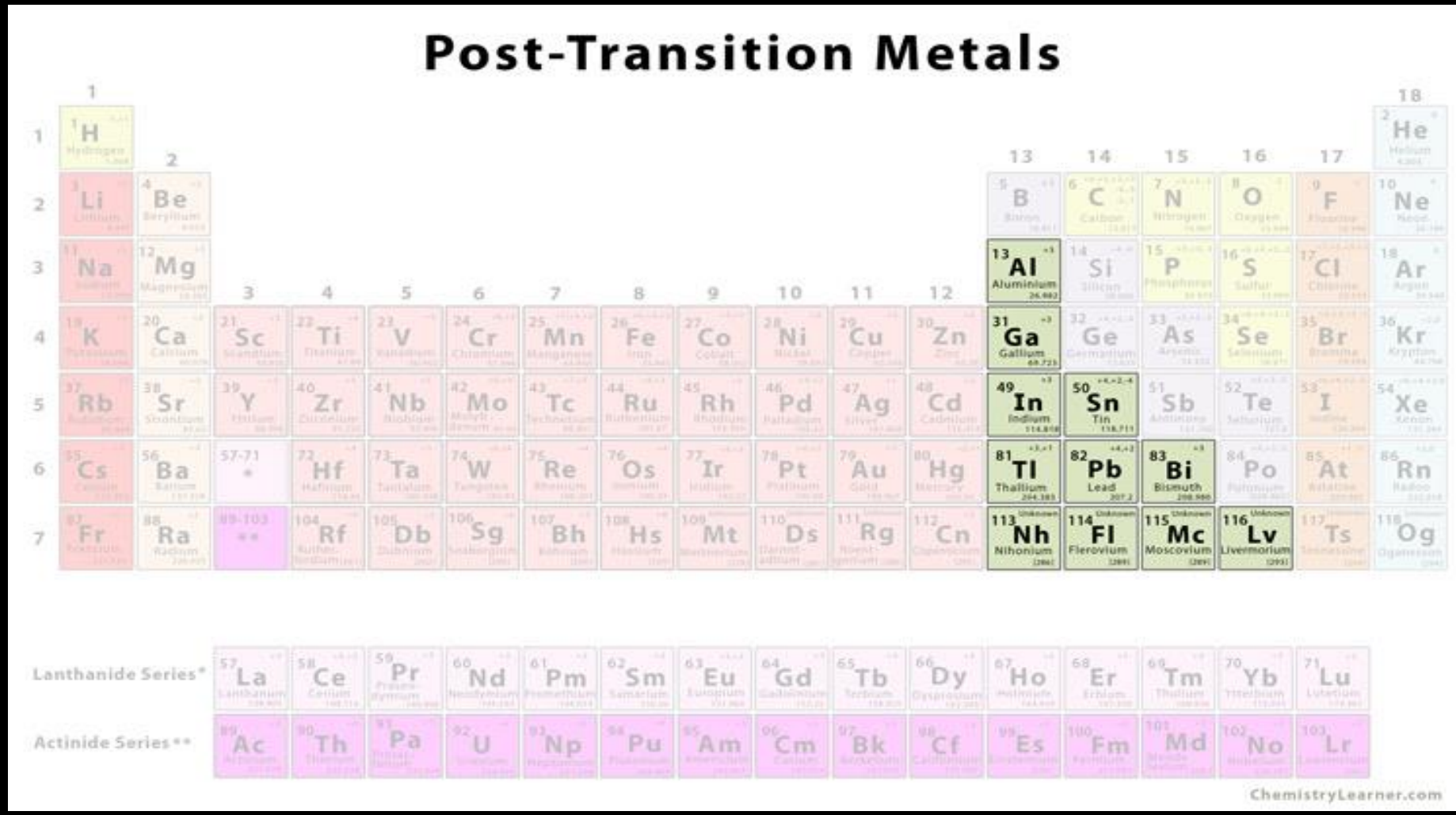
- **Boron trifluoride (BF_3), Beryllium hydride (BeH_2), Aluminum chloride ($AlCl_3$)**

- Although atoms with less than an octet may be stable, they will usually attempt to form a fourth bond to get eight electrons.
- For example BF_3 is stable, but it will form BF_4^- when possible.

More than Octet (18-Electron Rule)

- The ions of some transition and post-transition elements do not usually obey the octet rule.
- For transition metals, the 18-electron rule replaces the octet rule, due to the involvement of d orbitals of these atoms.

Post-Transition Metals



- **Note that when these atoms form positive ions, electrons are always lost first from the shells with the highest value of the principal quantum number (n).**
- **Consider the electron configurations of the ions of the transition elements iron and zinc and the post-transition elements gallium and tin.**

- A stable ion of iron with valence shell electron configuration is $3s^2 3p^6 3d^5$ which is not isoelectronic with a noble gas.
- Fe^{2+} is a well-known stable ion with a valence shell electron configuration 3s23p63d6 which is not isoelectronic with any of the noble gases.

Electron Configurations of Iron:

$_{26}Fe$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

$_{26}Fe^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

$_{26}Fe^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Electron configurations of zinc:

$_{30}Zn: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10} = [Ar]\ 4s^2 3d^{10}$

$_{30}Zn^{2+}: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10} = [Ar] 3d^{10}$

Zn^{2+} is also not isoelectronic with any of the noble gases.

Electron configurations of gallium:

The post-transition element gallium (Ga) loses electrons first from the 4*p* orbital and then from the 4*s* orbital to from a Ga^{3+} ion as

$$_{31}Ga: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^{10} 4p^1 = [Ar]\ 4s^2 3d^{10} 4p^1$$

$$_{31}Ga^{3+}: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} = [Ar] 3d^{10}$$

- On closely examining the electron configurations of Zn^{2+} and Ga^{3+}, we will realize that ions have completely-filled outer subshells and a noble gas core.
- Their valance electron configuration can be generally represented as $ns^2np^6nd^{10}$.

Exercise 2.4

1. From which orbital (s) do the heavier post-transition elements such as Pb and Sn lose electrons?
2. Can you write the electron configurations of Sn, Sn^{2+}, and Sn^{4+}? Check if any of these tin ions are isoelectronic with any of the noble gases.
3. Which group of ions of elements, in general, show more than the octet (18-electron rule)?

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3. Which group of ions of elements, in general, show more than the octet (18-electron rule)?

Covalent Bond Molecular Geometry

Formation of Covalent Bonding

- Consider the formation of a hydrogen molecule (H2).
- When two isolated hydrogen atoms come close together, electrostatic interactions begin to develop between them.
- The two positively charged nuclei repel each other, and the two negatively charged electrons repel each other, but each nucleus attracts both electrons and each electron is attracted to both nuclei (Figure 2.4).

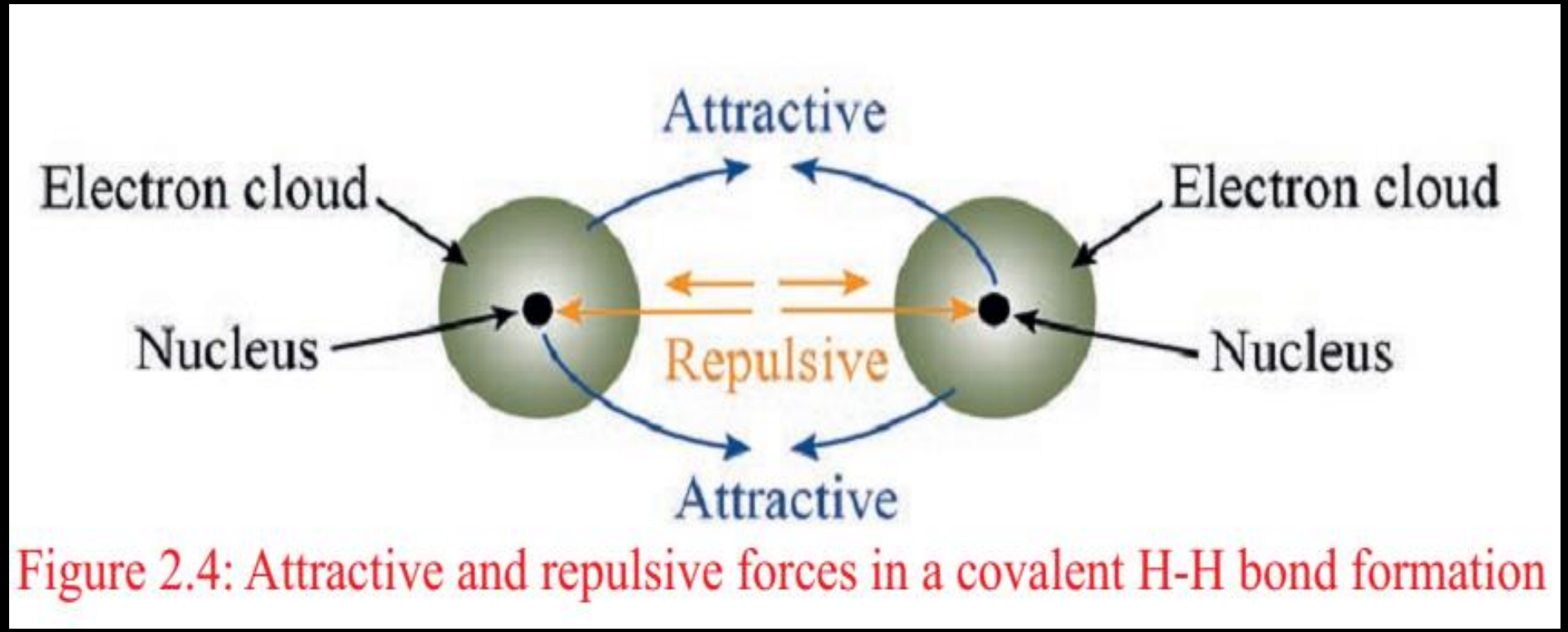
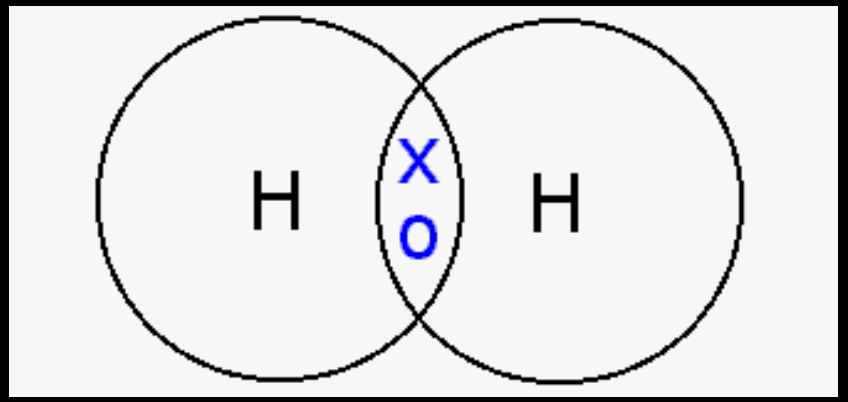
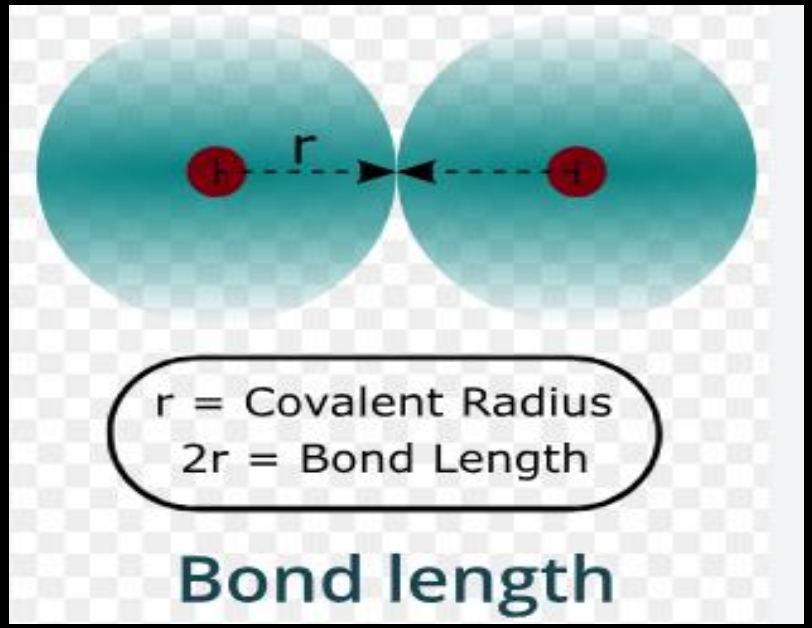


Figure 2.4: Attractive and repulsive forces in a covalent H-H bond formation

- If the attractive forces are stronger than the repulsive forces, a covalent bond is formed, with the two atoms held together and the two shared electrons occupying the region between the nuclei.
- The magnitudes of the various attractive and repulsive forces between nuclei and electrons in a covalent bond depend on how close together the atoms are.
- What happens if the hydrogen atoms are too far apart? What if the hydrogen atoms are too close together?



- There is an optimum distance between nuclei, called the bond length, where net attractive forces are maximized and the H–H molecule is most stable.
- In the H_2 molecule, the bond length is 74 pm.



- **On a graph of energy versus internuclear distance, the bond length is the H–H distance in the minimum energy. This is the most stable arrangement (Figure 2.5)**

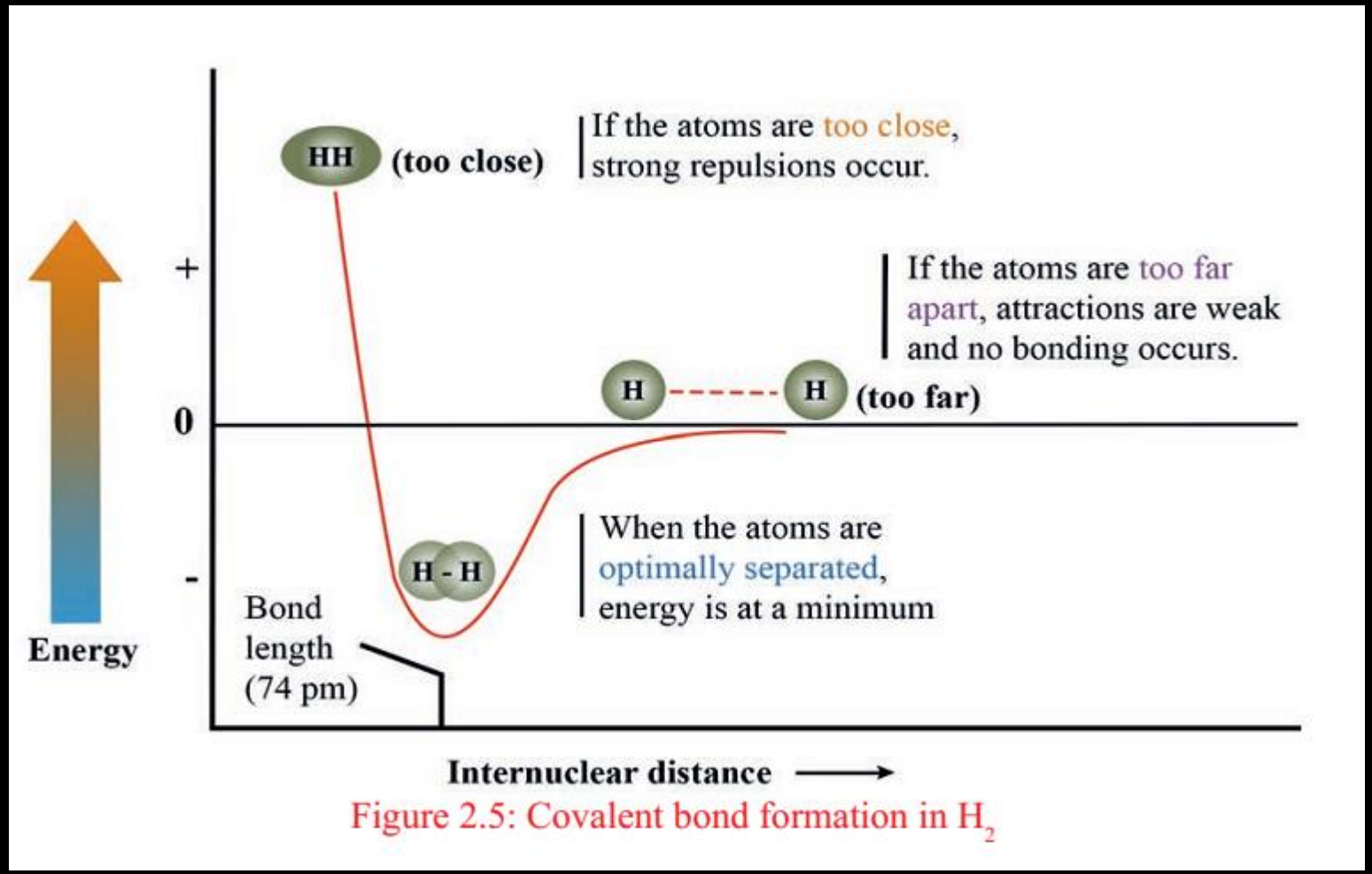


Figure 2.5: Covalent bond formation in H_2

- Therefore, a covalent bond is formed when a pair of electrons is shared between two atoms.
- Formation of a bond always results in greater electron density between the nuclei.
- Some examples of covalent molecules are

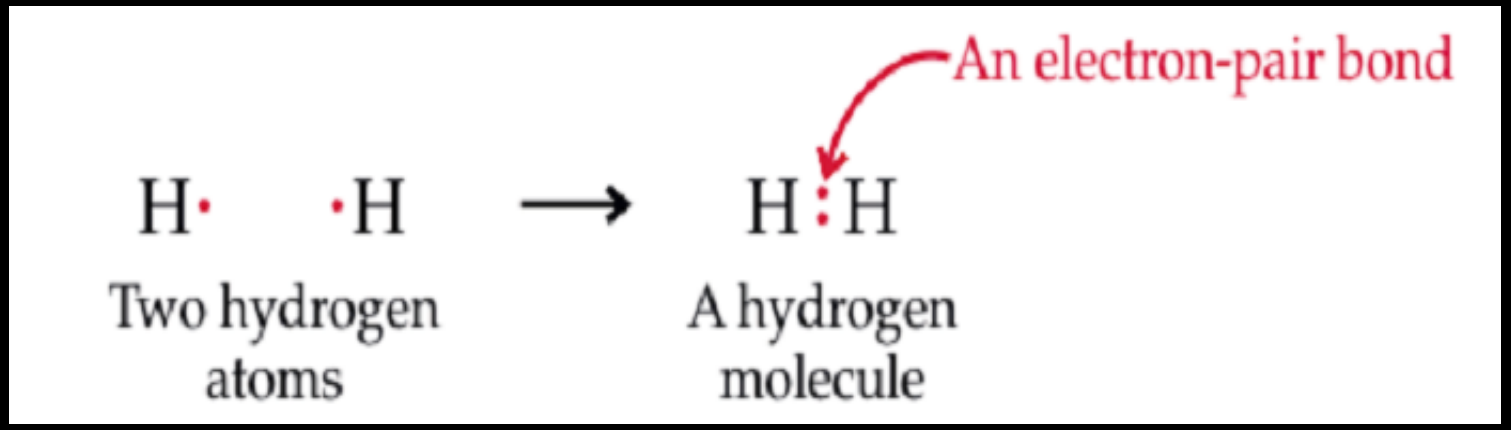
$HCl,\ H_2S,\ C_2H_4,\ N_2,\ CCl_4,\ BCl_3$

- Generally, substances that contain covalent bonds are called **molecules**.

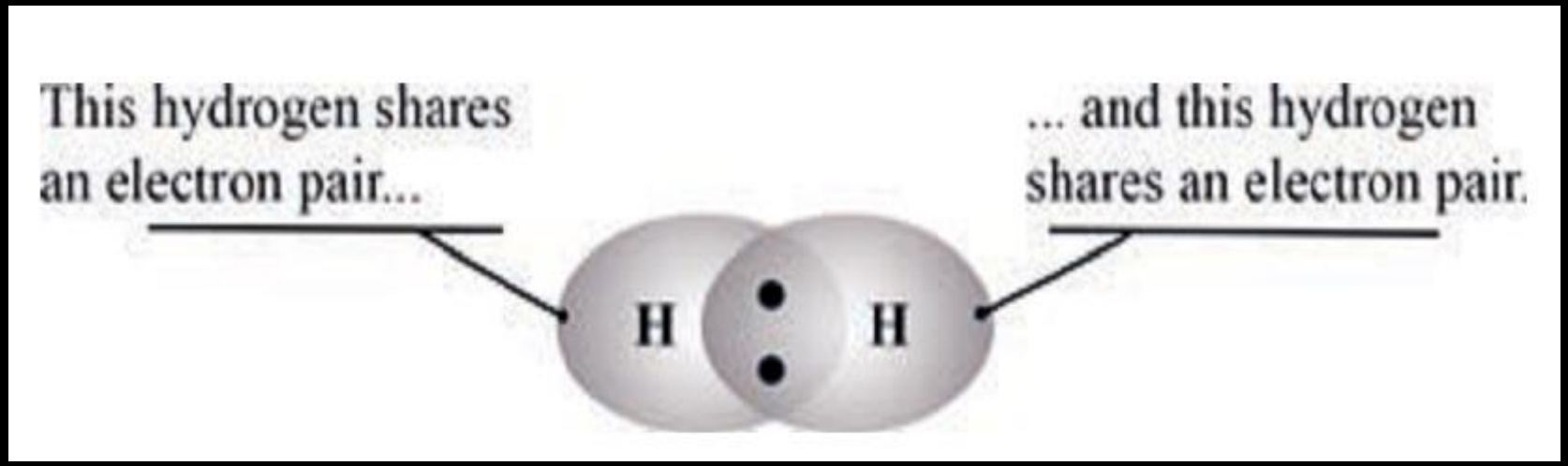
Representation of Covalent Bonds (Drawing Lewis Structures)

The representation of covalent bonding through Lewis symbols and shared electron pairs is called **a Lewis structure**.

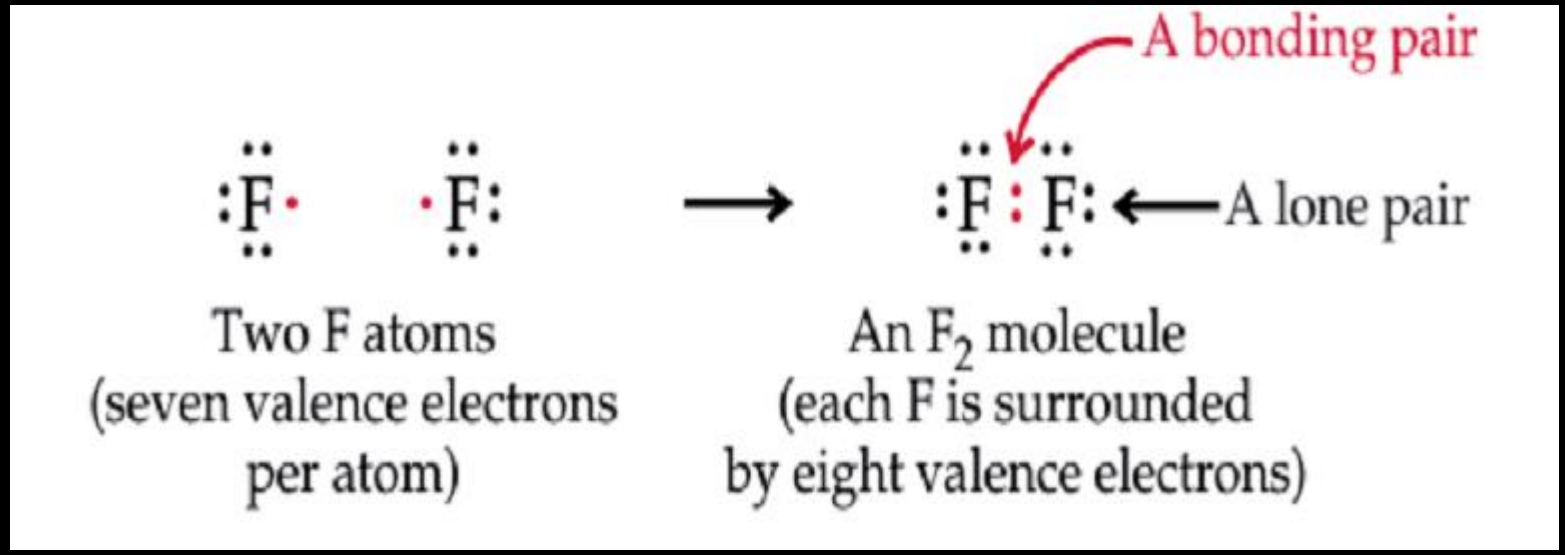
The Lewis structure for a hydrogen molecule formed from hydrogen atoms is:



- By sharing two electrons in a covalent bond, each hydrogen effectively has one electron pair and the stable, $1s^2$ electron configuration of helium.



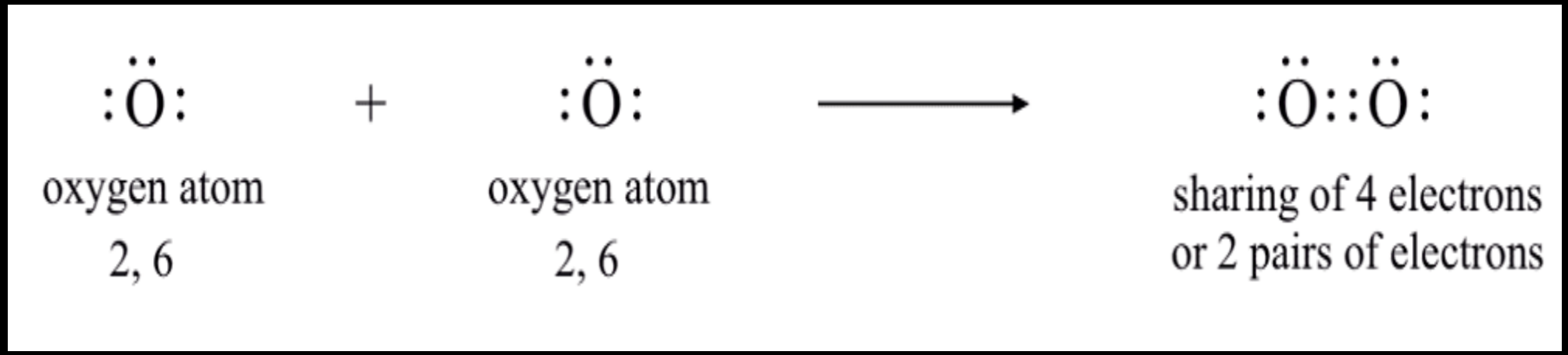
- **Similarly, fluorine has seven valence electrons, and an electron-dot structure for the F_2 molecule shows how a covalent bond can form:**



- The shared pairs of electrons in a molecule are called bonding pairs.
- The other electron pairs that stay with on atom and are not shared are called non-bonding pairs or lone pairs.

Do the fluorine atoms in a fluorine molecule (F2) obey the octet rule?

- **Note that in molecules such as O_2, N_2, and many others, the atoms share more than one pair of electrons, leading to the formation of multiple covalent bonds.**



Types of Covalent Bonds

- Atoms can form different types of covalent bonds.

  single bonds,

  double bonds

  triple bonds.

- In a **single bond** two atoms are held together by one electron pair
- If two atoms share two pairs of electrons, the covalent bond is called a **double bond**.
- A **triple bond** is formed when two atoms share three pairs of electrons

Steps to Writing a Lewis Formula:

- We can write the Lewis formula for a covalent compound of known geometry by using the following steps.

Steps to Writing a Lewis Formula

Step 1. Determine the total number of valence electrons.

For a **polyatomic anion**, which has one or more extra electrons, add one electron for each unit of negative charge.

Example: CO_3^{2-}

- For a **polyatomic cation**, which is missing one or more electrons, subtract one electron for each unit of positive charge.

Example: NH_4^+

Step 2. Write the skeletal structure.

- **The most electropositive atom usually occupies the central position. Connect bonded atoms with an electron-pair bond (a dash).**
- **Hydrogen is an exception; it is always a terminal atom, even when bonded to a more electronegative atom.**
- **Example:CO_3^{2-}** **Example:NH_4^+**

Step 3. Place electron pairs around terminal atoms so that each (except hydrogen) has an octet.

- Assign any remaining electrons as lone pairs around the central atom.

Example:CO_3^{2-}

Example:NH_4^+

Step 4: If at this stage, a central atom has fewer than eight electrons, a multiple bond(s) is likely.

- Move one or more lone-pair of electrons from a terminal atom(s) to a region between it and the central atom to form a double or a triple bond.
- Example: CO_3^{2-}

Example 2.2

Write the Lewis structure for nitrogen trifluoride (NF_3) in which all three F atoms are bonded to the N atom.

Exercise 2.5

1. Determine the total number of valence electrons for the following:

   a. CO_2 b. SO_4^{2-} c. NH_4^+ d. N_2O_4

2. Write a Lewis structure of

   a. nitrogen trichloride, NCl_3 b. chlorate ion, ClO_3^-

   c. phosphonium ion, PH_4^+

3. Draw a Lewis structure for SF_4 and HCOOH (formic acid).

4. Which of the following atoms O, He, F, H, and P cannot be used as a central atom in a Lewis structure? Explain.

5. Write a Lewis structure for carbonyl sulphide, COS.

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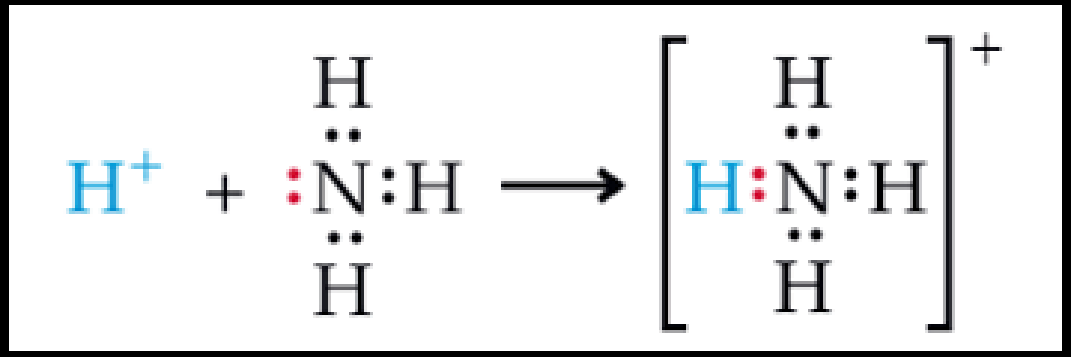
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Coordinate-Covalent Bonding

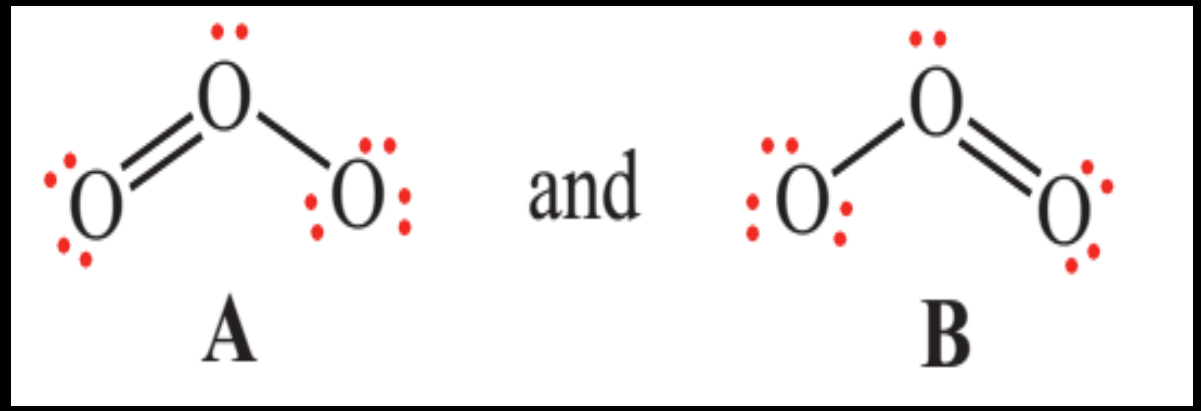
- Most covalent bonds form when two atoms each contribute one electron.
- However, bonds can also form when one atom donates both electrons (a lone pair) to another atom that has a vacant valence orbital.
- Such kind of bonds is called **coordinate covalent bonds or dative bonds.**
- The ammonium ion (NH_4^+), for example, forms when the lone-pair electrons from the nitrogen atom of ammonia, NH_3, bond to H^+.

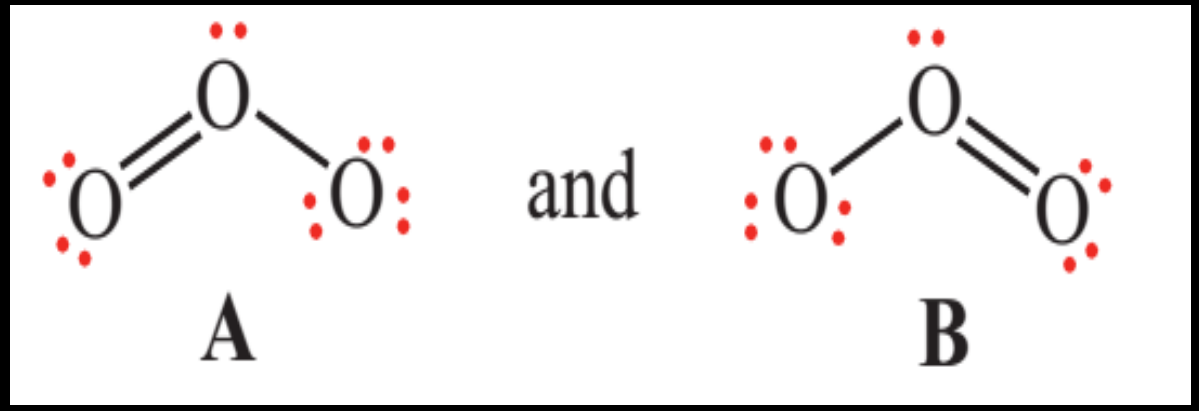


- Some examples of molecules which contain coordinate-covalent bonds include NH_3, BCl_3, H_3O^+ and $AlCl_4^-$.

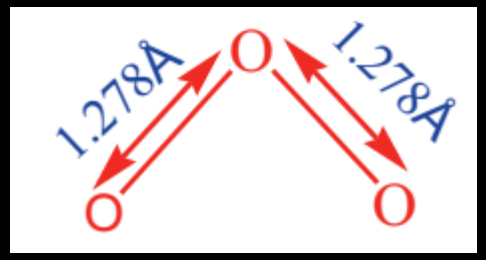
Resonance Structures

- Sometimes more than one valid Lewis structure is possible for a given molecule.
- The molecule is shown more correctly with two Lewis structures, called resonance structures (or resonance forms), and a two headed resonance arrow (↔) between them.

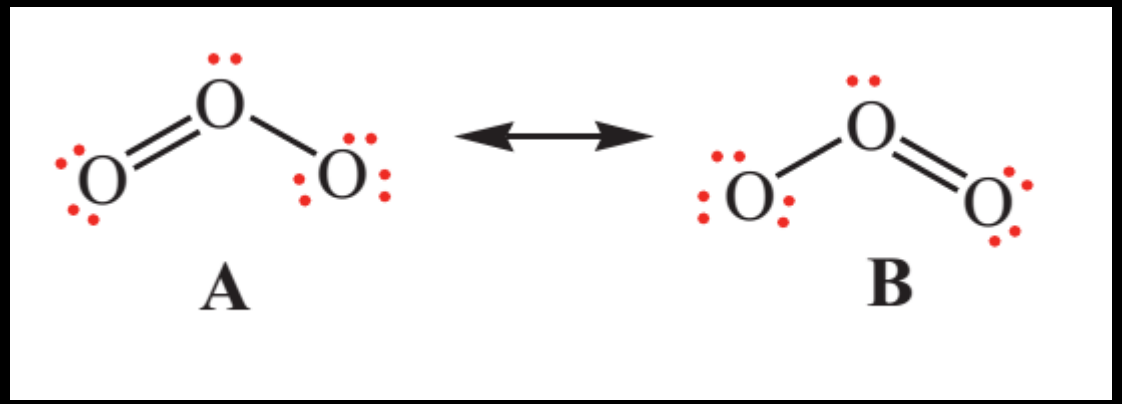


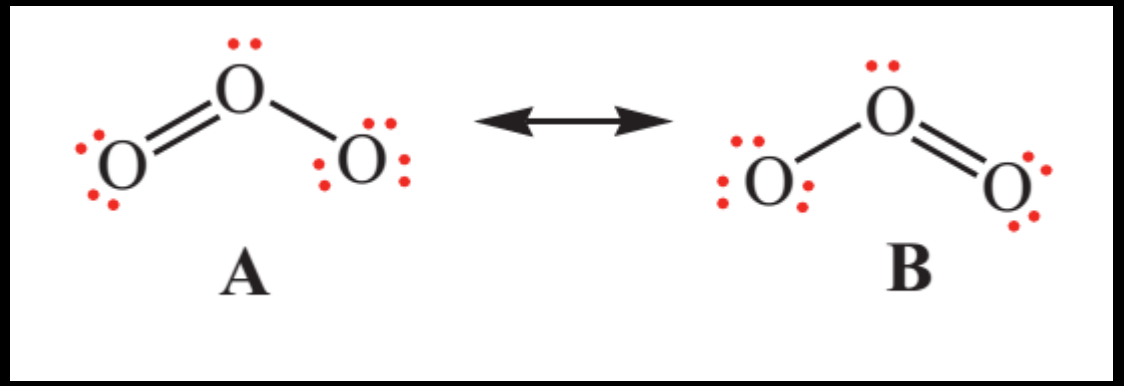


- In formula A, the oxygen–oxygen bond on the left is a double bond and the oxygen– oxygen bond on the right is a single bond. In formula B, the situation is just the opposite.
- These are not two different O_3molecules, just different Lewis structures for the same molecule. However, neither one of these two Lewis structures accounts for the known bond lengths in O_3(1.278 Å).



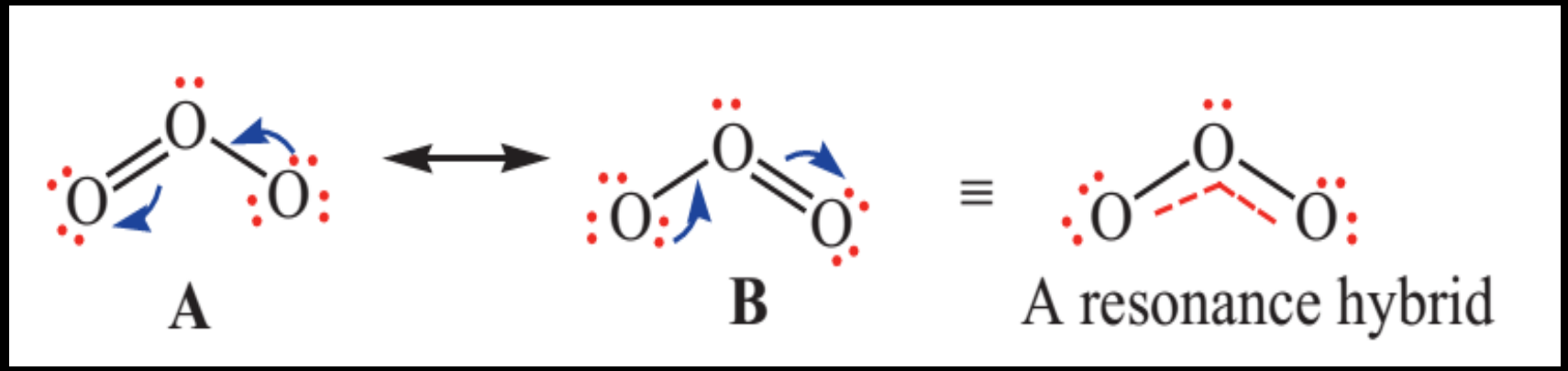
- Since both the bonds are identical, which one is a double bond? Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in O3 are identical, with properties that lie between those of an O–O bond and an O=O bond, something like a **"one-and-a-half" bond.**





- Unfortunately, this notation can be misinterpreted. It does not mean that the ozone molecule flips back and forth between two forms.
- There is only one ozone molecule.
- The double-headed arrow means that you should form a mental picture of the molecule by joining the various resonance formulas.

- Resonance structures have the same relative placement of atoms but different locations of bonding and lone electron pairs.
- Our need for more than one Lewis structure to depict the ozone molecule is the result of **electron-pair delocalization**.
- You can convert one resonance form to another by moving lone pairs to bonding positions, and vice versa:



- This description of O_3 is called resonance, in which two or more possible Lewis structures can be written and the true structure is a composite or hybrid of them.
- The different structures used to represent the molecule or ion are called resonance forms or resonance contributors or resonance structures.

Example 2.4

Write two equivalent Lewis structures for the nitirite ion, NO_2^-. Describe its resonance hybrid structure.

Exercise 2.6

1. Write three equivalent structures for the SO_3 molecule that obey the octet rule.
2. Draw Lewis structures of all the important resonance forms of each of the following:

   a. NO_2F (N central) b. HNO_3 c. NO_2^-

Exceptions to the Octet rule in Covalent Bonding

Although many Lewis structures follow the octet rule, there are exceptions. There can be categorized into three groups:

i. Less than octet (central atom is deficient of electrons)

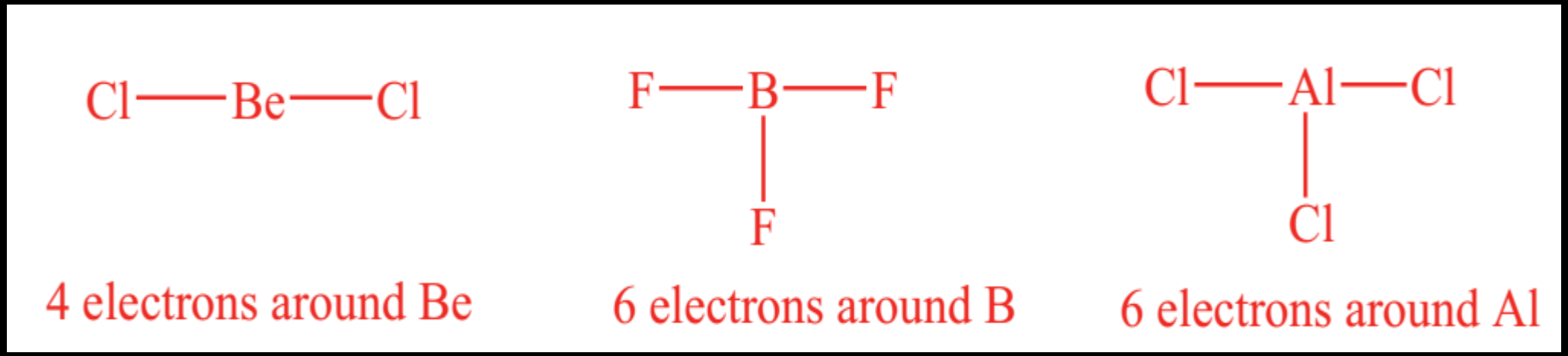
ii. More than octet (central atom has excess of electrons)

iii. Molecules containing an odd number of electrons

Less than octet (central atom is deficient of electrons)

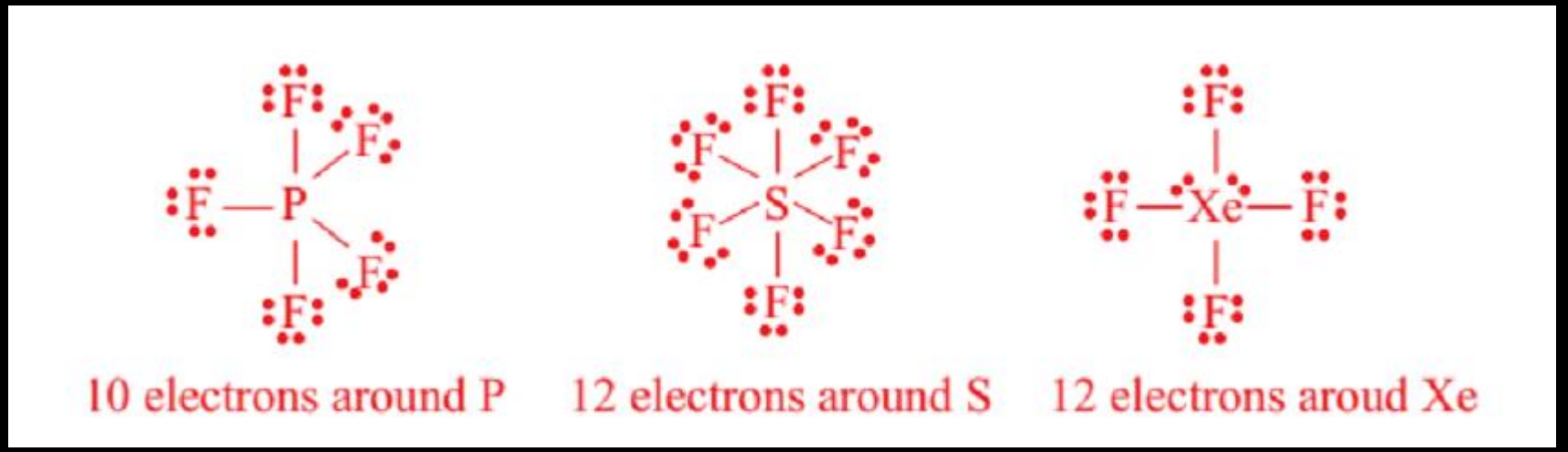
- Electron-deficient compounds are compounds in which an element has an incomplete octet.
- The central atoms of such molecules have fewer than eight electrons (below octet).
- This group consists of molecules containing central atoms from Group IIA and IIIA.

- For example, $BeCl_2$, $BF_3$and $AlCl_3$, whose Lewis formulas are shown:



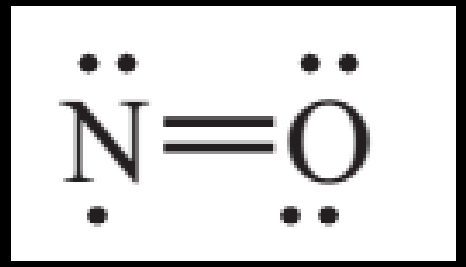
ii. More than octet (central atom has excess of electrons):

- Elements with an expanded valence (also called an expanded octet) have more than 8 electrons (often 10 or 12) in a Lewis structure.
- Elements in the third period and below, such as phosphorus, sulfur, and bromine, often have an expanded valence because of their larger radii (when compared to the second-row elements) and the availability of empty d orbitals in the valence shell. For example PF5, SF6 and XeF4



iii. Molecules containing an odd number of electrons:

- Even if stable molecules of this kind (free radicals) are rare, they do exist. Free radicals can also be electron-deficient compounds.
- Some examples are ClO_2, NO and NO_2 having 19, 11 and 17 valence electrons, respectively.
- For example, the best way to suggest the Lewis-like structure for the NO molecules is:



Exercise 2.7

1. Suggest the Lewis-like structure for NO_2 and ClO_2 molecules.
2. The following do not obey the octet rule. Draw a Lewis structure for each one and state the type of octet rule exception:

   a. BH_3 b. AsF_4^- c. $SeCl_4$ d. PF_6^-

Polar and Non-Polar Covalent Molecules

- When the atoms are alike in a covalent bond, as in the case of the H–H bond of H_2, the bonding electrons are shared equally.
- That is, the electrons spend the same amount of time near each nucleus.
- The bond formed is called a **non-polar covalent bond**.

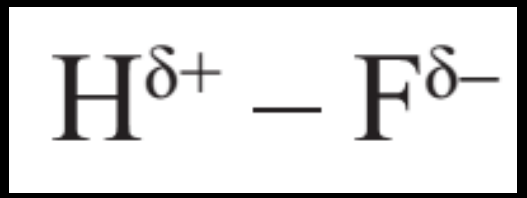
Table 1.4: (a) Electronegativity values (on Pauling scale) across the periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

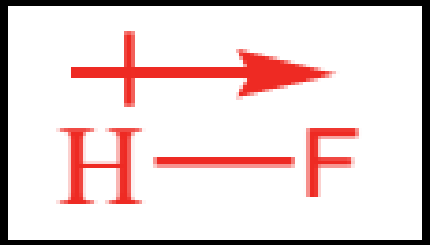
Table 1.4: (b) Electronegativity values (on Pauling scale) down a group

Atom (Group IA)	Electronegativity value	Atom (Group VIIA)	Electronegativity value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

- In a covalent bond between atoms of different electronegativity, there is an **unequal sharing of an electron pair** and the electrons spend more of their time around the more electronegative atom.
- Such a bond is said to be **polar covalent bond.**
- The H–F bond is a polar bond because fluorine is more electronegative than the hydrogen atom.
- The bonding electrons spend more time near the fluorine atom than the hydrogen atom.



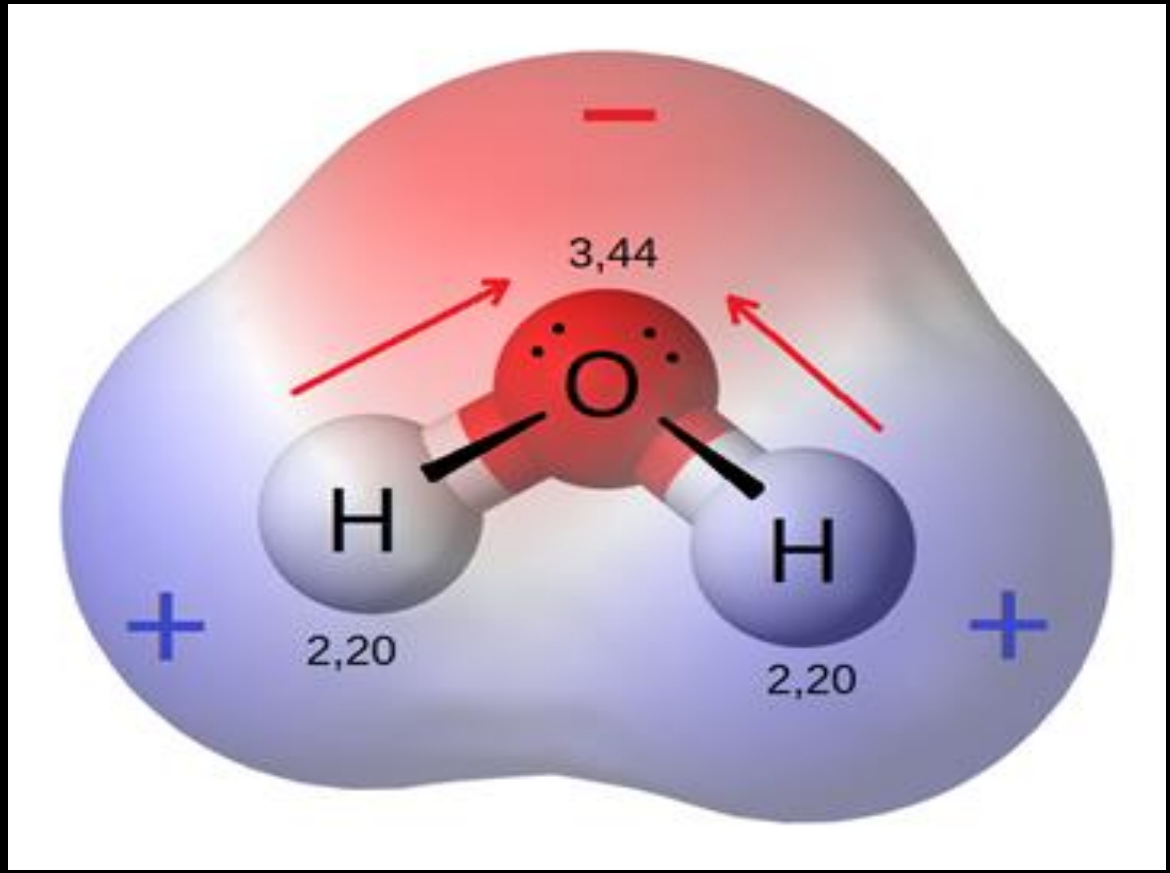
- In the representation the δ^+ and δ^- (read "delta plus" and "delta minus") signify that one end (H) is partially positive and the other end (F) is partially negative.
- The term "partial charge" implies something less than the full charges of the ions that would result from complete electron transfer.



- For a diatomic molecule having a polar covalent bond, such as HF, we can describe a quantity called **the dipole moment**, which is a vector sum of the bond moments in a molecule.
- **Bond moment** is a measure of polarity of a diatomic covalent bond.
- **The dipole moment (μ)** is defined as the product of the magnitude of the charge (δ) at either end of the dipole multiplied by the distance (d) that separates the charge.

$$\mu = \delta \times d$$

- **The SI-unit of dipole moment is coulomb-metre (C.m).**
- **A very polar molecule is one with a large dipole moment, while a non-polar molecule will have a zero-dipole moment.**


−
3,44
O
H
H
+
+
2,20
2,20

Note:

- For a diatomic molecule, the bond moment is the dipole moment.
- The dipole moment of a polyatomic molecule (three or more atoms) depends on the geometry of the molecule.
- If the bond moments are equal in magnitude but opposite in direction, then they will cancel each other and the resultant dipole moment will be zero, provided that the vector sum of the bond moments is zero.

Exercise 2.8

1. Both CO_2 and BCl_3 have zero dipole moments, but the C = O and B – Cl bond moments are not zero. Explain.
2. Compare the dipoles in the covalent molecules HF, HCl, HBr, and HI. Explain your answer.
3. For each of the following bonds, indicate the positive end with δ^+ and the negative end with δ^-. Draw an arrow to show the dipole for each.
   a. N and F b. Si and Br c. C and O d. P and Br e. N and P

Molecule will be non-polar

- If the molecular shape around the central atom has no lone pair or if it either square planar or linear
- All the terminal atom around the central atom is the same

Classify the following molecules as polar or non-polar

$CHCl_3$

CCl_4

NF_3

BCl_3

SO_3

CO_2

SO_2

Classify the following molecules as polar or non-polar

$CHCl_3$

CCl_4

NF_3

BCl_3

SO_3

CO_2

SO_2

Properties of Covalent Compounds

- Many of the covalent compounds are found in gaseous state at room temperature.
- Unlike melted ionic compounds, liquid covalent compounds do not conduct electricity.
- They have low melting and boiling points.
- Most covalent compounds are soluble in non-polar solvents.

Generally:

- **Covalent compounds exist as separate molecules because electrically neutral atoms form them and the forces of attraction between these molecules are relatively weak.**
- **Due to weak intermolecular forces, many covalent molecules or covalent compounds are liquids or gases at room temperature.**
- **However, some covalent molecules like iodine are solids at room temperature.**

- Covalent compounds are volatile.
- Generally, they have low melting points and boiling points.
- Covalent compounds are generally insoluble in water.
- Most covalent compounds are soluble in non-polar solvents
- Non-polar covalent compounds are non-electrolytes because they do not conduct electricity.

Classify the following molecules as polar or non-polar

$CHCl_3$

CCl_4

NF_3

BCl_3

SO_3

CO_2

SO_2

Molecular geometry

- **Molecular geometry** is the three-dimensional arrangement of atoms in a molecule.
- There is a simple procedure that enables us to predict the geometry of a molecule or ion if we know the number of electrons surrounding a central atom in its Lewis structure.
- The basis of this approach is the assumption that electron pairs in the valence shell of an atom repel one another.

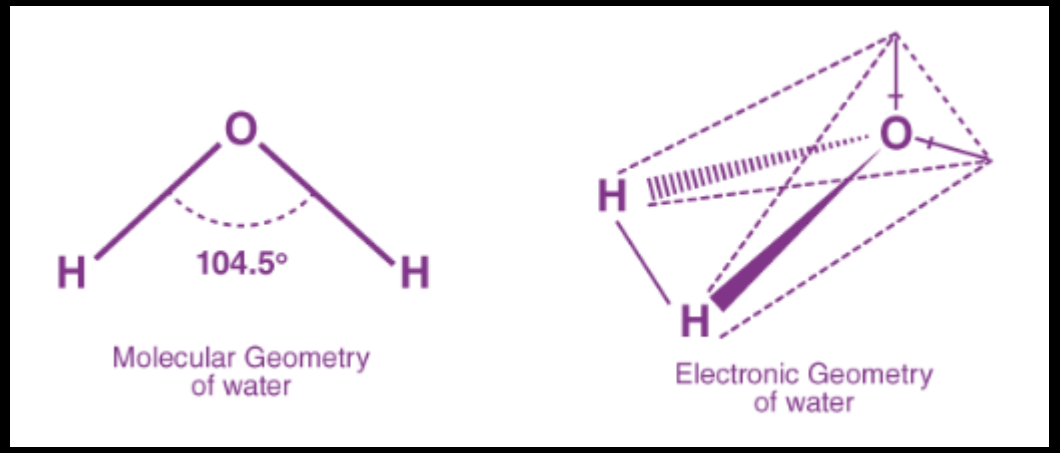
Valence Shell Electron Pair Repulsion (VSEPR) Theory

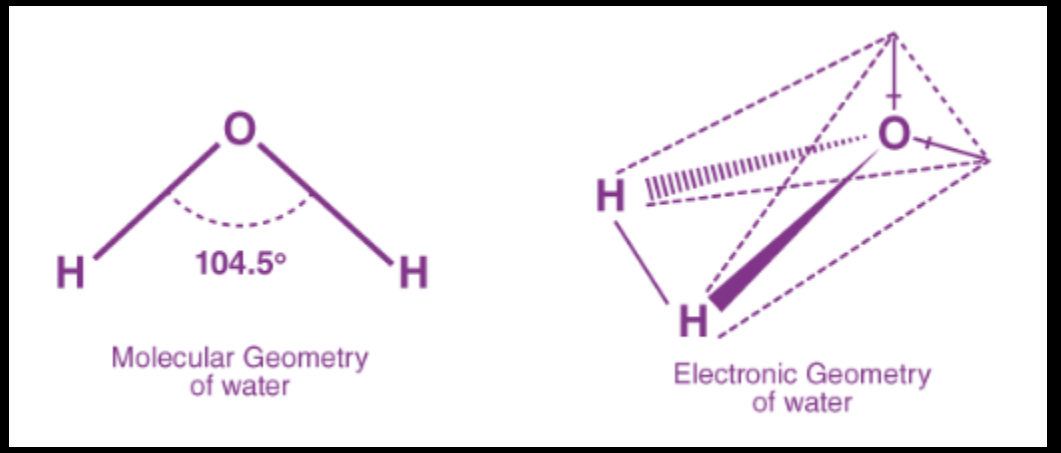
- In a covalent bond, a pair of electrons, often called the **bonding pair**,is responsible for holding two atoms together.
- However, in a polyatomic molecule, where there are two or more bonds between the central atom and the surrounding atoms, the repulsion between electrons in different bonding pairs causes them to remain as far apart as possible.
- The geometry that the molecule ultimately assumes (as defined by the positions of all the atoms) minimizes the repulsion. This approach to the study of molecular geometry is called the **valence-shell electron-pair repulsion (VSEPR) model.**

- **The basic principle of VSEPR theory** is that the pair of valence-shell electron pairs around the central atom arrange as far away from one another as possible to minimize electron-pair repulsions.
- The arrangements that best minimize repulsions naturally depend on the number of electron sets.
- Once we have counted the number of electron groups surrounding the central atom, we can determine its specific shape from the number of atoms bonded to the central atom.

Electron Pair Arrangement and Molecular Shape

- The **electron pair arrangement** is defined by the orientation/distribution of pairs of electrons, both bonding and non-bonding (lone pair), around the central atom.
- The **molecular shape** is defined by the relative positions of the atomic nuclei.
- Molecular shapes that occur when all the surrounding electrons are bonding differ from molecular shapes when some of the electrons are non-bonding.
- Thus, the same electron set arrangement can give rise to different molecular shapes.


O
H
104.5°
H
Molecular Geometry
of water
O
H
H
Electronic Geometry
of water


O
H
104.5°
H
Molecular Geometry
of water
O
H
H
Electronic Geometry
of water

- For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as

    1. molecules in which the central atom has no lone pair and
    2. molecules in which the central atom has one or more lone pairs.

1.Molecules in which the central atom has no lone pair

- Consider molecules that contain atoms of only two elements, A and B, of which A is the central atom.
- These molecules have the general formula ABx, where x is an integer 2, 3, ... (If x = 1, we have the diatomic molecule AB, which is linear by definition.)
- In the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangements of electron pairs and the B atoms around the central atom A are: linear, trigonal planar, tetrahedral, trigonalbipyramidal and octahedral, respectively.

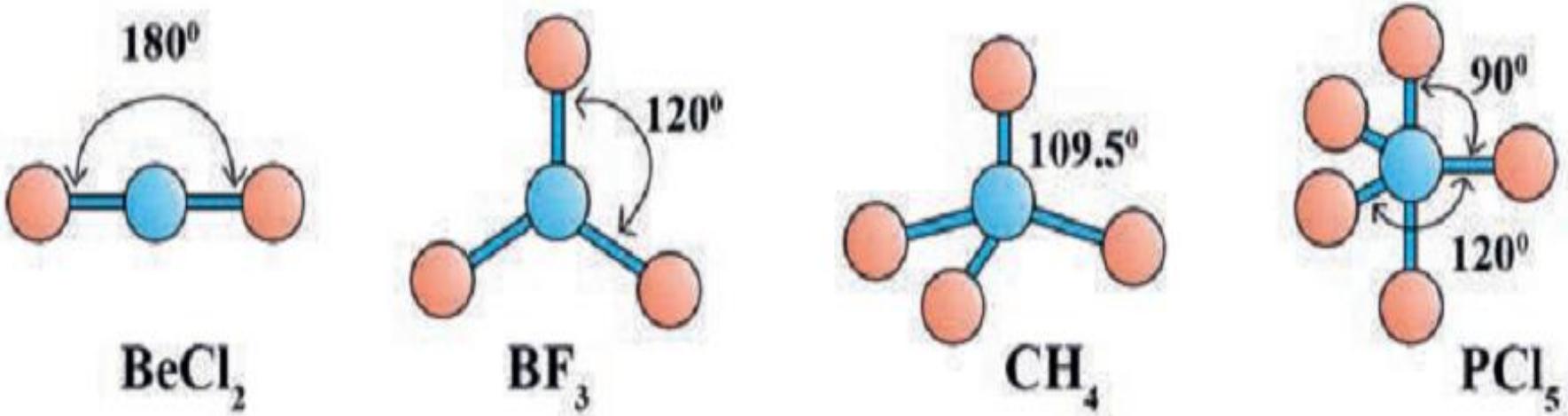


Figure 2.7: The shapes of molecules in which the central atom has no lone pair

- In the case of multiple (double or triple)bonds the counting is not different, because a double bond is considered as one set and a triple bond as another set of electrons.

For example, in the case of CO_2, O=C=O, there are two sets of electrons around the central atom, acetylene, C_2H_2, H–C≡C–H, two sets of electrons around each of the central atoms.

2.Molecules in which the central atom has one or more lone pairs

- In such molecules there are three types of repulsive forces—those between bonding pairs, those between lone pairs, and those between a bonding pair and a lone pair.
- In general, according to the VSEPR model, the repulsive forces decrease in the following order:
- Lone pair vs lone pair > lone pair vs bonding pair > bonding pair vs bonding pair
- Why is that repulsions exerted by lone pair is greater than that of bonding pair?

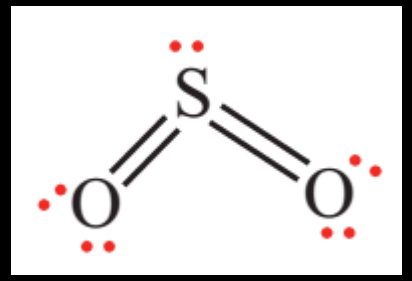
- To keep track of the total number of bonding pairs and lone pairs, we show molecules with lone pairs as AB_xE_y, where A is the central atom, B is a surrounding atom, and E is a lone pair on A.
- Both x and y are integers; x= 2, 3, . . . , and y= 1, 2, ... Thus, the values of x and y indicate the number of surrounding atoms and number of lone pairs on the central atom, respectively.
- The simplest such molecule would be a triatomic molecule with one lone pair on the central atom and the formula is AB_2E.

AB_2E: Sulfur Dioxide (SO_2)

The Lewis structure of sulfur dioxide is:

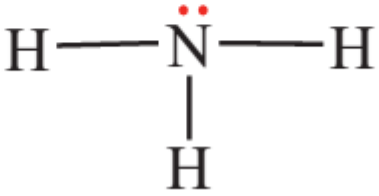


- **Electron arrangement:**
- **Molecular Shape:**
- **Bond angle:**

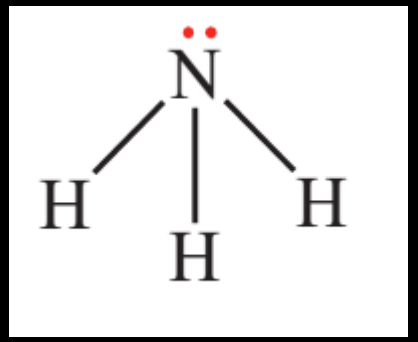


AB_3E: Ammonia (NH_3)

The ammonia molecule contains of three bonding pairs and one lone pair:



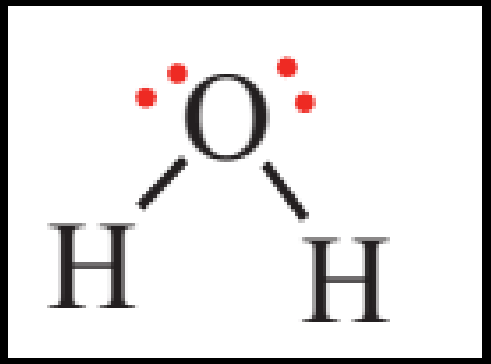
- **Electron arrangement:**
- **Molecular Shape:**
- **Bond angle:**



AB_2E_2: Water (H_2O)

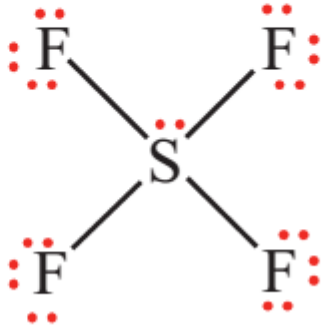
A water molecule contains two bonding pairs and two lone pairs:

- **Electron arrangement:**
- **Molecular Shape:**
- **Bond angle:**

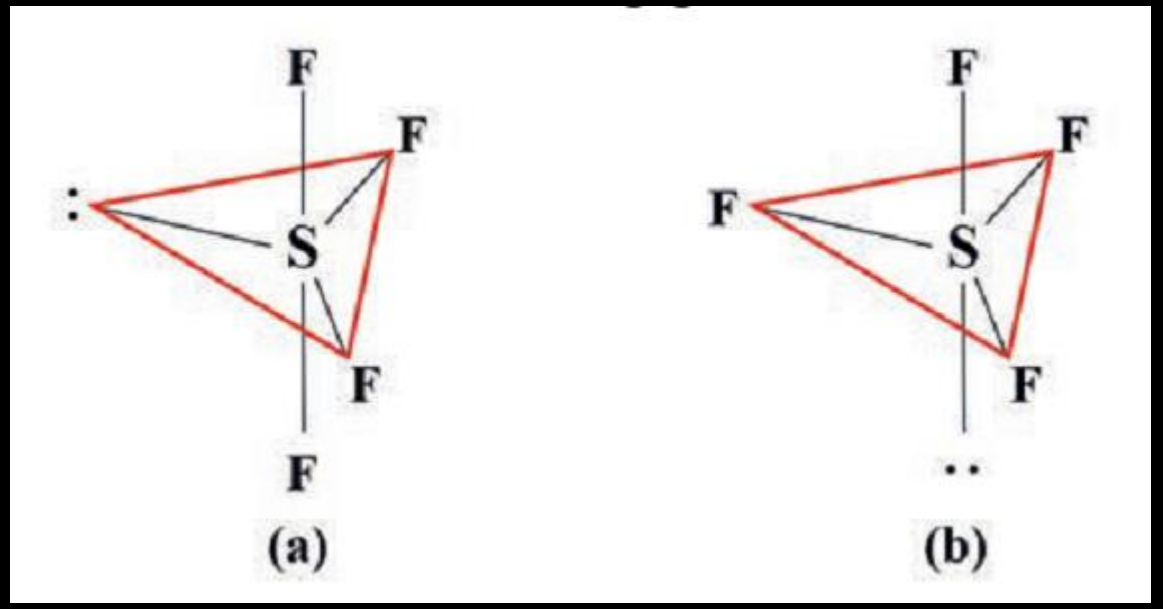


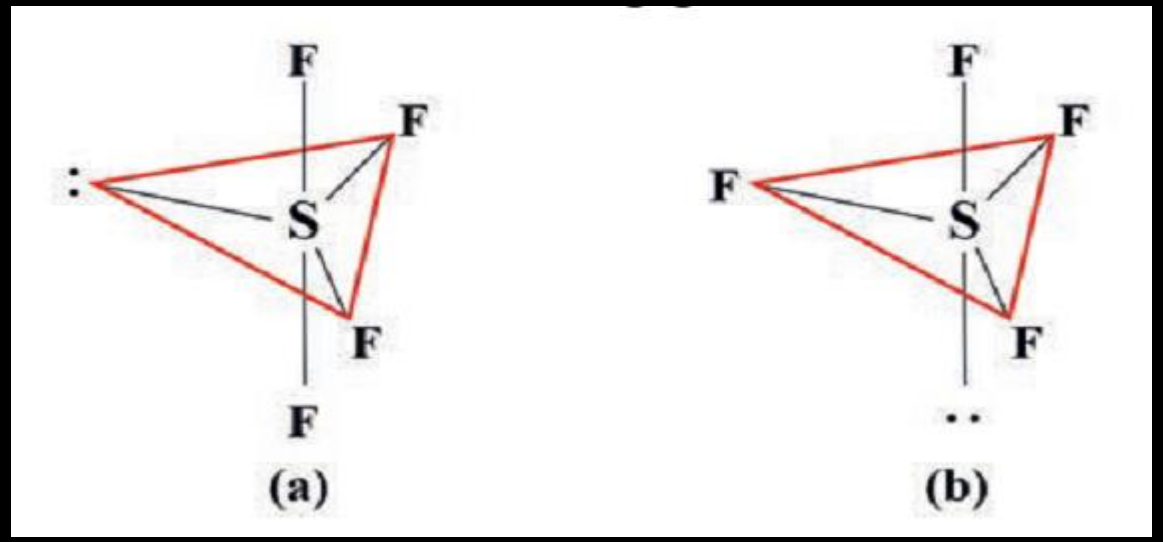
AB_4E: Sulfur Tetrafluoride (SF_4)

The Lewis structure of SF_4 is:

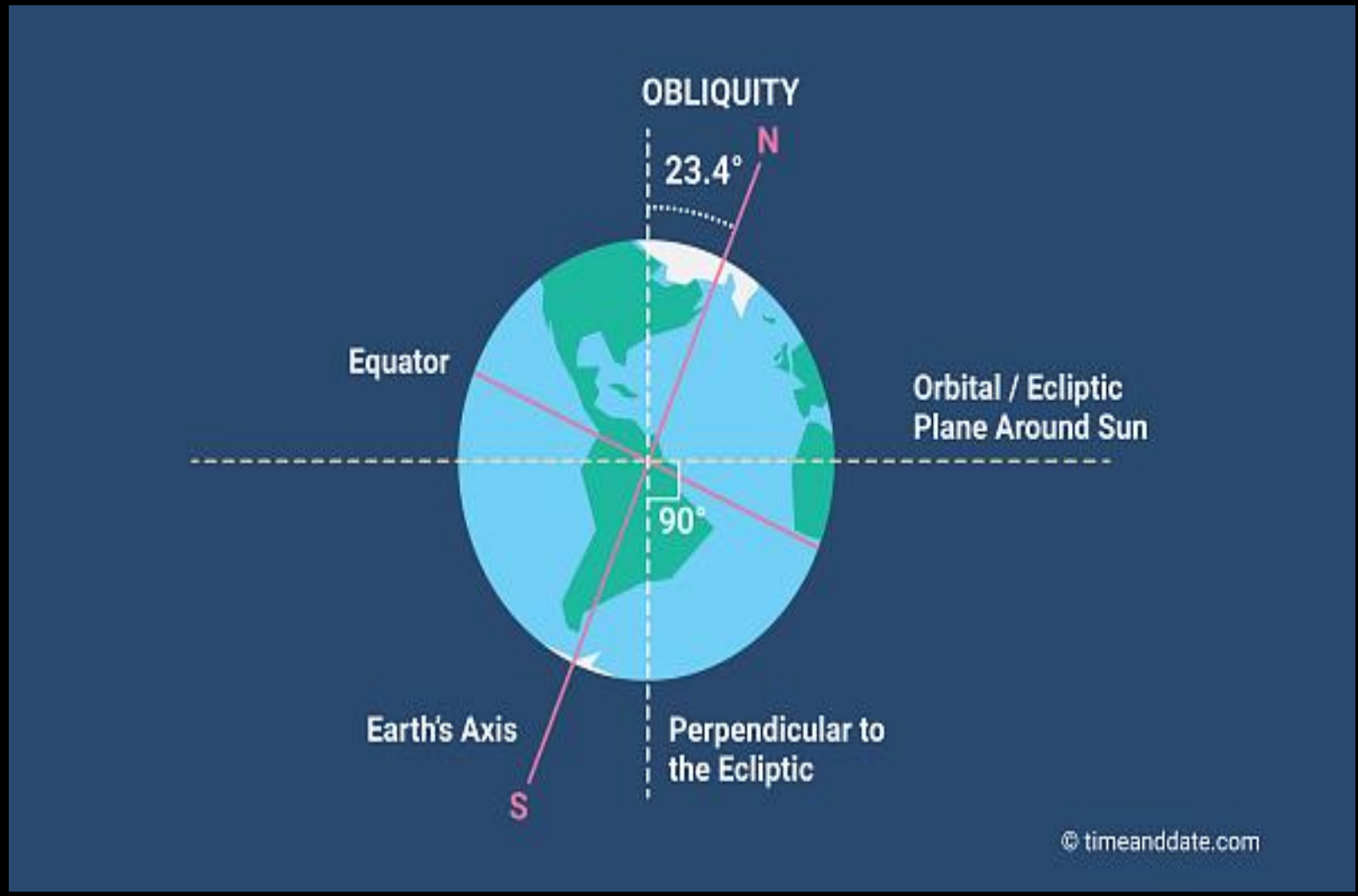


- **Electron arrangement:**
- **Molecular Shape:**
- **Bond angle:**





- In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position.
- The axial position has three neighboring pairs at 90° and one at 180°, while the equatorial position has two neighboring pairs at 90° and two more at 120°.


OBLIQUITY
23.4°
N
Equator
Orbital / Ecliptic
Plane Around Sun
90°
Earth's Axis
Perpendicular to
the Ecliptic
S
© timeanddate.com

Below ToP Valley SS Teacher Live

	Set of Electron Pair	Bonding Pair	Lone Pair	Molecular shape
2				
3				
4				
5				

Guidelines for Applying VSEPR Model

1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom (the atom that is bonded to more than one other atom).

2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs).

- Treat double and triple bonds as though they were single bonds.
- If there is more than one central atom, treat each central atom separately.

3. Use the VSEPR geometry to predict the shape of the molecule.

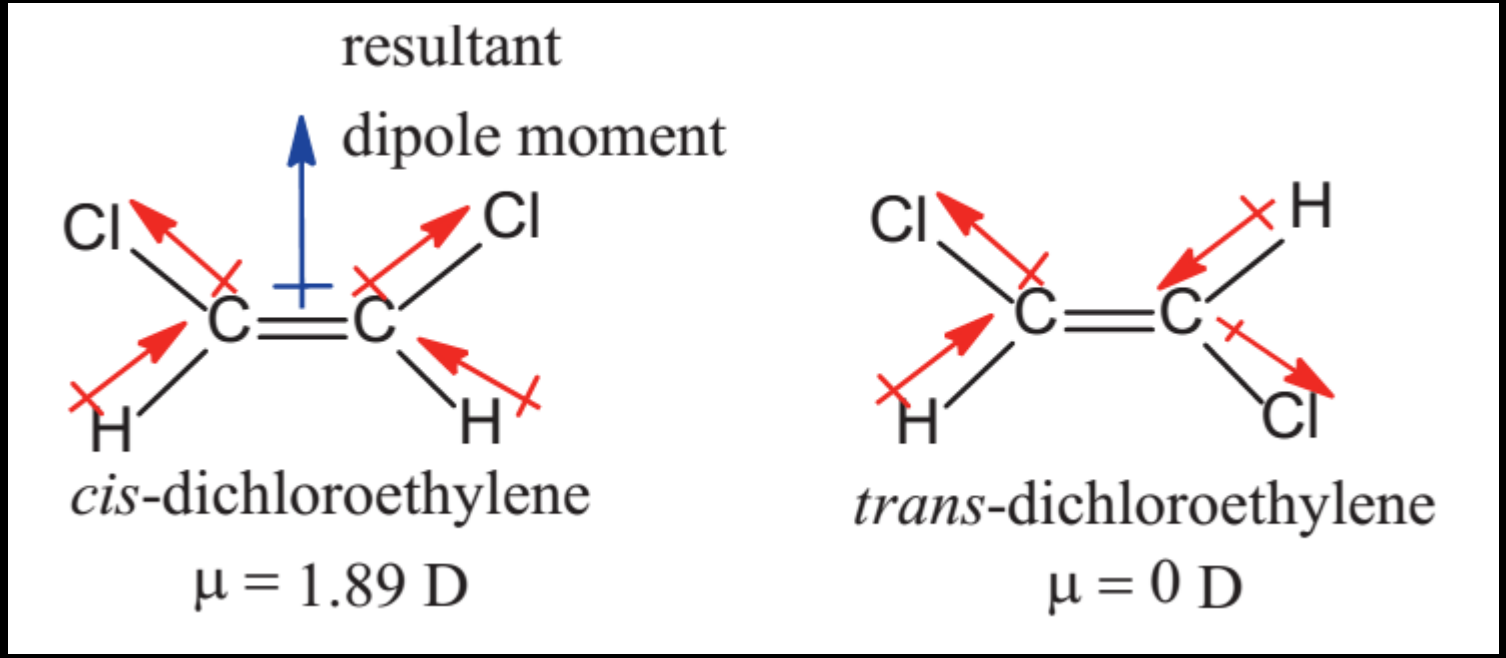
4. In predicting bond angles, note that a lone pair repels another lone pair or a bonding pair more strongly than a bonding pair repels another bonding pair.

Molecular Shape and Molecular Polarity

- Many aspects of molecule's chemical behaviour can be understood if we know the geometry (shape) of a substance.
- Molecular shape affects many properties of the molecule like molecular polarity, which in turn influence melting and boiling points, solubility, and even reactivity.
- Molecular polarity is created by molecules with a net imbalance of charge.
- In molecules with more than two atoms, both shape and bond polarity determine the molecular polarity.

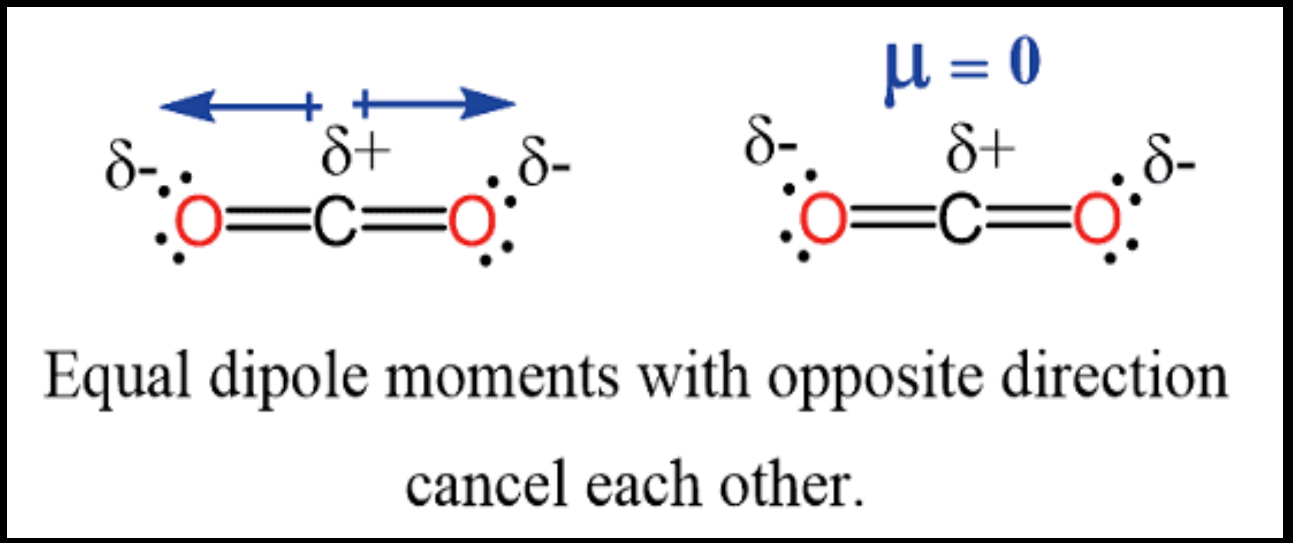
Bond Polarity and Dipole Moment

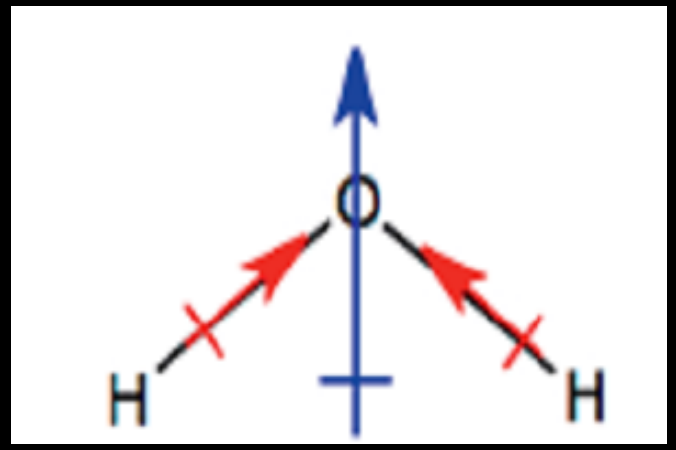
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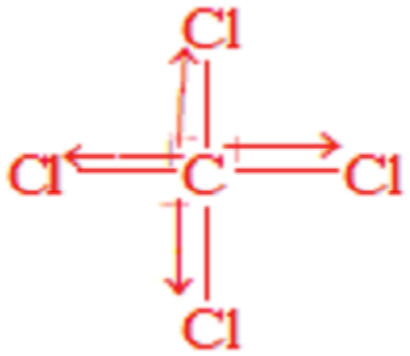

resultant
dipole moment
Cl
Cl
C
C
H
H
cis-dichloroethylene
μ = 1.89 D
Cl
H
C
C
H
Cl
trans-dichloroethylene
μ = 0 D

- Diatomic molecules containing atoms of different elements (for example, HCl, CO, and NO) have dipole moments and are called **polar molecules.**
- Diatomic molecules containing atoms of the same element (for example, H_2, O_2, and F_2) are examples of **non-polar molecules** because they do not have dipole moments.
- For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment.
- Polar bonds do not necessarily lead to polar molecules.

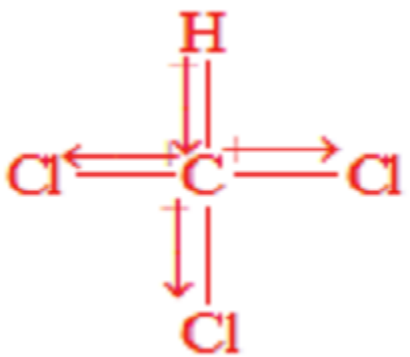
- **For example,**


δ-
δ+
δ-
O=C=O
μ = 0
δ-
δ+
δ-
O=C=O
Equal dipole moments with opposite direction cancel each other.

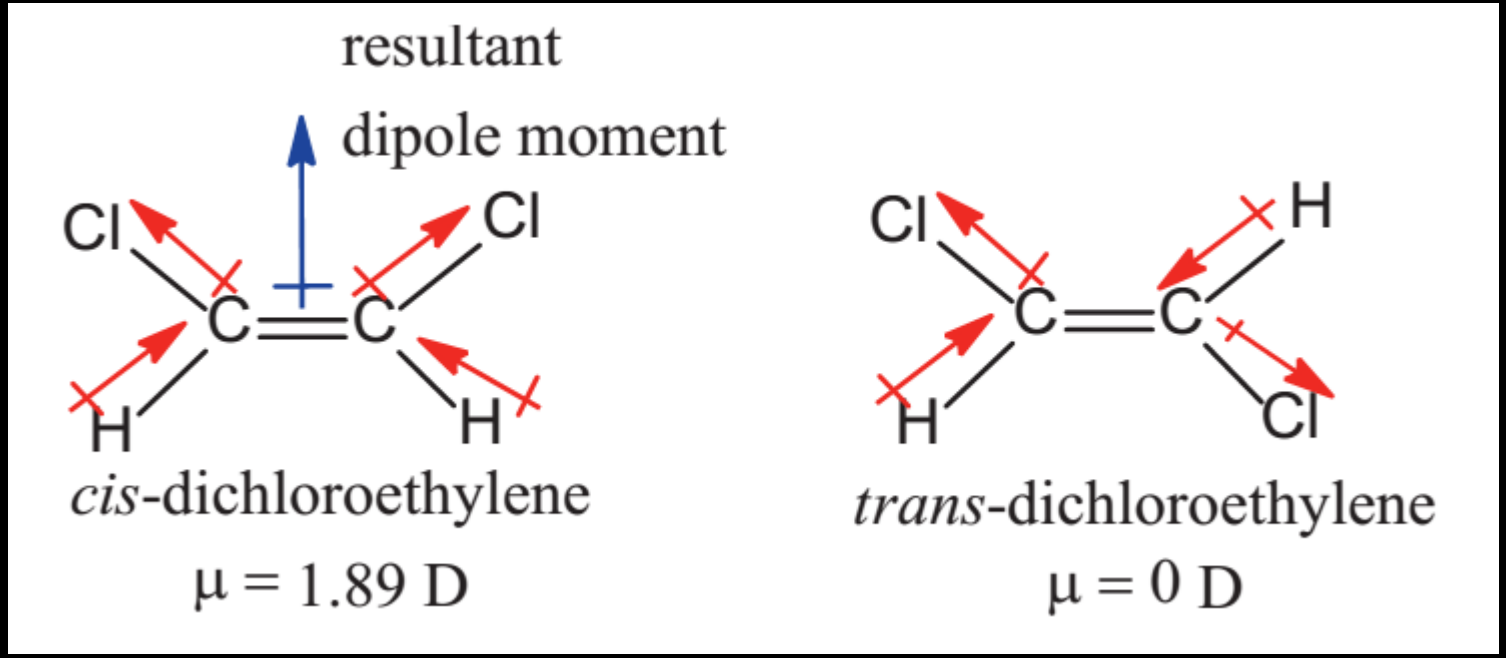

O
H
H



$\mu = 0$ D



$\mu = 1.02$ D


resultant
dipole moment
Cl
Cl
C
C
H
H
cis-dichloroethylene
μ = 1.89 D
Cl
H
C
C
H
Cl
trans-dichloroethylene
μ = 0 D

Intermolecular force in the covalent bond

- There are two types of force that hold matter together. These are
  intramolecular forces
  intermolecular forces.
- **Intramolecular force** is a chemical bond (ionic, covalent or metallic) that exists within a particle (molecule or polyatomic ion) and affects the chemical property of the species.

- **Intermolecular force** are those bonds that hold particles (ions or molecules) together.
- A glass of water for example, contains many molecules of water.
- These molecules are held together by intermolecular forces, whereas the intramolecular forces hold the two hydrogen atoms to the oxygen atom in each molecule of water.
- Intermolecular forces are relatively weak as compared to intramolecular forces, because they typically involve lower charges that are farther apart.
- However, the strength of the intermolecular forces is important because they affect physical properties of the species such as melting point and boiling point.

- Three types of attractive force are known to exist between neutral molecules:

  Dipole–dipole forces

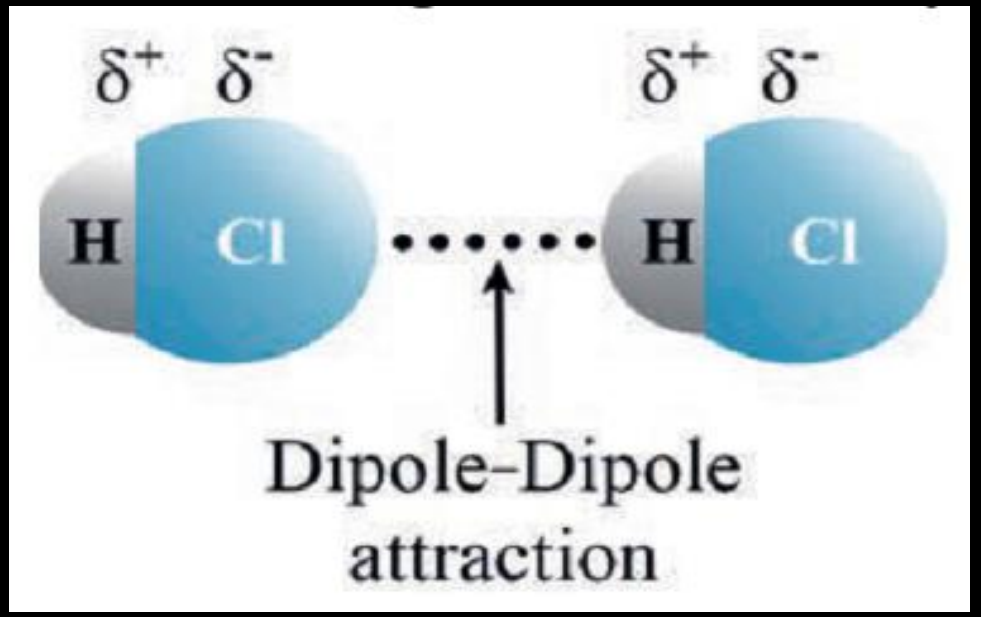
  London (or dispersion) forces,

  Hydrogen bonding forces.

- The term van der Waals forces are a general term for those intermolecular forces that include dipole–dipole and London forces.
- Van der Waals forces are the weak attractive forces in a large number of substances, including Cl_2, and Br_2.

Dipole-Dipole forces

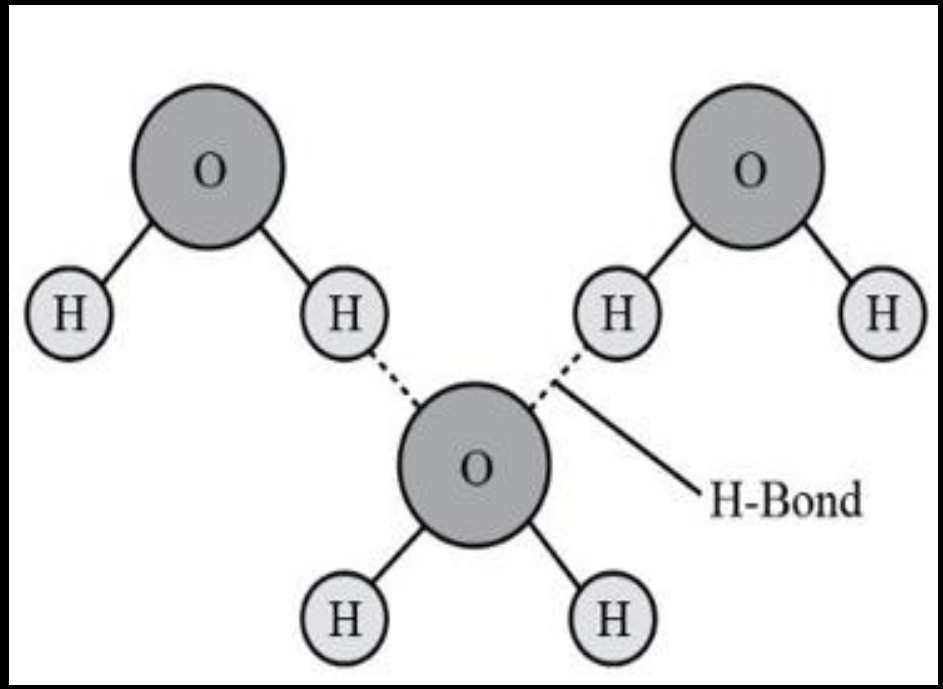
- Dipole-dipole forces act between the molecules possessing permanent dipole.
- When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another.
- Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter delta (δ).



- **This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.**
- **The attractive force decreases with the increase of distance between the dipoles.**

Hydrogen Bonding

- Polar molecules containing hydrogen atoms bonded to highly electronegative atoms of nitrogen, oxygen, or fluorine form especially strong dipole–dipole attractions.
- This type of attraction, called a hydrogen bond, occurs between the partially positive hydrogen atom in one molecule and the partially negative nitrogen, oxygen, or fluorine atom in another molecule.
- The atom sequence that leads to an H bond (dotted line) is indicated below.
- Hydrogen bonds are the strongest type of attractive forces between polar covalent molecules.


O
O
H
H
H
H
O
H-Bond
H
H

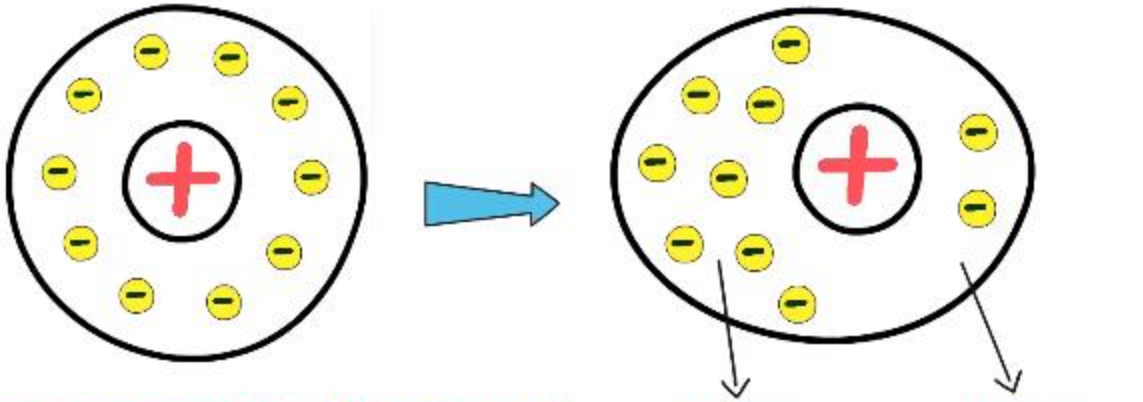
Dispersion or London Forces

- Usually, the electrons in a non-polar covalent molecule are distributed symmetrically.
- However, the movement of the electrons may place more of them in one part of the molecule than another, which forms a temporary dipole.
- These momentary dipoles align the molecules so that the positive end of one molecule is attracted to the negative end of another molecule.

TEMPERORY DIPOLE?

NEUTRAL ATOM

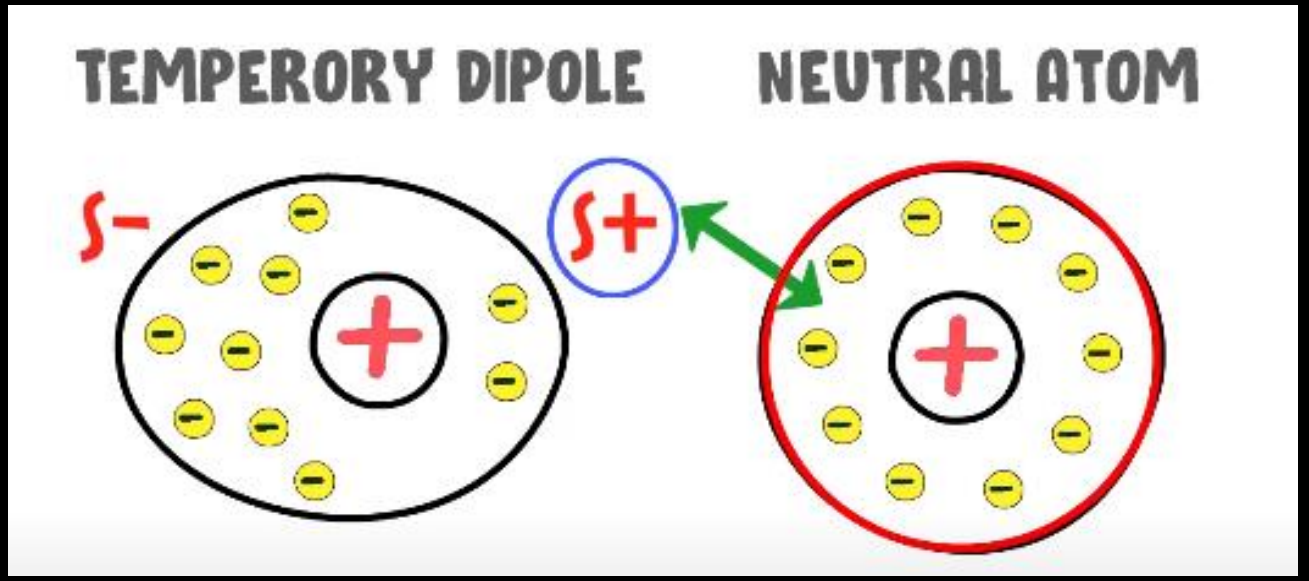
THERE WILL BE
A time when...



Electrons are equally distributed
Electrons constantly revolve...

More Electrons

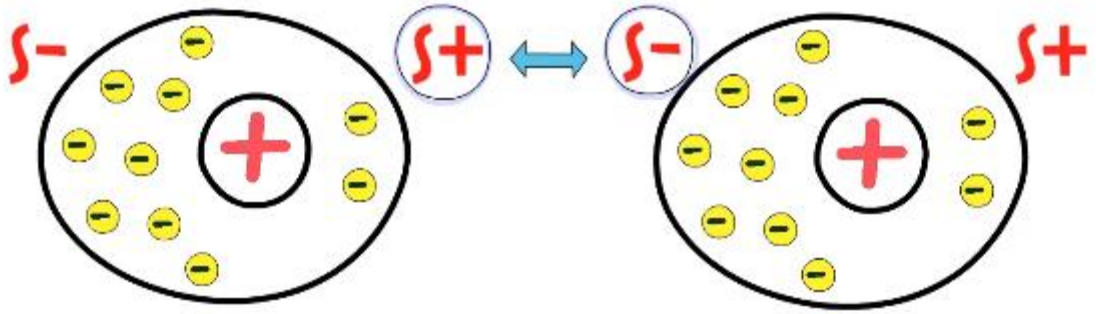
Less Electrons


TEMPERORY DIPOLE
NEUTRAL ATOM
δ−
δ+

INDUCED DIPOLE ?

TEMPERORY DIPOLE

INDUCED DIPOLE



LONDON DISPERSION FORCE

- These weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei are called **London forces or dispersion forces.**
- They are present between all particles (atoms, ions, and molecules).
- dispersion forces are the weakest intermolecular force

- **London forces tend to increase with molecular weight, why do you think this is?**
- For molecules of about the same molecular weight, the strength of the dispersion forces is affected by molecular geometry (shape).
- Shapes that allow more points of contact have more area over which electron clouds can be distorted, so stronger attractions result.
- This is probably the reason why n-pentane has a higher boiling point (36 °C) than its isomers 2-methylbutane (28 °C), and 2, 2-dimethylpropane (9.5 °C).

Easy trick to identify intermolecular forces

Hydrogen bonding	dipole-dipole bond	London dispersion
• H - F,O,N	Polar molecule	non-polar molecule
Hydrogen bonded to F,O,N		polar molecule

Example :Which type of intermolecular force is dominant

ICl

CH_4

CH_3OH

HI

CH_3COOH

PCl_3

Cl_2

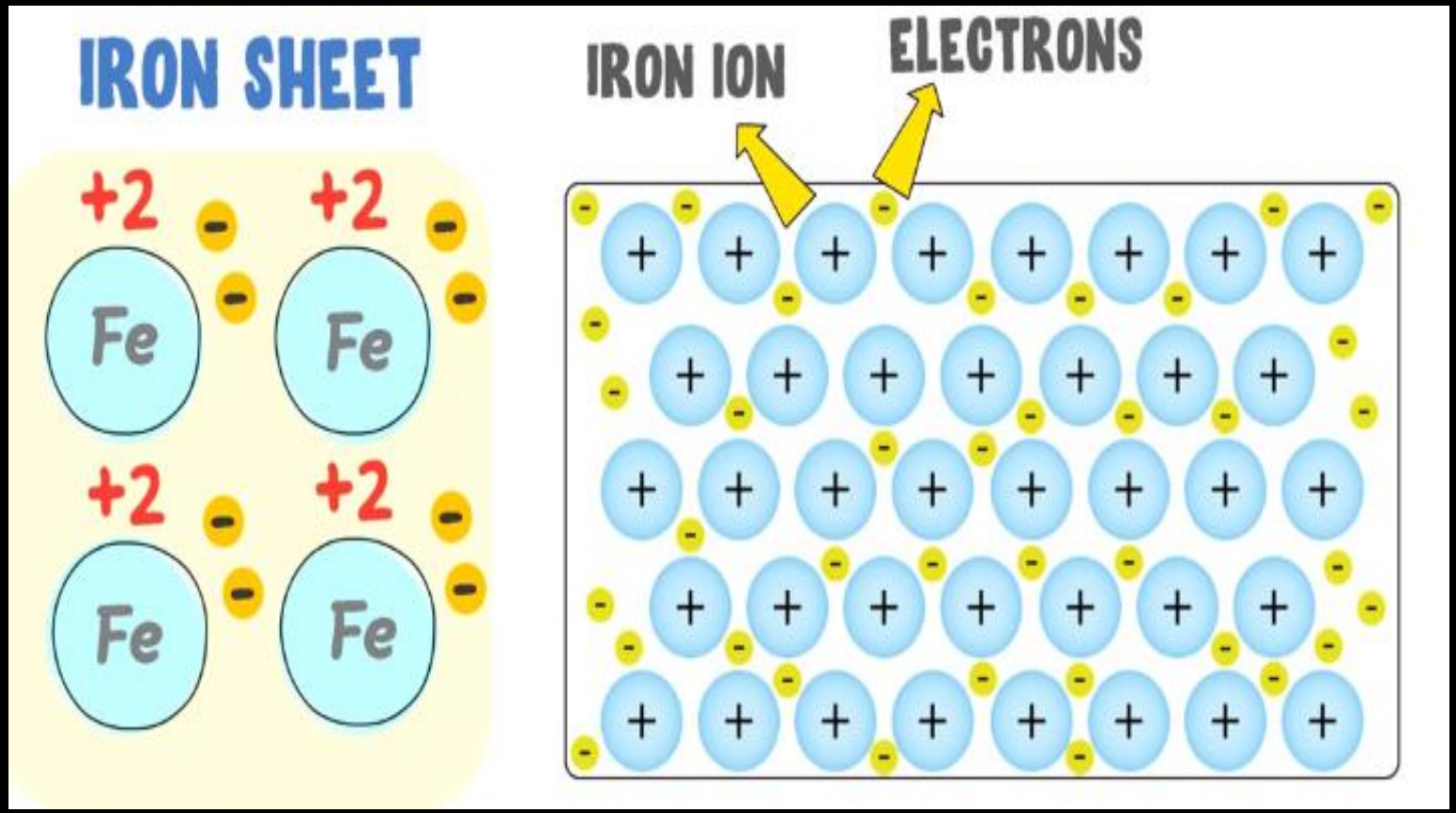
CH_3NH_2

Metallic bonding

Formation of metallic bond

- Metallic bonds are the chemical bonds that hold atoms together in solid metals such as copper, iron, and aluminum.
- In these metals, each metal atom is bonded to several neighboring atoms.
- Metallic bonding is the sharing of free electrons (delocalized electrons) among a lattice of positively charged metal ions.
- The bonding electrons are relatively free to move throughout the three-dimensional structure.

How is a metallic bond different from that of covalent and ionic bonds?


IRON SHEET
IRON ION
ELECTRONS
+2
+2
+2
+2
Fe
Fe
Fe
Fe

The strength of the metallic bond depends on:

1.The number of electrons in the delocalized “sea” of electrons.

- More delocalized electrons result in a stronger bond and a higher melting point.

2. The packing arrangement of the metal atoms.

- The more closely packed the atoms are the stronger the bond is and the higher the melting point.

Electron-sea model

- The electron-sea model is a very simple model, which pictures the metal as an array of metal cations in a “sea” of electrons.
- It proposes that all the metal atoms in a sample pool their valence electrons to form an electron “sea "that is delocalized throughout the piece.
- The metal ions (nuclei plus core electrons) are submerged within this electron sea in an orderly array.

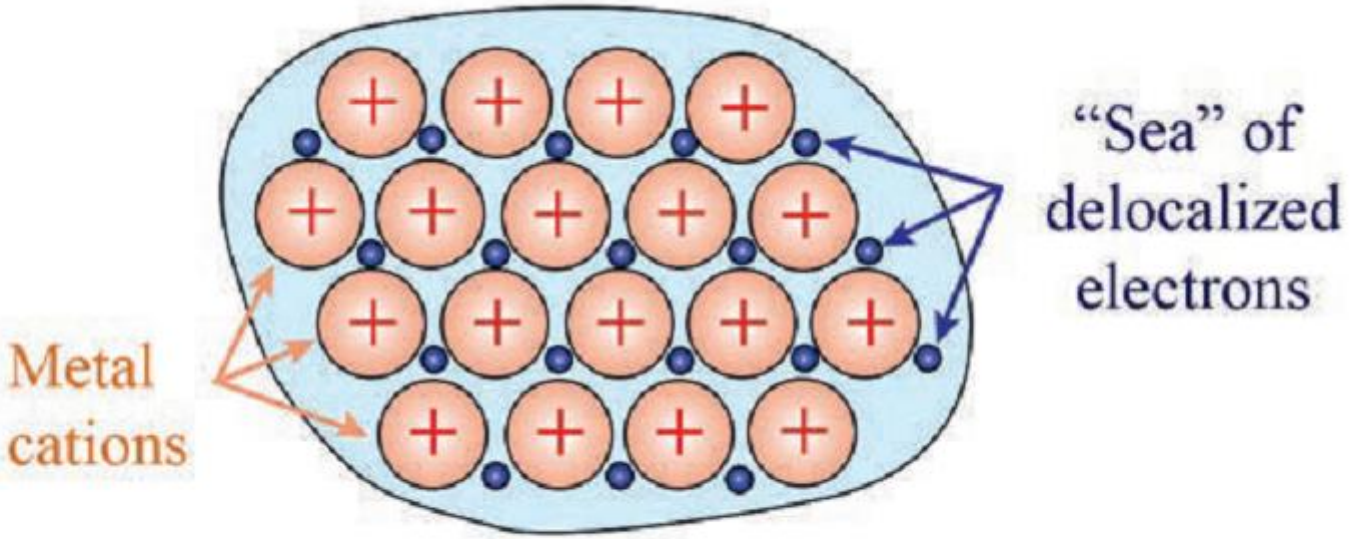


Figure 2.8: The electron-sea model for the electronic structure of metals



- The metal ions are not held in place as rigidly as the ions in an ionic solid, and no two metal atoms are bonded through a localized pair of electrons as in a covalent bond.
- Rather, the valence electrons are shared among all the atoms in the sample, and the piece of metal is held together by the mutual attraction of the metal cations for the mobile, highly delocalized valence electrons.
- The mobile electrons, known as **conduction electrons**, can transfer thermal vibration from one part of the structure to another i.e., metals can conduct heat.
- They are good conductors of electricity also.

Properties of metallic bonding

- The general properties of metals include malleability and ductility and most are strong and durable.
- They are good conductors of heat and electricity.
- Their strength indicates that the atoms are difficult to separate.

To what do properties of metals like malleability and ductility refer?

- The regularity, but not rigidity, of the metal-ion array and the mobility of the valence electrons account for the physical properties of metals

- **The delocalized electrons are not attached to atoms, so they can move through the metal easily.**
- **This makes metals good conductors of electricity and heat, even when they are solid.**

Why do not ionic compounds conduct electricity when they are in solid form? But conductor when they are dissolved in water?

- **The electrostatic bonds between the metal ions and the delocalized electrons are hard to break, so metals are strong.**
- **Many metals can be flattened into sheets (malleable) and pulled into wires (ductile).**
- **The combination of strength and malleability means that metals are easy to bend but hard to break. This makes them extremely useful for making things.**

- **Metals have moderate to high melting points because the attractions between the cations and the delocalized electrons are not broken during melting, but boiling points are very high because each cation and its electron(s) must break away from the others.**
- **The alkaline earth metals [Group IIA(2)] have higher melting points than the alkali metals [Group IA(1)] because of greater attraction between their 2+ cations and twice the number of valence electrons.**

Chemical Bonding Theories

- The Lewis model, one of the earliest models of covalent bond formation, represents chemical bonds by an electron dot formula.
- However, it fails to explain the formation of chemical bonds.
- It gives no idea about the shapes of polyatomic molecules.
- Similarly, the VSEPR theory gives the geometry of simple molecules but, theoretically, it does not explain them and it has limited applications.

- **Covalent bonds are more accurately explained using modern bonding theories:**

  The valence bond theory (VBT)

  The molecular orbital theory(MOT)

- **The valence bond (VB) theory** assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms.
- It give us a picture of individual atoms taking part in the bond formation.
- **The molecular orbital (MO) theory**, assumes the formation of molecular orbitals from the atomic orbitals.

Valence Bond (VB) Theory

The valence-bond approach is the most useful approach to answer questions such as:

- what is a covalent bond, and what characteristic gives it strength?
- How can we explain molecular shapes based on the interactions of atomic orbitals?
- The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons.

By overlap, we mean that the two orbitals share a common region in space.

For example, consider the formation of the H_2 molecule from two hydrogen atoms.

- Each atom has the electron configuration $1s^1$.
- As the H atoms approach each other, their 1s orbitals begin to overlap and a covalent bond forms.
- Electron density is higher in the overlap region than anywhere else, and the build-up of negative electron charge between the positive nuclei provides the electrostatic attraction that holds the atoms together

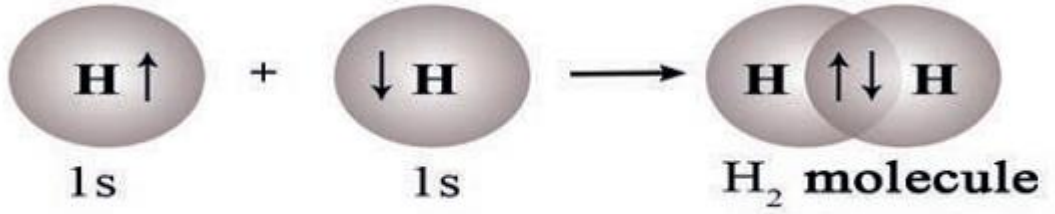


Figure 2.9: Atomic orbital overlap and bonding in H_2

- **How is the strength of the bond between any two atoms affected by the extent of the overlap between the two orbitals?**

- When two atoms are brought closely together, the repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction and the bond becomes unstable.
- There is a condition of optimal orbital overlap that leads to maximum bond strength (bond energy)at a particular internuclear distance (bond length)

- The bond strength depends on the attraction of the nuclei for the shared electrons, so the greater the orbital overlap, the stronger (more stable) the bond.
- The extent of overlap depends on the shapes and directions of the orbitals.
- An s orbital is spherical, but p and d orbitals have more electron density in one direction than in another.
- Thus, whenever possible, a bond involving p or d orbitals will be oriented in the direction that maximizes overlap.

- In the HF bond, for example, the 1s orbital of H overlaps the half-filled 2p orbital of F along the long axis of that orbital.
- Any other direction would result in less overlap and, thus, a weaker bond.

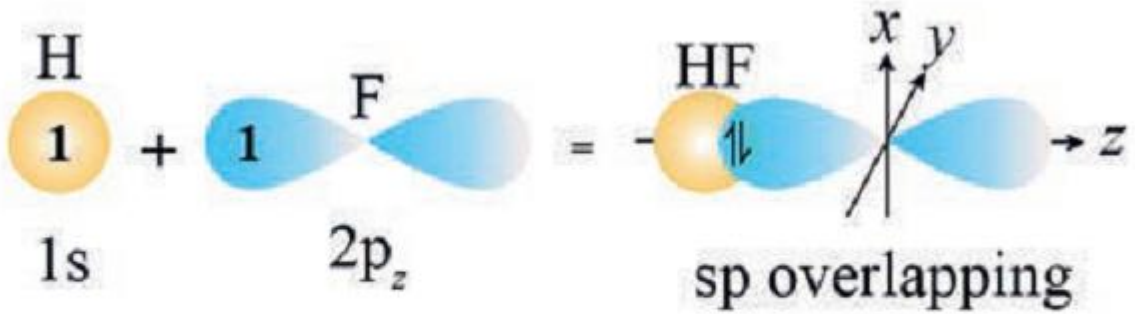


Figure 2.10: Orbital and spin pairing in the formation of a HF molecule

- Similarly, in the F–F bond of F_2, the two 2p orbitals interact end-to-end, that is along the orbital axes, to attain maximum overlap

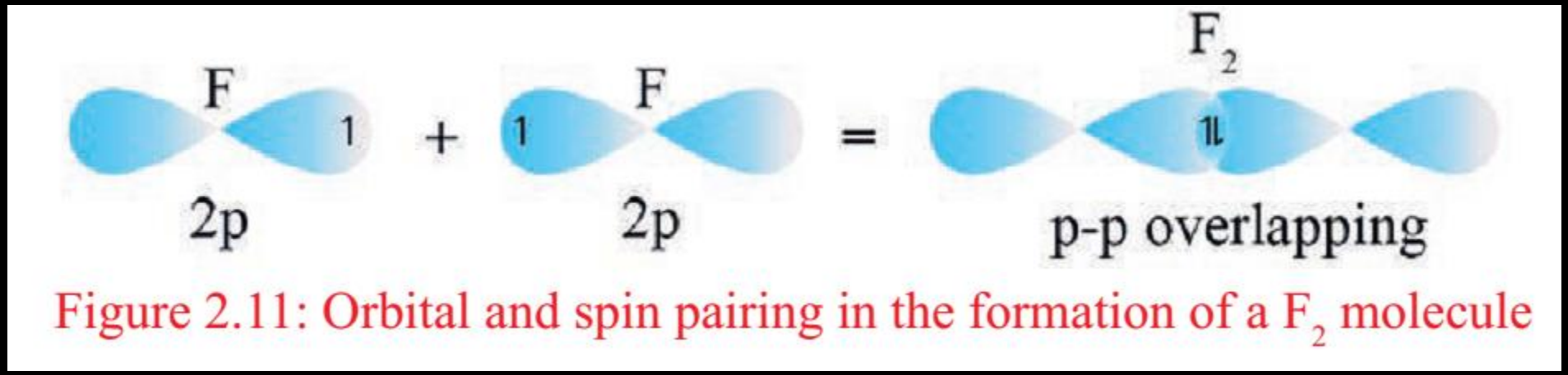


Figure 2.11: Orbital and spin pairing in the formation of a F_2 molecule

- When two atomic orbitals overlap to build up electron density along the two axis between the two nuclei, the resulting localized bond is called a **sigma bond (σ)**.
- Such an overlap is sometimes referred to as a **head on, end-to-end, end on or linear overlap.**
- In Figures 2.9, 2.10 and 2.11, head-to-head overlap resulted in sigma bonds.

- The shape of p atomic orbitals allows them to overlap not only in a head-to-head fashion.
- If they are oriented in a parallel position, they can overlap sideways or laterally as .A bond formed in this way is called **pi-bond (π).**

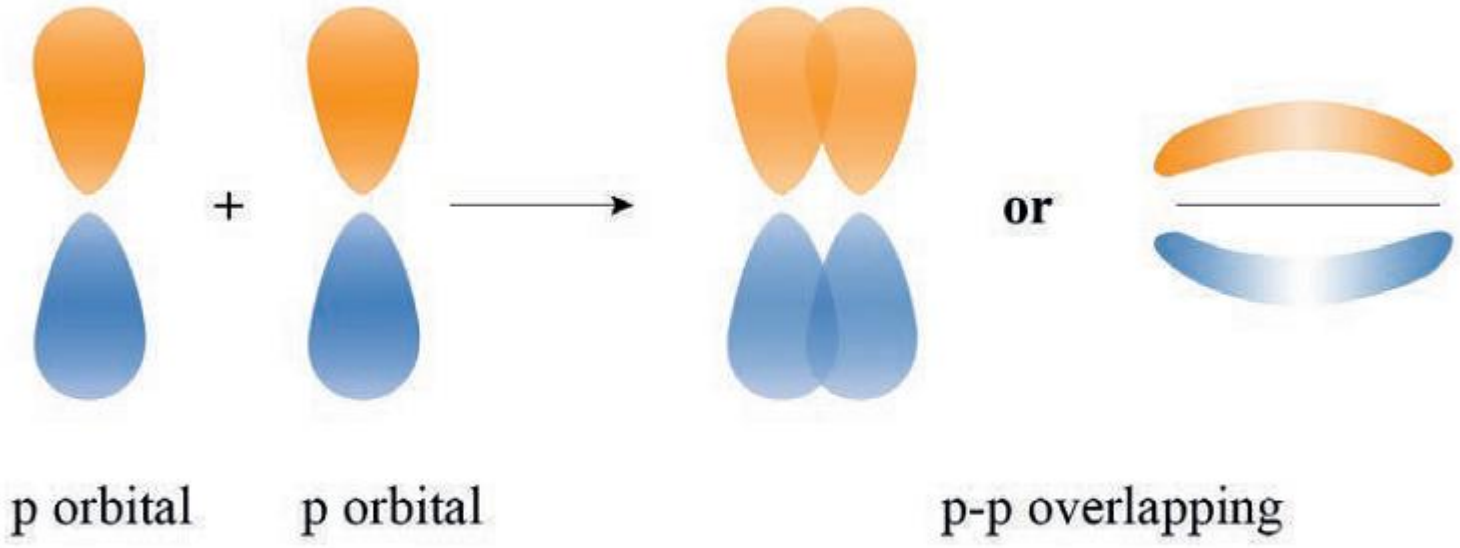


Figure 2.12: Formation of a pi bond (π bond) by the overlap of two half-filled p orbitals that are perpendicular to the internuclear axis

- Note that the directional nature of p orbital allows to overlap in two ways: **end-to end or sideways**.
- These two modes give rise to the two types of covalent bond: **sigma (σ)** and **pi (π) bond**, respectively.
- However, s-s and s-p will always overlap along the nuclear axis, resulting only in **sigma bonds**.
- Pi bonds are present in molecules containing multiple bonds.

- All of the electron density in a π bond is found in lobes above and below the line connecting the atomic centers: one above and one below the sigma bond axis.
- One πbond holds two electrons that occupy both regions of the bond.
- A double bond always consists of **one σ** and **one π bond**.
- The double bond increases electron density between the nuclei.
- A triple bond consists of **one σ** and **two π bonds**.

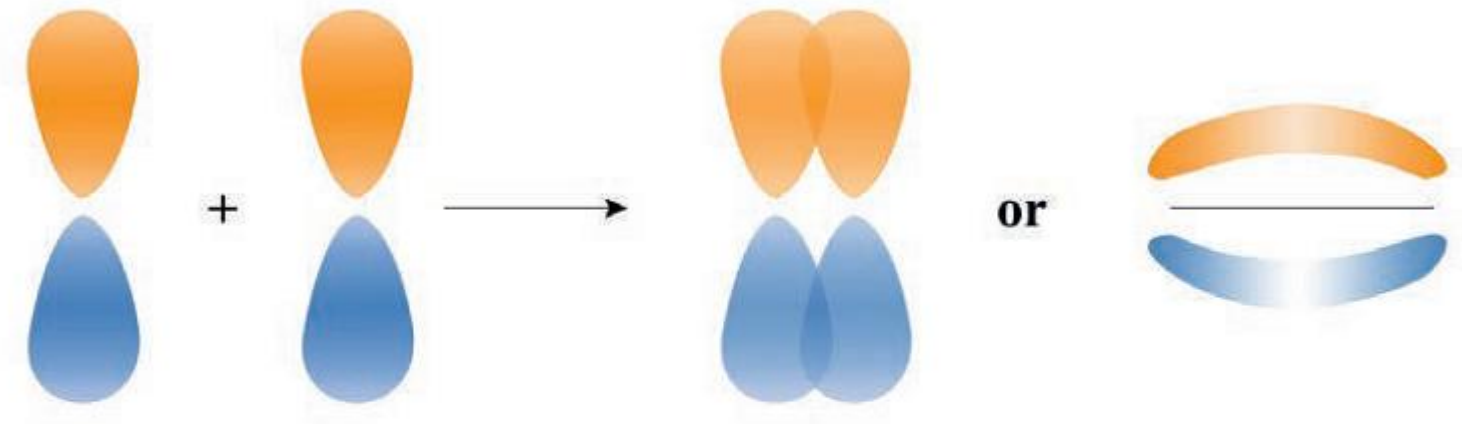


Figure 2.12: Formation of a pi bond (π bond) by the overlap of two half-filled p orbitals that are perpendicular to the internuclear axis

VALENCE BOND THEORY

1) COVALENT BOND

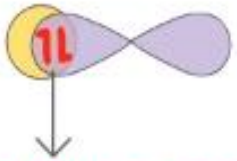
Formed by overlapping of two atomic orbitals.

H Cl



They combine together...

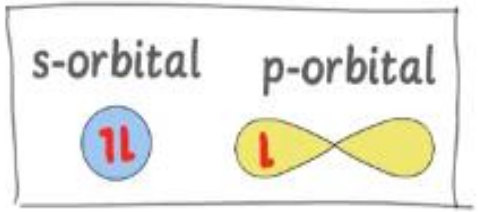
HCl



Overlapping Region

2) TYPE OF ORBITALS

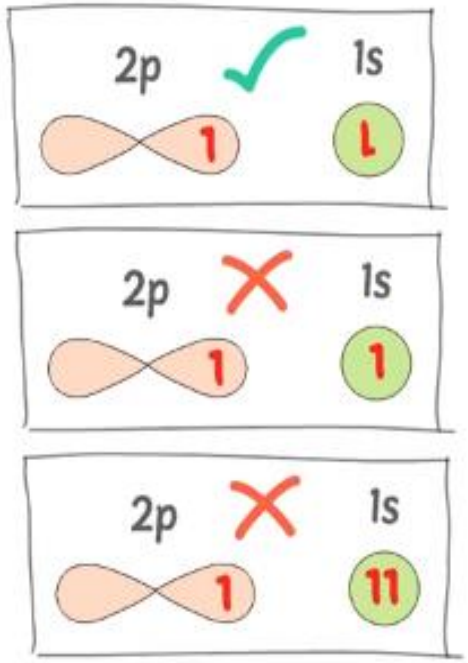
Only half filled orbitals overlap...



NO COVALENT BOND

3) SPIN OF ELECTRONS

Spin must be opposite in overlapping orbitals...



4) IDENTITY OF ORBITALS

Orbitals retain their identity after overlapping.

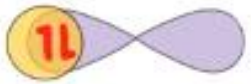
H Cl



Spherical Dumbbell

High Energy

HCl



Spherical Dumbbell

Lower Energy

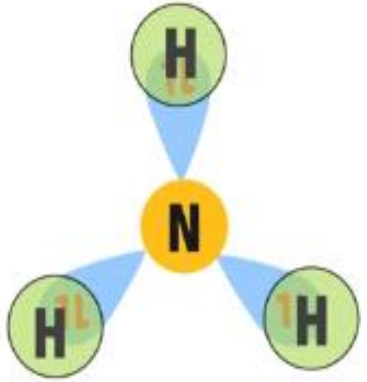
5) NUMBER OF BONDS

1 Unpaired Electron 1 Bond

2 Unpaired Electrons 2 Bonds

3 Unpaired Electrons 3 Bonds

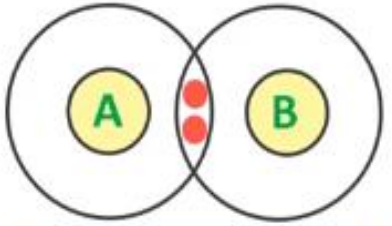
4 Unpaired Electrons 4 Bonds



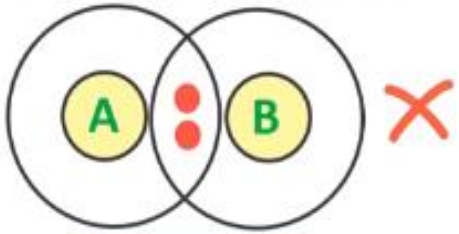
3 Unpaired Electrons 3 Bonds

6) INTENSITY OF OVERLAPPING

Overlapping should take place at optimum position.



Minimum Repulsion

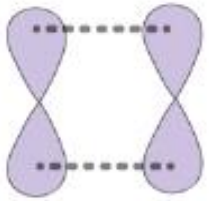


Maximum Repulsion

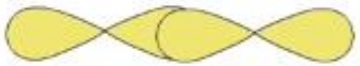
7) BOND ENERGY & LENGTH

The extent of overlapping decides
Bond Energy, Bond Strength, Bond Length

↑ OVERLAPPING ↑ BOND STRENGTH



Minimum Overlapping
Smaller Bond Energy
High Bond Length



Maximum Overlapping
High Bond Energy
Smaller Bond Length

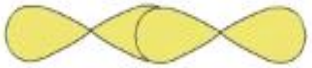
8) SIGMA AND Pi BONDS

Two types of overlapping.

AXIAL OVERLAPPING

Head 2 Head

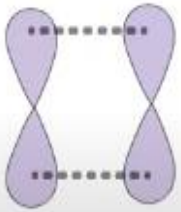
σ



Sigma Bond

PARALLEL OVERLAPPING

Side 2 Side



Hybridization of Orbitals

What is hybridization?

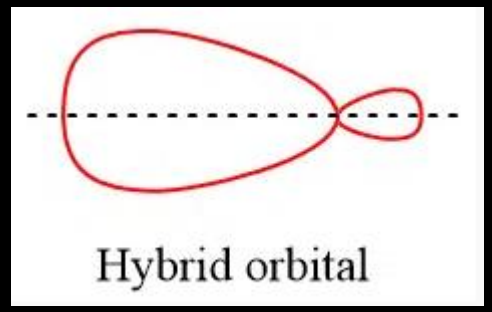
- It is an imaginary mixing process in which the orbitals of an atom rearrange themselves to form new orbitals called **hybrid orbitals.**

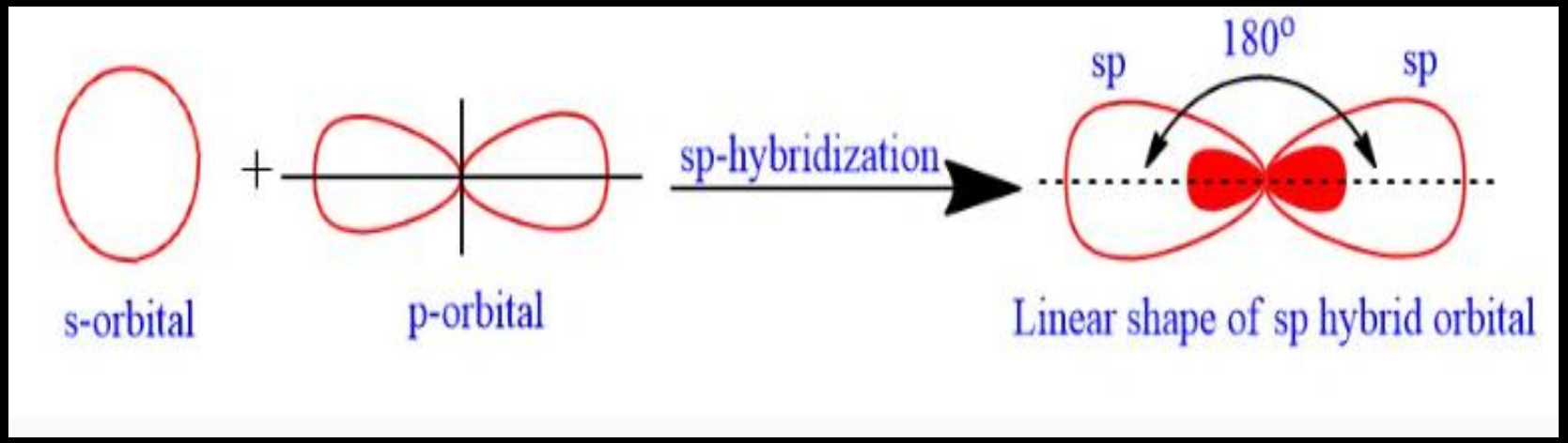
Why we study hybridization?

- Predicting Molecular Geometry
- Explaining Bond Angles
- understanding Molecular Stability

Key Features of Hybridization

- The orbitals involved in hybridization must only have a slight variation in energy.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixed.
- Half filled, completely filled and vacant orbitals can take part in hybridization
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if the hybridization of the molecule is known.
- The bigger lobe of the hybrid orbital always has a positive sign, while the smaller lobe on the opposite side has a negative sign.


Hybrid orbital


sp
180°
sp
sp-hybridization
s-orbital
p-orbital
Linear shape of sp hybrid orbital

Hybrid Orbitals

2	→	sp	→	linear
3	→	sp^2	→	trigonal
4	→	sp^3	→	tetrahedral
5	→	sp^3d	→	trigonal bipyramidal
6	→	sp^3d^2	→	octahedral

- **Based on the types of orbitals involved in mixing, the hybridization can be classified as**

  sp

  sp^2

  sp^3

  sp^3d

  sp^3d^2

  sp^3d^3

Sp hybrid orbital

- sp type of hybridization involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.
- The two equivalent hybrid orbitals formed are oriented in a linear arrangement
- Each sp hybrid orbitals has 50% s-character and 50% p-character.
- This type of hybridization is also known as diagonal hybridization.

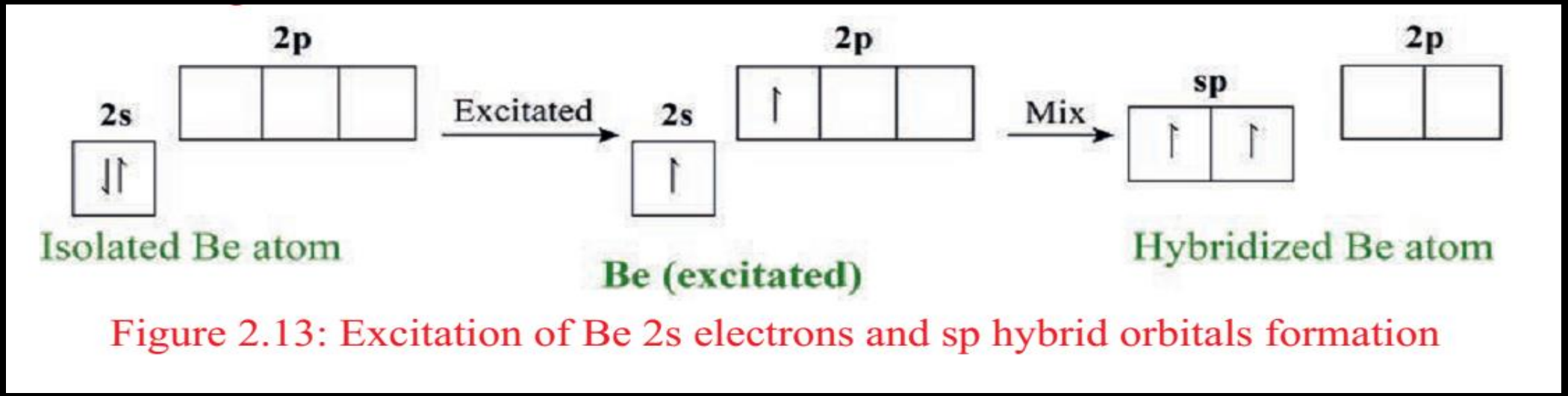
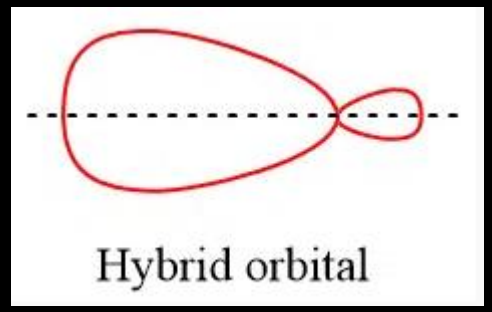
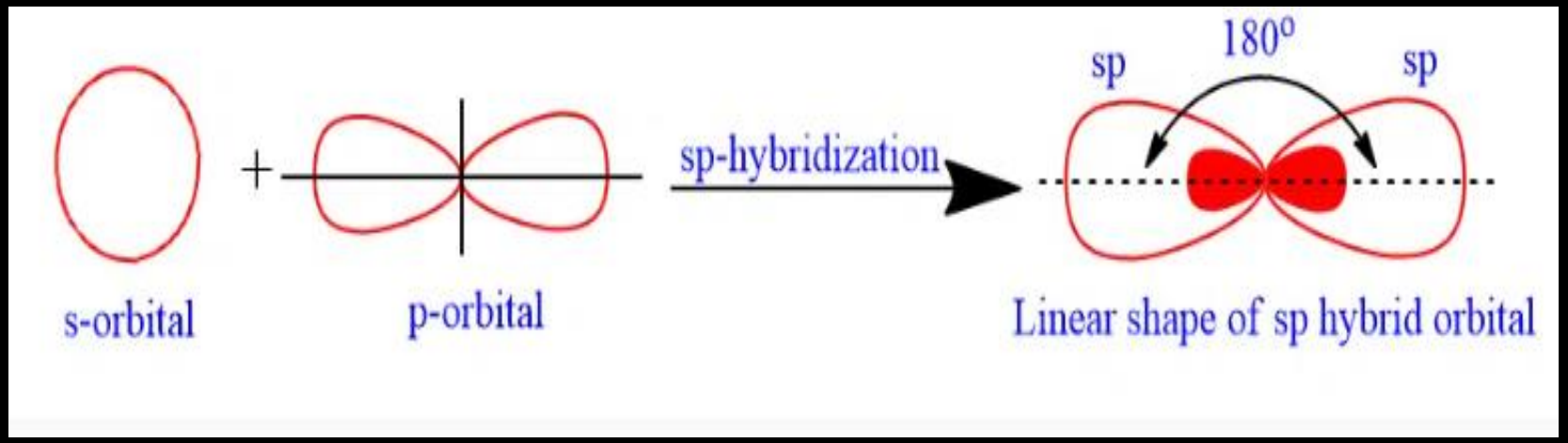


Figure 2.13: Excitation of Be 2s electrons and sp hybrid orbitals formation


Hybrid orbital


sp
180°
sp
sp-hybridization
s-orbital
p-orbital
Linear shape of sp hybrid orbital

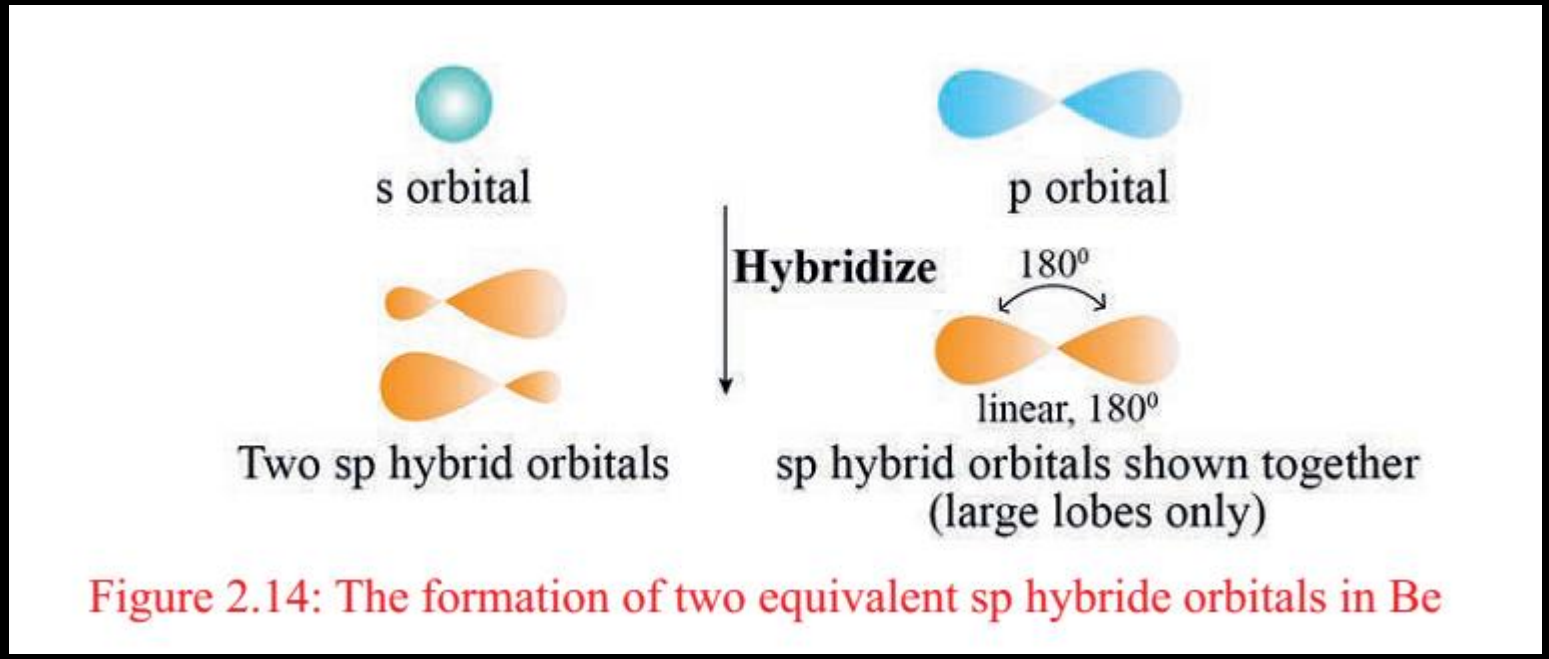


Figure 2.14: The formation of two equivalent sp hybride orbitals in Be

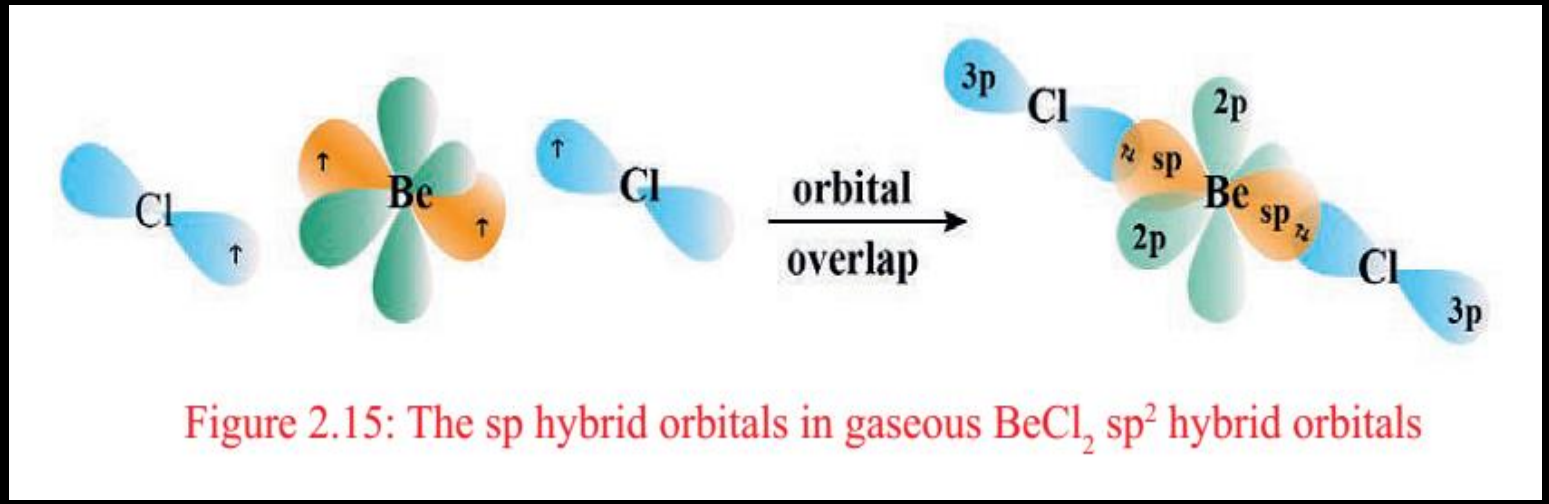


Figure 2.15: The sp hybrid orbitals in gaseous $BeCl_2$ sp^2 hybrid orbitals

Sp^2 hybridization

- In this hybridization there is involvement of one s and two p-orbitals in order to form three equivalent sp^2 hybridized orbitals.
- The three equivalent hybrid orbitals formed are oriented in a trigonal planar arrangement
- Each sp^2 hybrid orbitals has 33.33% s-character and 66.77% p-character.

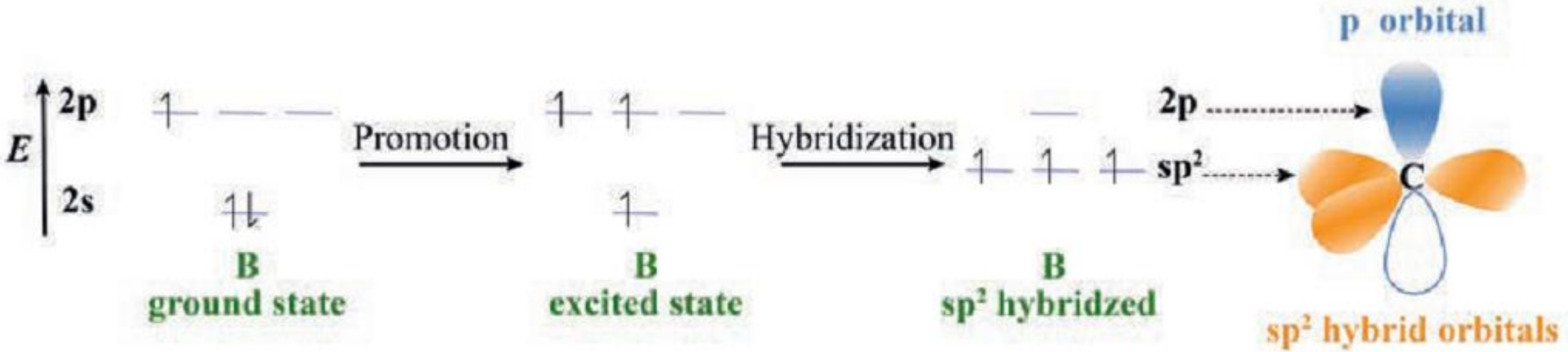
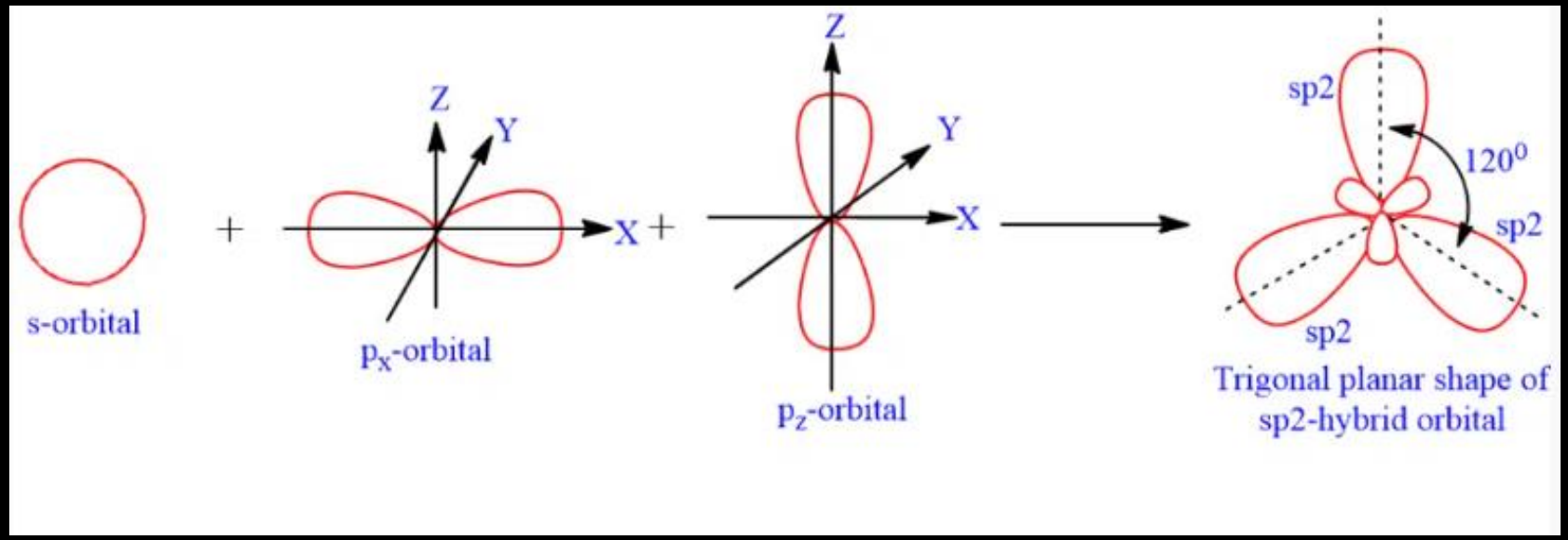
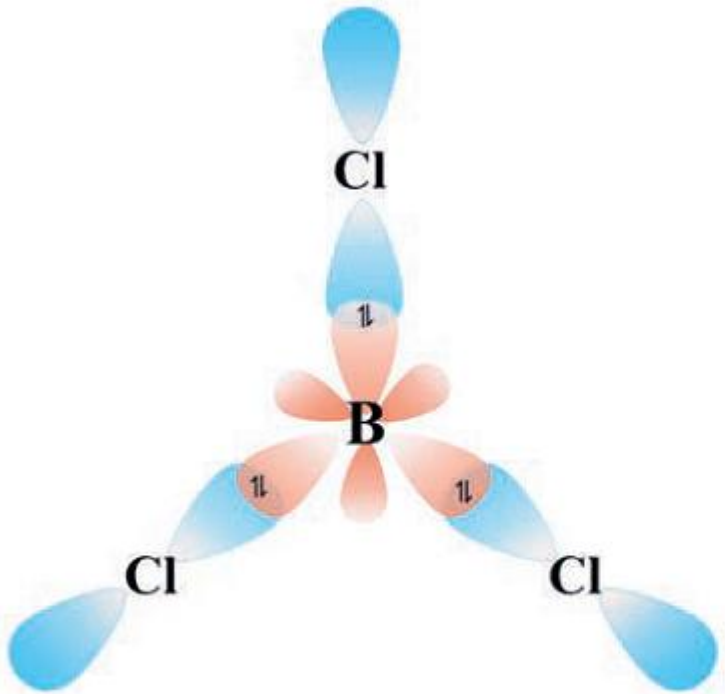


Figure 2.16: Excitation of boron 2s electrons and sp^2 hybrid orbitals formation





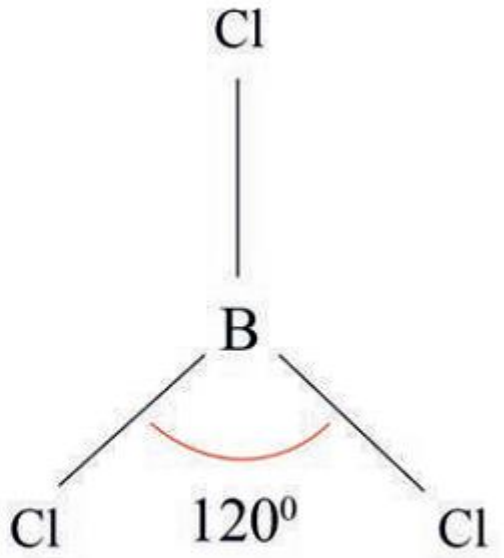


Figure 2.17: sp^2 hybrid orbitals and bonding in BCl_3

Sp^3 hybridization

- In this hybridization there is involvement of one s and three p-orbitals in order to form three equivalent sp^3 hybridized orbitals.
- The four equivalent hybrid orbitals formed are oriented in a Tetrahedral arrangement
- Each sp^3 hybrid orbitals has 25% s-character and 75% p-character.

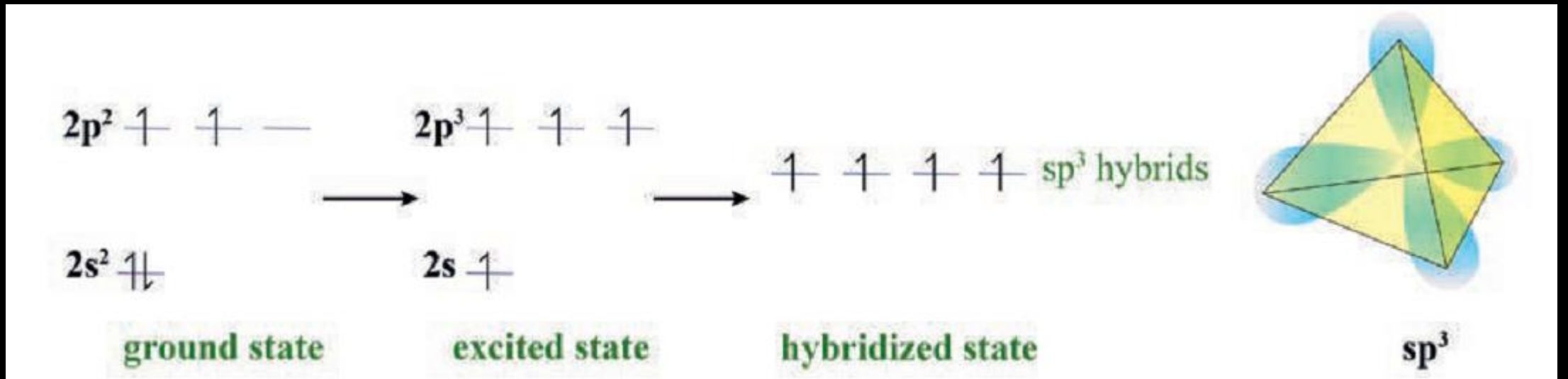


Figure 2.18: Excitation of carbon 2s electrons and sp^3 hybrid orbitals formation

Sp^3d hybridization

- In this hybridization there is involvement of one s ,three p-orbitals and one d orbitals in order to form five equivalent sp^3d hybridized orbitals.
- The five equivalent hybrid orbitals formed are oriented in a trigonal bipyramidal arrangement
- Each Sp^3d hybrid orbitals has 20% s-character , 60% p-character and 20% d character.

Sp^3d^2 hybridization

- In this hybridization there is involvement of one s ,three p-orbitals and two d orbitals in order to form six equivalent sp^3d^2 hybridized orbitals.
- The six equivalent hybrid orbitals formed are oriented in a Octahedral arrangement
- Each Sp^3d^2 hybrid orbitals has 16.67% s-character , 50% p-character and 33% d character.

Multiple bonds and hybridization

Hybrid Orbitals

2	→	sp	→	linear
3	→	sp^2	→	trigonal
4	→	sp^3	→	tetrahedral
5	→	sp^3d	→	trigonal bipyramidal
6	→	sp^3d^2	→	octahedral

Easy trick to find hybridization of central atom

- **Hybrid orbital** = lone pair + number of surrounding atom
- **Lone pair of electron**= G.n of central atom – Valency of atom

Lone pair of electron= G.n of central atom – Valency of atom

Trick To Calculate Lone Pair of Electrons

	G-1	G-2	G-3	G-4	G-5	G-6	G-7	G-8
	H	Mg	B	C	N	O	F	He
	Na	Ca	Al	Si	P	S	Cl	Xe
Valency	1	2	3	4	3	2	1	0

Identify the hybridization of the central atom

CO_2

$S0_2$

BF_4^-

SF_4

SF_6

CO_3^{2-}

NH_4^+

Molecular Orbitals Theory(MOT)

- The molecular orbital theory assumes that when atoms come together, their orbitals not only overlap, but are also simultaneously transformed into new orbitals.
- These new orbitals, called **molecular orbitals (MOs)** These play the same role for molecules that atomic orbitals play for atoms.
- Note that atomic orbitals are the allowed states for an electron moving in the field of one nucleus, whereas molecular orbitals are the allowed states for an electron moving in the field of several nuclei (atoms present in the molecules).

Bonding and Anti-Bonding Molecular Orbitals

- In contrast to VB theory, in which one bonding orbital is formed as a result of the interaction of two atomic orbitals, in MO theory two molecular orbitals result from the combination of two atomic orbitals.
- In mathematical terms, the two molecular orbitals result from the addition of the atomic orbitals that overlap.

- The molecular orbitals that results from the addition of the atomic orbitals that overlap is called a **bonding orbital.**
- In a bonding molecular orbital, because the electron density is concentrated between the two nuclei, the energy of the system is lowered compared with that of isolated atomic orbitals.

- The molecular orbital that results from the subtraction of atomic orbitals that overlap is called an **antibonding molecular orbital**.
- In antibonding molecular orbitals, the electron density is concentrated away from the region between the two nuclei.
- That is, anti-bonding molecular orbitals have a region of zero electron density (a node) between the nuclei.
- The net effect of having a low electron density between the nuclei is that the two nuclei repel each other. Therefore, energy of an
- antibonding orbital is increased compared with that of the two isolated atomic orbitals.

Example: Which of the following is a characteristics of antibonding molecular orbitals?(UEE 2004)

A. It is a molecular orbital with high probability of finding electrons parallel to the region between bonded atoms

B. It has no electrons

C. It is a molecular orbital with high probability of finding electrons away from the region between bonded atoms

D. It is a molecular orbital with high probability of finding electrons in the region between bonded atoms

Electron Configuration of Diatomic Molecules

- **Electrons occupy molecular orbitals following the same rules that apply to the filling of atomic orbitals: the aufbau principle and the Pauli Exclusion Principle and Hund's rule are obeyed.**

a. In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is: $\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}(\pi_{2p_y}=\pi_{2p_z})\sigma_{2p_x}(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

b. For simple homonuclear diatomic molecules (total electrons greater than 14) the $(\pi_{2p_y}=\pi_{2p_z})$ comes after σ_{2p_x} and the order is:

$\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}\sigma_{2p_x}(\pi_{2p_y}=\pi_{2p_z})(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

- **Note:**
- **The number of molecular orbitals formed must equal the number of atomic orbitals available for combination.**
- **Unfilled molecular orbitals are considered to be there, even when there are no electrons in them.**

Bond border

- MO theory uses the term “bond order” to indicate whether a covalent bond is single (bond order = 1), double (bond order = 2) or triple (bond order = 3).
- **Bond order** is defined as the number of electrons in bonding MOs minus the number in antibonding MOs, divided by two:

$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{Number of } e^- \text{ in}\\ \text{bonding MOs}\end{pmatrix} - \begin{pmatrix}\text{Number of } e^- \text{ in}\\ \text{anti-bonding MOs}\end{pmatrix}\right]$$

a. In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is: $\sigma_{1s}\sigma^{*}_{1s}\sigma_{2s}\sigma^{*}_{2s}(\pi_{2p_y}=\pi_{2p_z})\sigma_{2p_x}(\pi^{*}_{2p_y}=\pi^{*}_{2p_z})\sigma^{*}_{2p_x}$

b. For simple homonuclear diatomic molecules (total electrons greater than 14) the $(\pi_{2p_y}=\pi_{2p_z})$ comes after σ_{2p_x} and the order is:

$\sigma_{1s}\sigma^{*}_{1s}\sigma_{2s}\sigma^{*}_{2s}\sigma_{2p_x}(\pi_{2p_y}=\pi_{2p_z})(\pi^{*}_{2p_y}=\pi^{*}_{2p_z})\sigma^{*}_{2p_x}$

- A bond order greater than zero indicates that the molecule is stable relative to the separate atoms, whereas a bond order of zero implies no net stability.
- In general, the higher the bond order, the stronger the bond.

Example: Find the bond order and the molecules exist or doesn't exist

N_2

O_2

Ne_2

a. In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is: $\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}(\pi_{2p_y}=\pi_{2p_z})\sigma_{2p_x}(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

b. For simple homonuclear diatomic molecules (total electrons greater than 14) the

$(\pi_{2p_y}=\pi_{2p_z})$ comes after σ_{2p_x} and the order is:

$\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}\sigma_{2p_x}(\pi_{2p_y}=\pi_{2p_z})(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

Magnetic Properties

- Molecules with unpaired electrons exhibit paramagnetic properties. The species is attracted by an external magnetic field.
- When all the electrons are paired, there is diamagnetism. Such species are not attracted (and, in fact, are slightly repelled) by a magnetic field.

Example: Classify the following molecules as **paramagnetic or diamagnetic** substance

NO

O_2

CN^-

a. In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is: $\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}(\pi_{2p_y}=\pi_{2p_z})\sigma_{2p_x}(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

b. For simple homonuclear diatomic molecules (total electrons greater than 14) the $(\pi_{2p_y}=\pi_{2p_z})$ comes after σ_{2p_x} and the order is:

$\sigma_{1s}\sigma^*_{1s}\sigma_{2s}\sigma^*_{2s}\sigma_{2p_x}(\pi_{2p_y}=\pi_{2p_z})(\pi^*_{2p_y}=\pi^*_{2p_z})\sigma^*_{2p_x}$

Types of Crystal

The crystalline solids can be classified as

- Ionic crystals
- Molecular crystals
- Covalent network crystals
- Metallic crystals

Types of Solid

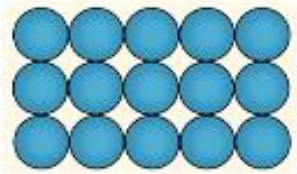
- Depending on the arrangement of atoms, there are two types of solid
  - Crystalline
  - Amorphous
- all crystals are solids, but not all solids are crystals

TYPES OF SOLIDS

CRYSTALLINE SOLIDS

1) Regular arrangement of particles.

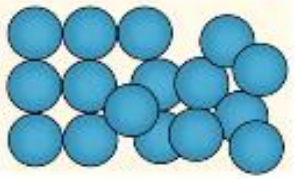
REGULARLY ARRANGED



AMORPHOUS SOLIDS

1) Irregular arrangement of particles.

IRREGULARLY ARRANGED



Crystalline solid

- Composed of one or more crystals.
- Each crystal has a well-defined, ordered structure in three dimensions.
- A structural unit of a crystalline solid has a characteristic repetitive pattern.

Example:metal,ionic compounds, sugar

The crystalline solids can be classified as ionic, molecular, covalent network and metallic.

Amorphous solid

- An **amorphous solid** has a disordered structure; it lacks the well-defined arrangement of basic units (atoms, molecules, or ions) found in a crystal.
- **Example:** Plastics, glass, rubber, metallic glass, polymers
- A glass is an amorphous solid obtained by cooling a liquid rapidly enough that its basic units are “frozen” in random positions before they can assume an ordered crystalline arrangement.

Ionic Crystals

- Ionic crystals consist of ions held together by ionic bonds
- The structure of an ionic crystal depends on the charges on the cation, anion and on their radii.
- The properties of ionic solids are direct consequences of the strong interionic forces, which create a high lattice energy.
- Ionic solids have high melting points, an indication of the strong attraction force holding the ions together.

Molecular Crystals

- Contains molecules
- Molecular solids are made up of discrete molecules that interact via intermolecular forces.
- Various combinations of dipole-dipole, dispersion and hydrogen-bonding forces

- The fundamental unit of a molecular solid is molecules or monatomic elements.
- Such solids are common among organic compounds and simple inorganic compounds.
- Molecular crystals are usually transparent, brittle, and break easily when stressed.
- They are usually non-conductors of heat and electricity and usually have low melting points.

Covalent Network Crystals

- In this type of crystalline solids, separate particles are not present.
- Instead, strong covalent bonds link the atoms together throughout the network of covalent solid.
- As a consequence of the strong bonding, all these substances have extremely high melting and boiling points, but their conductivity and hardness depend on the nature of their bonding.
- graphite and diamond are examples of network covalent solids

- **The most important network covalent solids are the silicates.**
- **In a covalent network solid, the whole crystal is one giant molecule.**
- **The fundamental units are atoms covalently bonded to their neighbours.**
- **These crystals are usually hard, non-conductors of heat and electricity, and have high melting points.**

Metallic Crystal

- The strong metallic bonding forces hold individual atoms together in metallic solids.
- Bonding in metals can be explained as a network of positive ions immersed in a sea of electrons.
- That is, the electrons in the valence shell of the metal atoms are highly delocalized.
- For this reason, metals are very good conductors of electricity.
- Metallic bonding forces are stronger than those arising from intermolecular forces, so metallic solids have higher melting points than molecular solids.