Pre-University Remedial Chemistry Course

March 2023

1. Atomic Structure and Periodicity

1.1 The concept of the atom

- The Greek philosopher ,Democritus expressed the belief that all matter consists of very small, indivisible particles, which he named *atomos (meaning* uncuttable or indivisible)
- His idea was not accepted by many of his contemporaries (notably Plato and Aristotle).
- John Dalton, formulated a precise definition of the indivisible building blocks of matter that we call atoms

Dalton’s Atomic Theory

- ✓ *Elements are composed of extremely small particles, called atoms.*
- ✓ *All atoms of a given element are identical, having the same size, mass, and chemical properties.*
- ✓ *Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.*
- ✓ *A chemical reaction involves only the separation, combination, or rearrangement of atoms*

How the Modern Theory Explains the Mass Laws

Activity

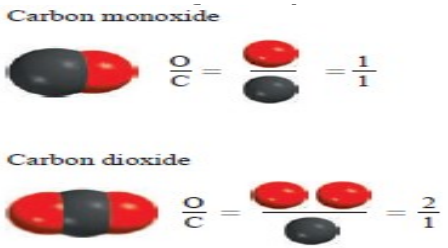
Write modern atomic theory

Which of Dalton's postulates inconsistent with later observations?

- Dalton's concept of an atom was far more detailed and specific than Democritus
- The third hypothesis suggests that, to form a certain compound, we need not only atoms of the right kinds of elements, but the specific numbers of these atoms as well
- Proust's ***law of definite proportions*** states that *different samples of the same*

compound always contain its constituent elements in the same proportion by mass.

- ***law of multiple proportions*** this law states, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers*
- Modern measurement techniques indicate that on combines with one atom of oxygen in carbon mon tom of arbon combines with two oxygen atoms in carbo



- Dalton's fourth hypothesis is another way of stating the ***law of conservation of mass,*** which is that *matter can be neither created nor destroyed.*

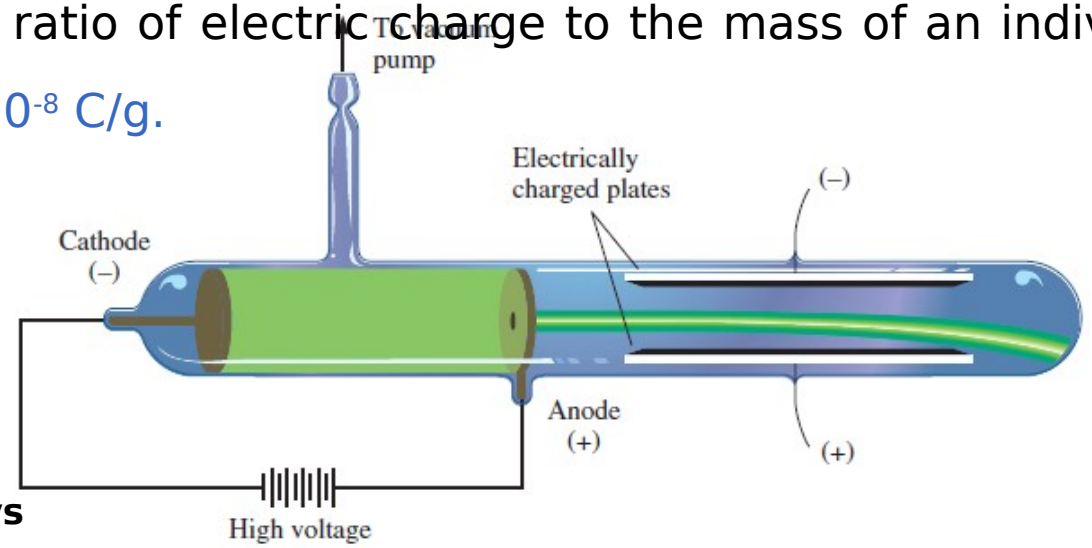
The Structure of the Atom

- On the basis of Dalton's atomic theory, we can define an ***atom*** as *the basic unit of an element that can enter into chemical combination.*
- Investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure;
- This research led to the discovery of three *subatomic particles*
  - ✓ *electrons*
  - ✓ *protons, and*
  - ✓ *neutrons*

1.2. Discoveries of subatomic Particles

Discovery of the Electron

- Some investigators tried passing current from a high-voltage source through nearly evacuated glass tubes fitted with metal electrodes that were sealed
- The rays were called **cathode rays because they originated at** the negative electrode (cathode) and moved to the positive electrode (anode).
- in place and connected to an external source of electricity.
- J. J. Thomson, used a cathode ray tube and his knowledge of electromagnetic theory to determine the ratio of electric charge to the mass of an individual electron (e^-/m) -1.76 x 10^{-8} C/g.



1 Formation of cathode rays

✓The rays were called **cathode rays because they originated** the negative electrode (cathode) and moved to the positive electrc (anode).

✓travel in a straight line,

✓in a magnetic field the path is bent, indicating that the particles are charged, and in an electric field the path bends toward the positive plate

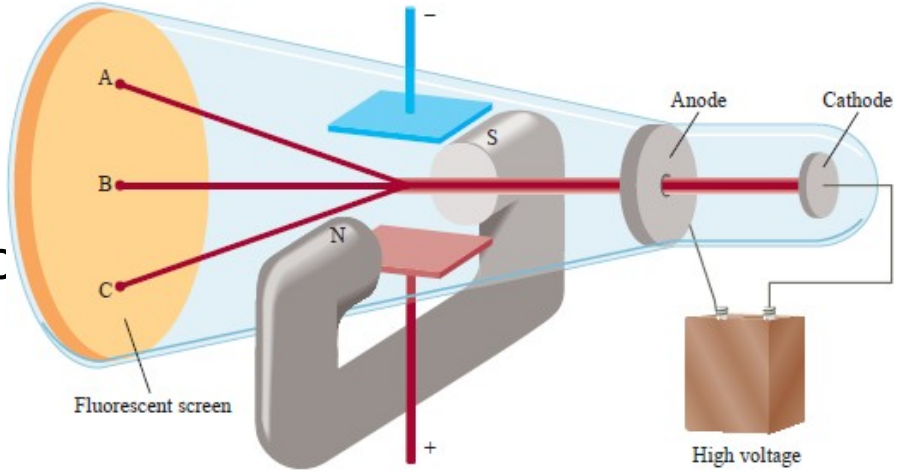


Fig.2 Thomson's cathode ray tube, which was used to measure the charge-to-mass ratio for the electron.

➢It was concluded that cathode rays consist of negatively charged particles found in all matter

➢The rays appear when these particles collide with the few remaining gas molecules in the evacuated tube. Cathode ray particles were later named *electrons.*

- After studying many droplets, Millikan calculated that the various charges of the droplets were always some *whole-number multiple of a minimum charge.*
- R. A. Millikan, an American physicist, found the charge of an electron to be 1.6022×10^{-19} C. From these data he calculated the mass of an electron

$$\text{mass of an electron} = \frac{\text{charge}}{\text{charge/mass}}$$

$$= \frac{-1.6022 \times 10^{-19}\ \text{C}}{-1.76 \times 10^{8}\ \text{C/g}}$$

$$= 9.10 \times 10^{-28}\ \text{g}$$

- This mass is 1/1837 the mass of a hydrogen atom

Radioactivity and Discovery of Nucleus

Radioactivity

- Radioactivity is the spontaneous emission of radiation from the unstable nuclei of certain isotopes.
- Isotopes that are radioactive are called radioactive isotopes or radioisotopes

e.g. $^{55}_{24}Cr$, $^{226}_{88}Ra$, $^{14}_{6}C$, $^{238}_{92}U$, $^{14}_{7}N$

- Radioactive decay is defined as a nuclear breakdown in which particles or (electromagnetic) radiation is emitted
- three types of rays were identified in the emanations from radioactive substances.

alpha (α) particles which consist of particles that have a mass that is about four times that of a hydrogen atom

- ✓ They also have a charge twice the magnitude of an electron but positive rather than negative.
- ✓ known to be a doubly-ionized helium atom, that is, He^{2+}

Beta (β) particles- consist of negatively-charged particles, identical to cathode rays

- are *electrons* and are deflected by the negatively charged plate.

Gamma (γ) rays- is a form of electromagnetic radiation much like the X-rays but of even higher energy

- Like X rays, rays have no charge and are not affected by an external electric or magnetic field.

Discovery of Nucleus

- In 1910, Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for *particles from a radioactive source*
- They observed that the majority of particles penetrated the foil either un deflected or with only a slight deflection.
- They also noticed that every now and then an α- *particle was scattered* (or deflected) at a large angle.
- In some instances, an α- *particle actually bounced back*

- From results of the α -scattering experiment, Rutherford devised a new model of atomic structure
- The atom's positive charges, are all concentrated in the *nucleus, a dense central core within the atom*

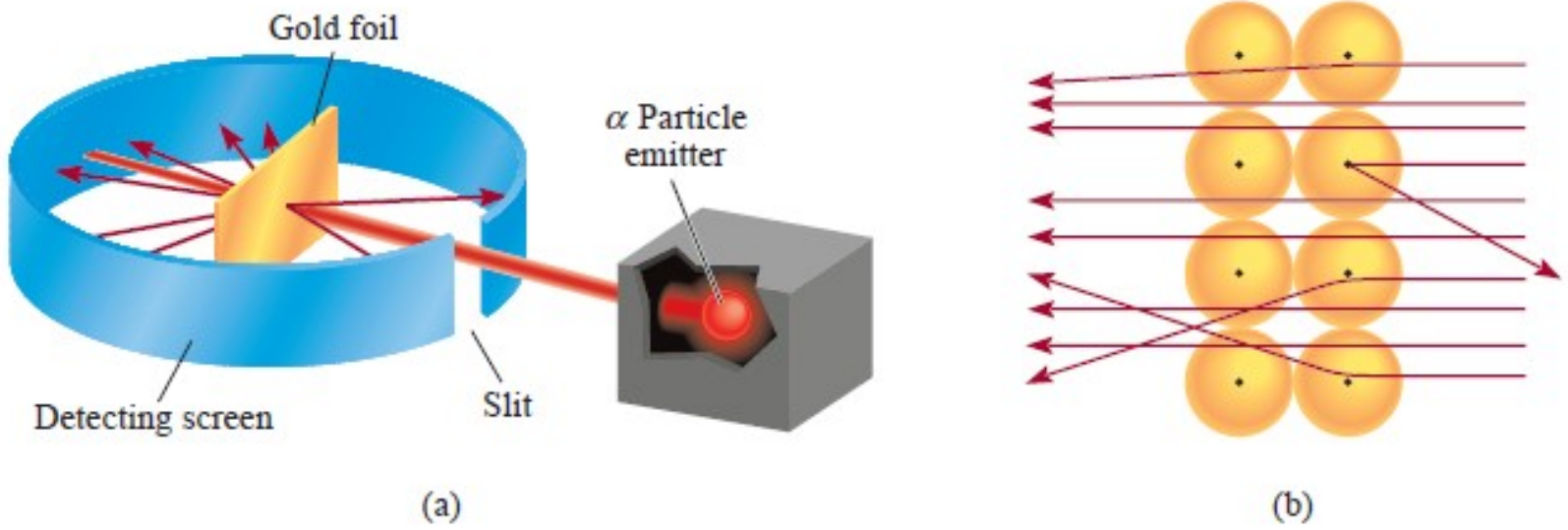
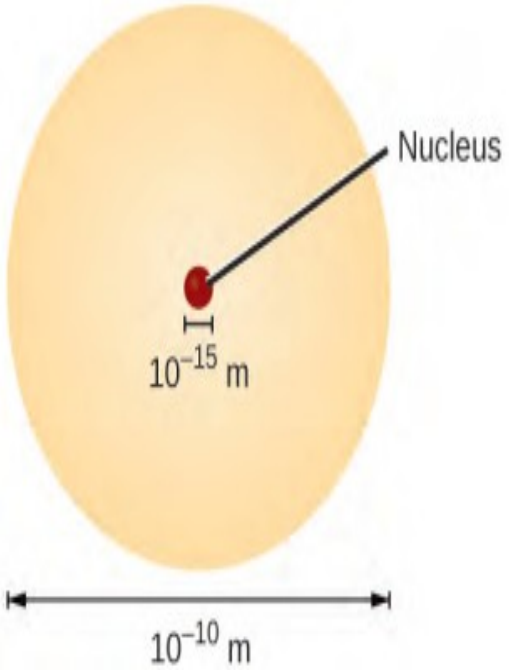
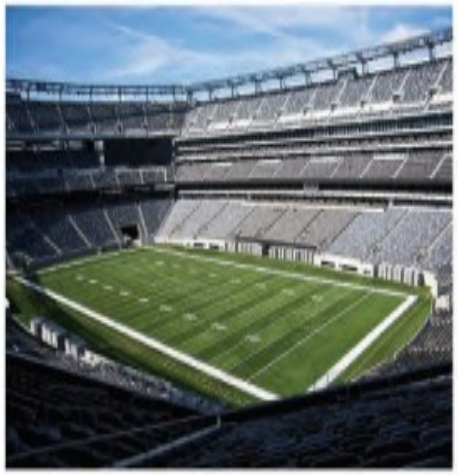


Figure 3 Rutherford's α -scattering experiment

- *What you conclude from the deflection of each rays?*

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







- ✚ Rutherford suggested that the smallest positive-ray particle was the fundamental unit of positive charge in all nuclei
- ✚ A **proton** is *a nuclear particle having a positive charge equal to that of the electron and a mass more than 1840 times that of the electron.*
- ✚ A proton has a mass of $mp = 1.67262 \times 10^{-27}$ kg

The Discovery of Neutron

- In 1932, James Chadwick, in 1932. When Chadwick bombarded a thin sheet of beryllium with *particles, a very high energy radiation similar to rays was emitted by the metal.*
- *The exp't revealed that electrically neutral particles having a mass slightly greater than that of protons obtained. Chadwick named these* particles ***neutrons.***
- It has an actual mass 1.674 $x10^{-24}$ g which is only very slightly greater than that of a proton.

Mass and Charge of Subatomic Particles

Name (Symbol)	Charge		Mass		Location in Atom
	Relative	Absolute (C)*	Relative (amu)†	Absolute (g)	
Proton (p^+)	1+	$+1.60218\times10^{-19}$	1.00727	1.67262×10^{-24}	Nucleus
Neutron (n^0)	0	0	1.00866	1.67493×10^{-24}	Nucleus
Electron (e^-)	1−	-1.60218×10^{-19}	0.00054858	9.10939×10^{-28}	Outside nucleus

1.3. The Bohr Theory of the hydrogen atom

- According to Rutherford's nuclear model, the atom consists of a nucleus with most of the mass of the atom and a positive charge, around which move enough electrons to make the atom electrically neutral.

- **Niels Bohr** introduced **the atomic Hydrogen model** in **1913**. He described it as a positively charged nucleus, comprised of protons and neutrons, surrounded by a negatively charged electron cloud.

Emission Spectra

- Is expressed as either ***continuous or line spectra*** of radiation emitted by substances.

- Bohr set down the following postulates to account for;
- The stability of the hydrogen atom (that the atom exists and its electron does not continuously radiate energy and spiral into the nucleus) and the line spectrum of the atom.

1. Energy-level Postulate - An electron can have only *specific energy values in an atom*, which are calle

- He formula for the energy lev e hydrogen atom.

$$E = -\frac{R_H}{n^2} \qquad n = 1, 2, 3, \ldots \infty \qquad \text{(for H atom)}$$

Rydberg constant,
RH = 2.179*10-18 J
n = principal quantum number

2. Transitions Between Energy Levels- An electron in an atom can change energy only by going from one energy level to another energy level.

- ✓ According to Bohr, the emission of light from an atom occurs as follows. An electron in a higher energy level (initial energy level, *Ei*) undergoes a transition to a lower energy level (final energy level, *Ef*), explained by Balmer's formula.

$$\Delta E = E_f - E_i$$

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

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

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

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

Examples

1. What is the wavelength of light emitted when the electron in a hydrogen atom transitions from an energy level with n = 4 to an energy level with n = 2?

❖ What are the limitations of Bohr's theory of a hydrogen atom?

- ✓ It violates the Heisenberg Uncertainty Principle.
- ✓ The Bohr atomic model theory made correct predictions for smaller sized atoms like hydrogen, but poor spectral predictions are obtained when larger atoms are considered.
- ✓ Failed to explain Stark effect when the spectral line gets split up into fine lines in the presence of electric field.

Beginning with Rutherford

Problems with Rutherford's Model

- It didn't explain WHY metals and metal compounds give off characteristic colors when they are flame tested
- It didn't explain why metals glow when heated – first red, orange yellow and then white
- It didn't explain the CHEMICAL properties of elements

Bohr's Theory

- Electrons are located at specific energy levels surrounding the nucleus
- The higher the energy level – the farther it is from the nucleus

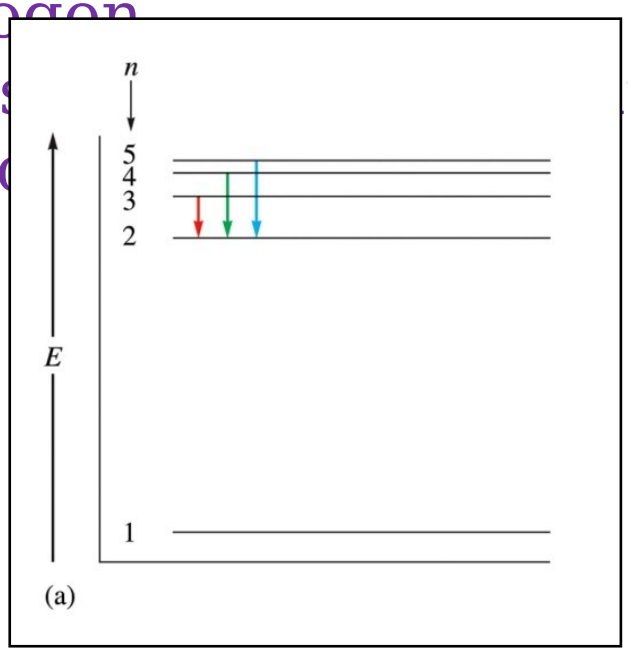
Bohr Model

- First model of the electron structure
- Gives levels where an electron is most likely to be found
- Incorrect today, but a key in understanding the atom

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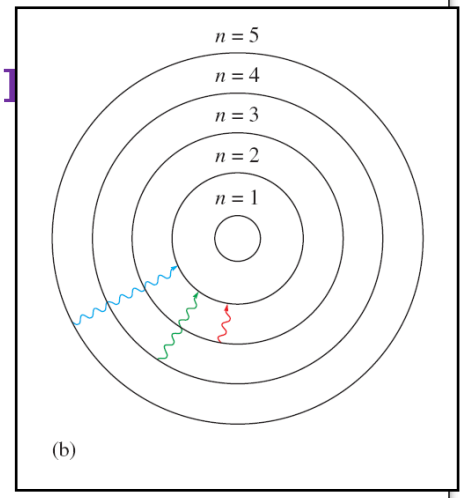
Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum.

- Ground state – lowest possible energy state (n = 1)
- Bohr's model is incorrect. This model only works for hydrogen
- Electrons [illegible] around the [illegible] circular [illegible]



Electronic Transitions in the Bohr Model for the Hydrogen Atom

a) An Energy-Level Diagram for Electronic Transitions



Electronic Transitions in the Bohr Model for the Hydrogen Atom

b) An Orbit-Transition Diagram, Which Accounts for the Experimental Spectrum

1.4 . The quantum mechanical model of the atom

❖ The Dual Nature of the Electron

- De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties.

- According to de Broglie, an electron bound to the nucleus behaves like a *standing **wave***.
- De Broglie deduced that the **particle and wave properties** are related by the expression

$$\lambda = h/mu$$

where λ, m, and u are the wavelengths associated with a moving particle, its mass, and its velocity, respectively.

Example

1. What is the wavelength (in picometers) associated with an electron, whose mass is 9.11 * 10-31 kg, traveling at a speed of 4.19*106 m/s?

Werner Heisenberg (**Heisenberg uncertainty principle): It is impossible to know** simultaneously both the momentum (mass times velocity) and the position of a particle with certainty.
The probability of finding the electron in a certain region in space is proportional to the square of the **wave function, ψ^2.**

The square of the **wave function, ψ^2**, defines the distribution of electron density in three-dimensional space around the nucleus (***schrodinger***).

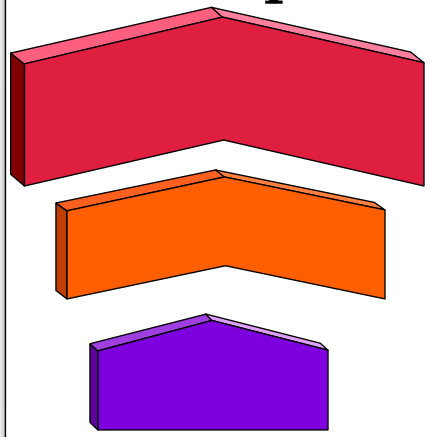
- He agreed that electrons have a specific amount of energy
- Quantum – the amount of energy needed to move from one energy level to another
- The electrons move in regions of probability around the nucleus called *Orbitals*

Cont'd…

- ✓ Quantum theory, also called wave mechanics, **describes the arrangement and space occupied by electrons.**
- ✓ **Orbitals** refers to the three-dimensional regions in space where there is a high probability of finding an electron around an atom.

haracteristics of Electrons

- Extremely small mass
- Located outside the nucleus
- Moving at extremely high speeds in a sphere
- Have specific energy levels



Energy of Electrons

- When atoms are heated, bright lines appear called line spectra
- Electrons in atoms arranged in discrete levels.
- An electron absorbs energy to “jump” to a higher energy level.
- When an electron falls to a lower energy level, energy is emitted.

Quantum numbers

- Quantum Numbers are used to define:
  - ✓ The energy of the electron
  - ✓ The electron's relative distance from the nucleus
  - ✓ The size and shape of the ORBITAL
  - ✓ The pairings of the electrons

- According to quantum mechanics, each electron in an atom is described by four different quantum numbers.

Cont'd

1. Principal Quantum Number (*n*)

- Average distance from the nucleus increases with increasing principal quantum number, therefore *n* designates the size of the electron cloud.

- Maximum of electrons in each energy level is calculated by $2n^2$ where n = the energy level (1-7).

2. The angular momentum quantum number (*l*)

- The number of sublevels equals the value of the principal quantum number (*n*) for that level.
- Sublevels are named in the following order - s, p, d, f.
- The *l* number designates the shape of the electron cloud

3. The magnetic quantum number (ml)

- The space occupied by a pair of electrons in a certain sublevel. Sublevel; **s** - **1** orbital

  p - **3** orbitals

  d - **5** orbitals

  f - **7** orbitals

- Each orbital can hold two electrons.
- *m* represents the orientation in space of the orbitals (x axis, y axis, z axis)

4. The spin quantum number (m_s)

- Distinguishes between the electrons in the same orbital.
- Describes the electrons spin as either clockwise or counter-clockwise

Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

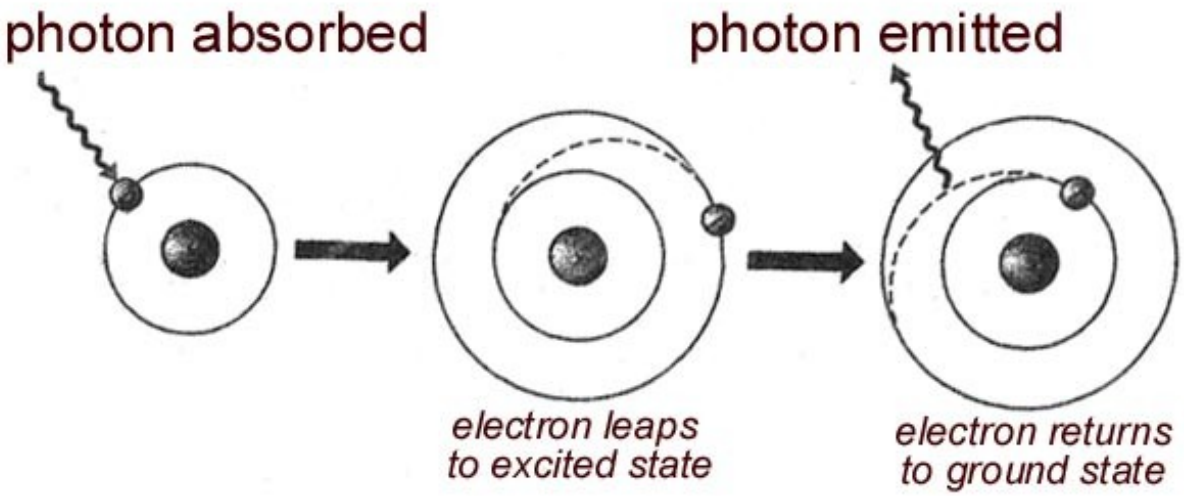
n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

Exercise

1. For principal quantum level $n = 3$, determine the number of allowed subshells (different values of l), and give the designation of each.
2. For $l = 2$, determine the magnetic quantum numbers (m_l) and the number of orbitals.

1.4.1 The electromagnetic radiation and atomic spectra

- Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or *quanta*.
- *Energy* is continuous, which meant that any amount of energy could be released in a radiation process.
- ***El*** *ssion and tr form of el*



- Light consists of electromagnetic waves.
- Electromagnetic radiation includes the following spectrum

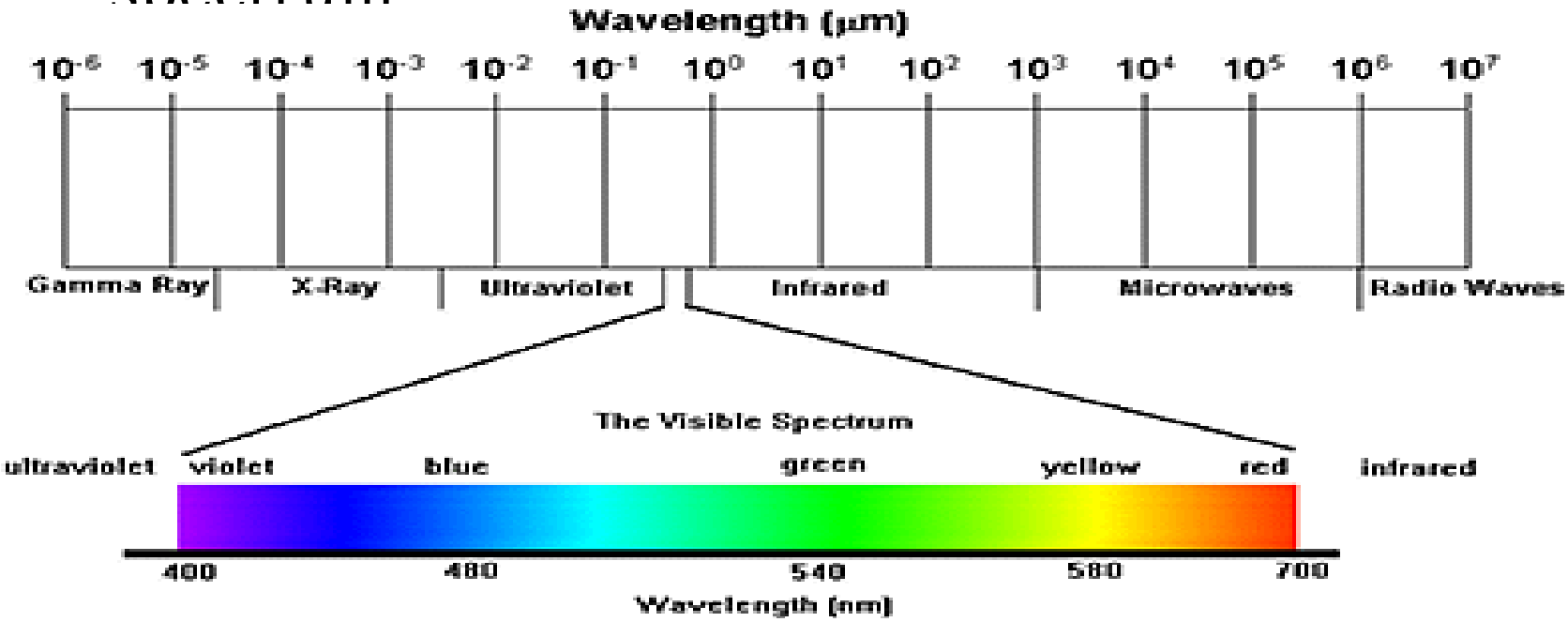
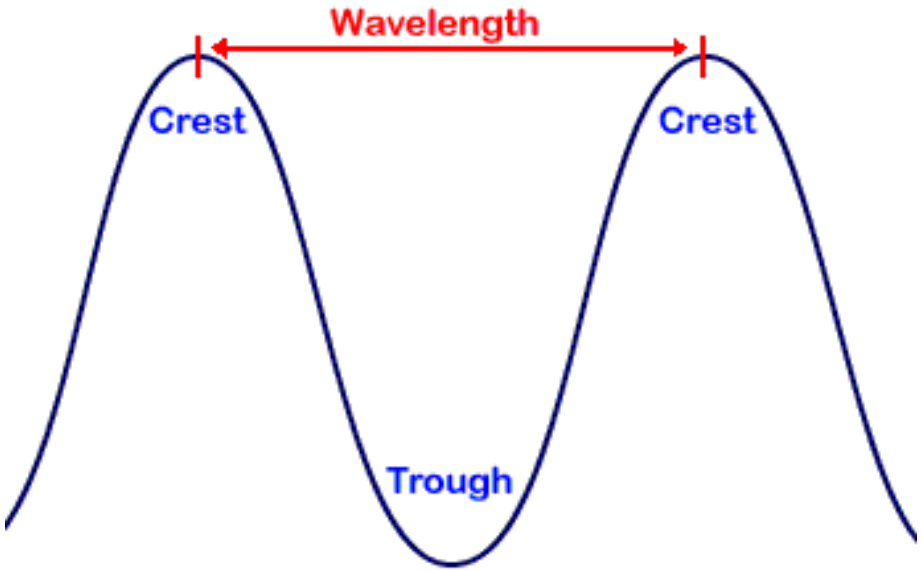
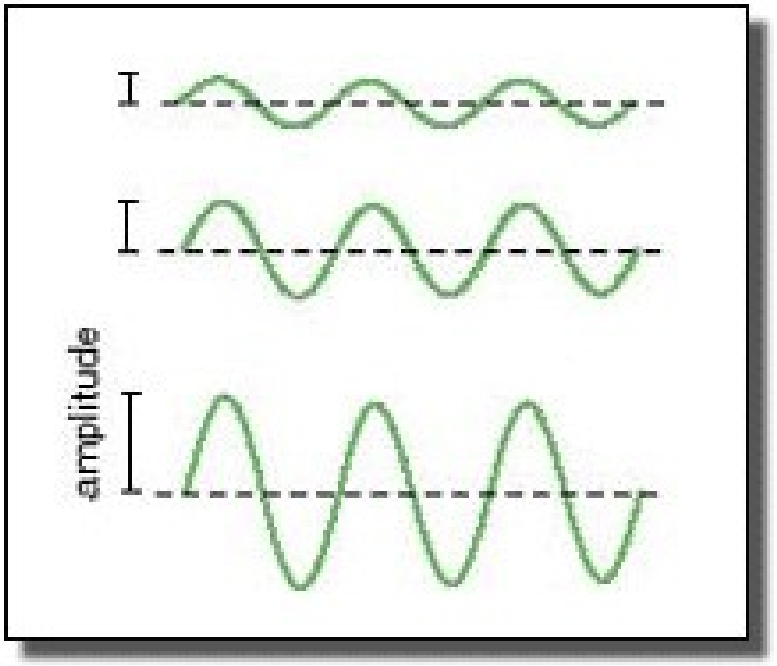


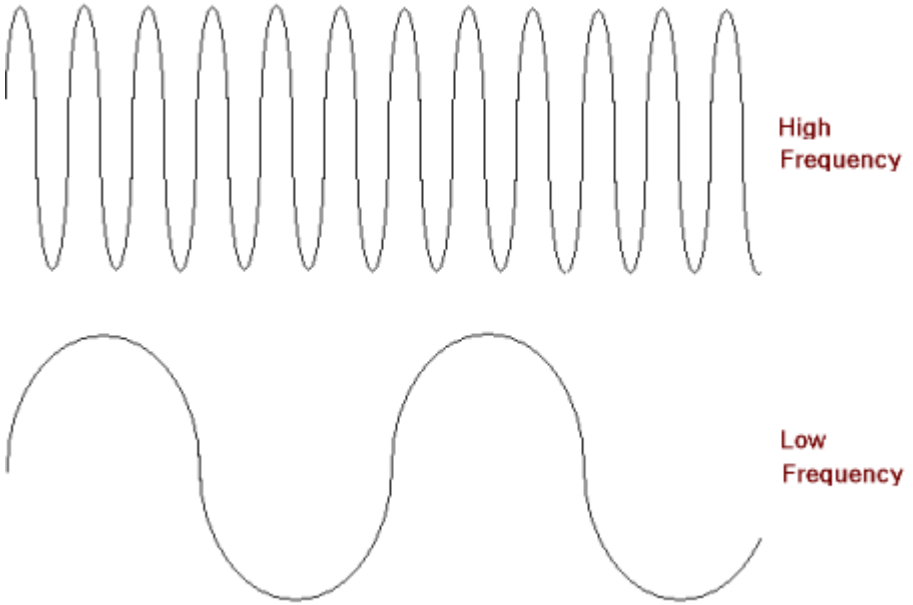
Fig. The electromagnetic spectrum showing the boundaries between different regions.

Waves

- *Parts of a wave:*
  - **Amplitude, crest, trough**
  - ***Frequency*** **"ν":** the number of oscillations of the field that occurs per second.
  - ***Wavelength,*** **"λ":** the linear distance between successive maxima or minima of a wave. Mostly measured in nm = 10^{-9}m.
  - ***Speed of light*** *can be expressed as* where "λ" is the wavelength;"ν"is the frequency, and "c"the speed of light in a medium.
  - ***wavenumber,*** "$\tilde{\nu}$" another unit used to describe the wave properties of electromagnetic radiation which is the reciprocal of wavelength (i.e. $\tilde{\nu} = 1/\lambda$)


Wavelength
Crest
Crest
Trough


amplitude


High
Frequency
Low
Frequency

Wave Equations

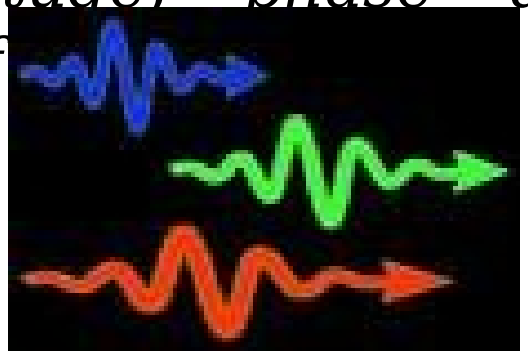
Frequency is inversely related to the wavelength by the speed of light.

$$\mathbf{c = \lambda\nu}$$

where λ = wavelength, ν = frequency, and c = speed of light = 3×10^8 m/s

Dual Nature of Light

- **EMR**, or ***light***, is described by the properties of both ***waves*** and ***particles*** *nature*.
- **Wave nature of light:** In dealing with phenomena such as reflection, refraction, interference, and diffraction, but electromagnetic radiation is conveniently modeled as waves.
- An electromagnetic *wave* is *characterized* by several fundamental properties, including its *frequency, velocity, amplitude, phase angle, polarization, and direction of*



- **Particle Nature of light:** When matter absorbs electromagnetic radiation it undergoes a change in energy.
  - ✓ The interaction between matter and EMR is easiest to understand if we assume that radiation consists of a beam of energetic particles called photons.
  - ✓ When a *photon* is absorbed by a sample it is "destroyed," and its energy acquired by the sample.
  - ✓ The energy of a photon, in joules, is related to its frequency, wavelength, and wavenumber.

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$$

$E \propto \tilde{\nu}$ and ν but $E \propto \frac{1}{\lambda}$

- ,where "h" is Planck's constant = 6.63×10^{-34} J s

NB:

E.g.1. The energy difference between the 3p and the 3s orbitals in a sodium atom is 2.107 eV. Calculate the (in nm) that would be absorbed in exciting the 3s electron to the 3p state (l eV = 1.60 X 10^{-19} J).

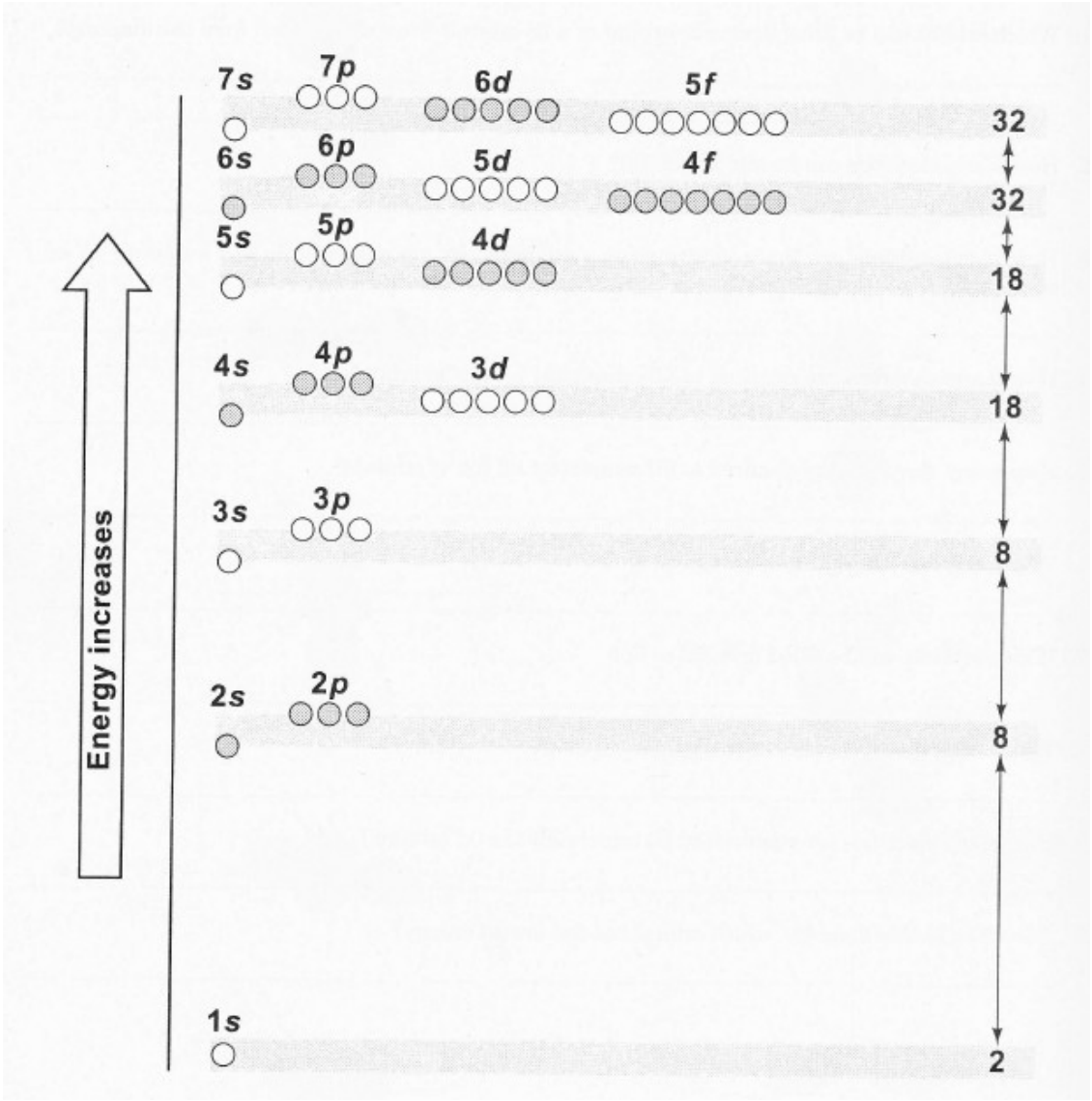
Solution :

$$\lambda = \frac{hc}{E} = \frac{6.63x10^{-34}J.S\ x\ 3x10^{8}m/s}{2.107eV\ x\ 1.6x10^{-19}J/eV} = 590nm$$

1.4.2 Electronic Configuration and Periodic Table

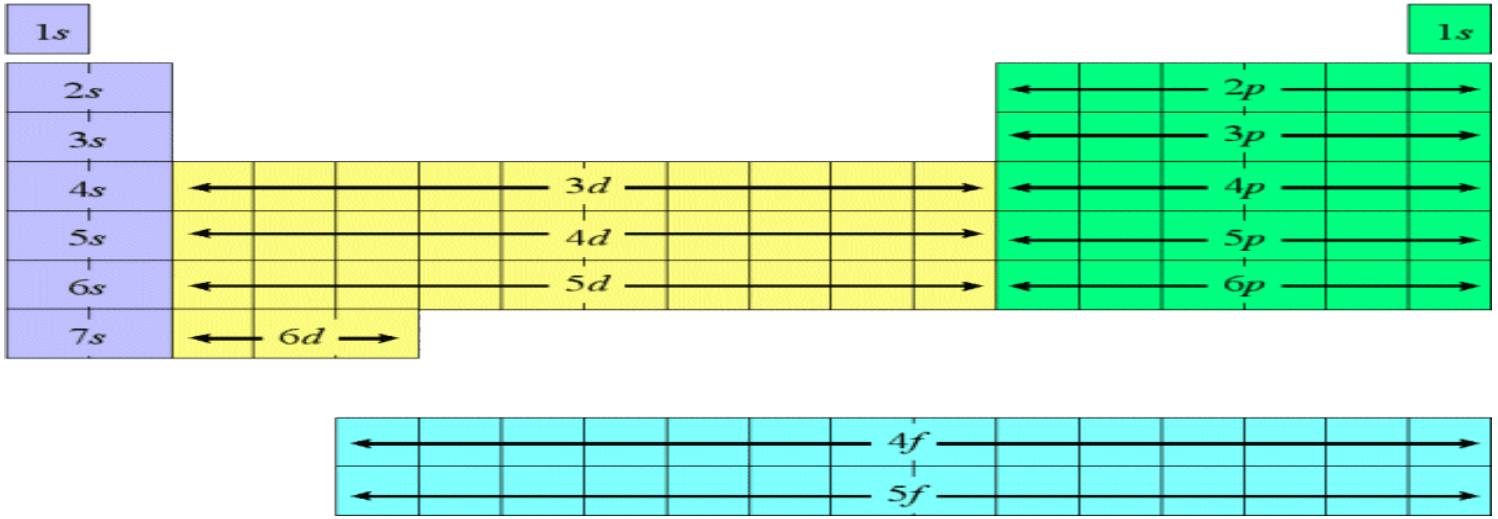
Electron Configurations

- **Aufbau Principle** – electrons enter orbitals of lowest energy first.
- **Pauli Exclusion Principle** – only 2 electrons can occupy an orbital and they must have opposite spins.
- **Hund's Rule** – When electrons occupy orbitals of equal energy (degenerate orbitals), one electron enters each orbital until all the orbitals contain one with parallel spins, then they will pair up.


Energy increases
7s
7p
6d
5f
32
6s
6p
5d
4f
32
5s
5p
4d
18
4s
4p
3d
18
3s
3p
8
2s
2p
8
1s
2

Periodic Table

- The periodic table is structured so that elements with the same type of valence electron configuration are arranged in columns.



- The left-most columns include the alkali metals and the alkaline earth metals. *In these elements the valence s orbitals are being filled*
- On the right hand side, the right-most block of six elements are those in which *the valence p orbitals are being filled*
- *In the middle is a block of ten columns that contain transition metals. These are elements in which d orbitals are being filled*
- *Below this group are two rows with 14 columns. These are commonly referred to the f-block metals. In these columns the f orbitals are being filled*

Important facts to remember:

- 2, 6, 10 and 14 are the number of electrons that can fill the s, p, d and f subshells (the l=0,1,2,3 azimuthal quantum number)
- The 1s subshell is the first s subshell, the 2p is the first p subshell
- 3d is the first d subshell, and the 4f is the first f subshell