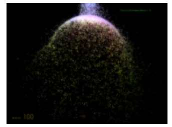
Chapter 4

Atomic Structure

Electromagnetic Radiation

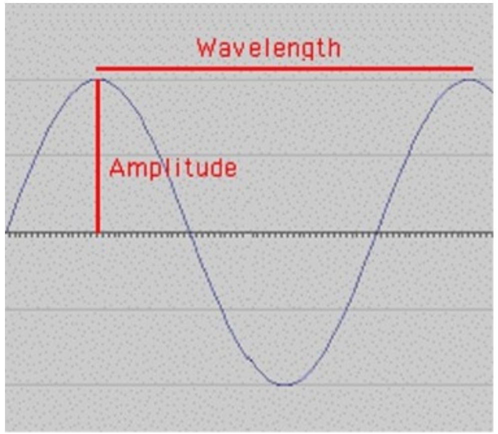
- Electromagnetic radiation has some of the properties of both a **particle** and a **wave**.



- ***Particles:*** *have a* definite **mass** and they occupy space.

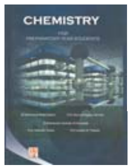
- ***Wave*** have **no mass** and yet they carry **energy** as they travel through space.

Waves have four other characteristic properties: speed, frequency, wavelength, and amplitude.



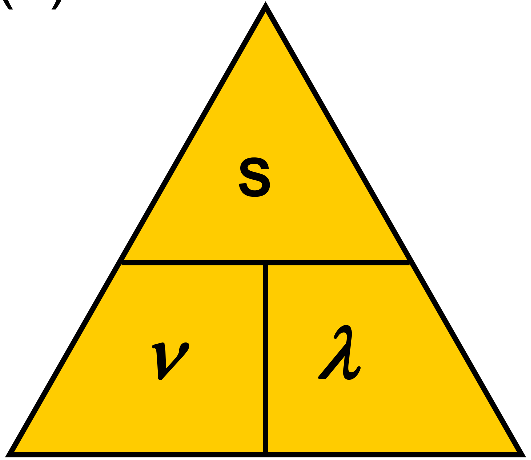
The **frequency** (*v*) is the number of waves (or cycles) per unit of time and its units of cycles per second (s-1) or hertz (Hz).

The **wavelength** (*l*) is the smallest distance between repeating points on the wave. The product of the frequency (*v*) times the wavelength (*l*) of a wave is therefore the speed (*s*) at which the wave travels through space.



The product of the frequency (ν) times the wavelength (λ) of a wave is therefore the speed (s) at which the wave travels through space.

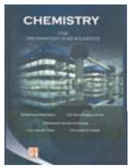
$s = \nu\lambda$ *or* $\nu = s/\lambda$



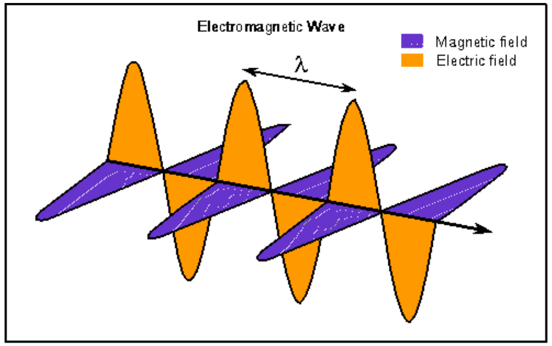
What is the speed of a wave that has a wavelength of 1 meter and a frequency of 60 cycles per second?

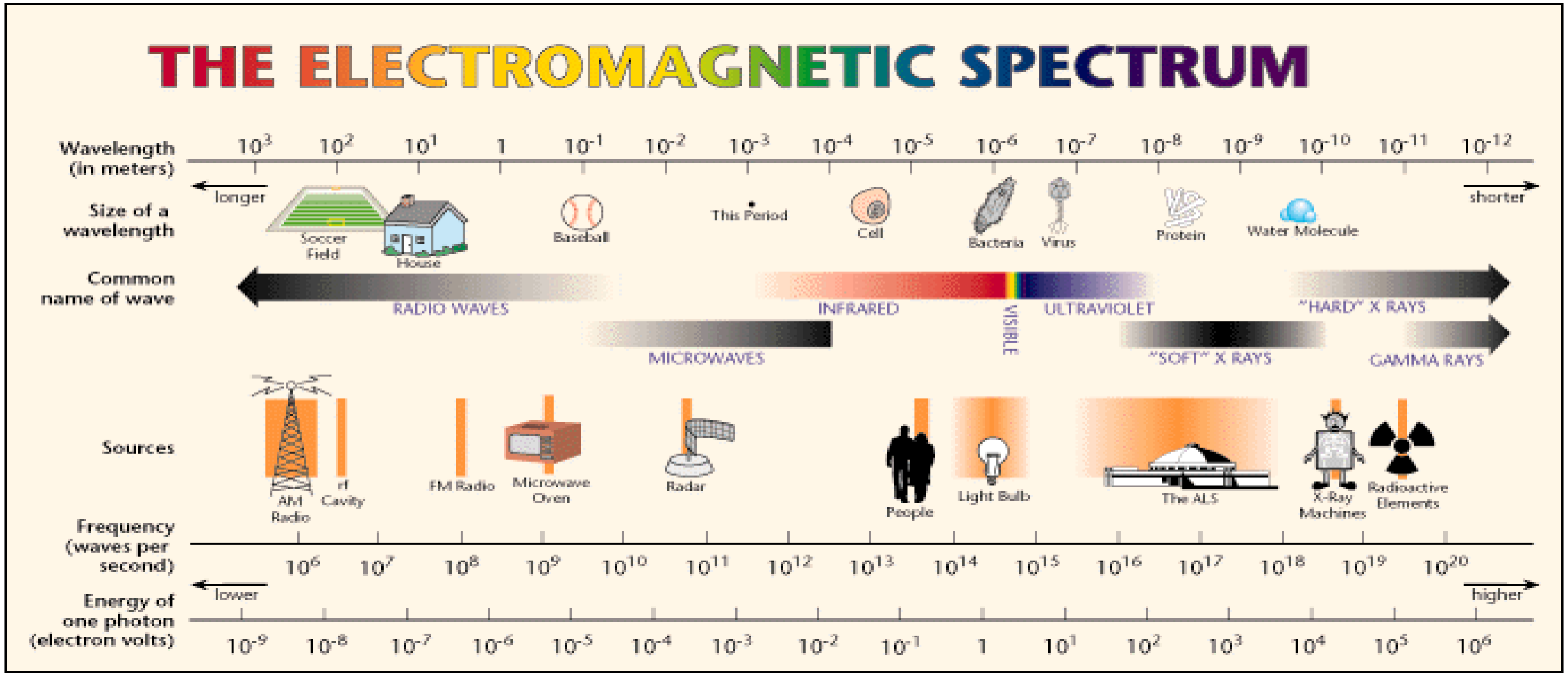
λ = 1 m and ν = 60 cycles per second (Hz)

$s = \nu\lambda$ = 60 (Hz) x 1 m = 60 m per second



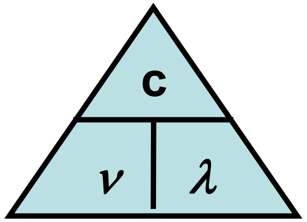
- Light is a wave with both *electric* and *magnetic* components. It is therefore a form of **electromagnetic radiation**.

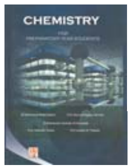




The product of the frequency times the wavelength of electromagnetic radiation is always equal to the speed of light (c), 3.00×10^8 m/s.

$$c = \nu\lambda \quad \textit{or} \quad \nu = c/\lambda$$





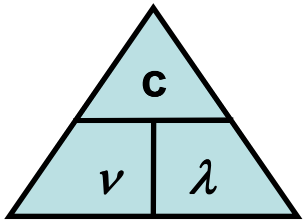
Calculate the frequency of red light that has a wavelength of 700.0 nm if the speed of light is 3.00 x 10^8 m/s.

λ = 700.0 nm = 700.0 x 10^{-9} m and c = 3.00 x 10^8 m/s

$c = \nu\lambda$ or $\nu = c / \lambda$

ν = 3.00 x 10^8 (m/s) / 700.0 x 10^{-9} (m)

ν = 4.29 x 10^{14} (s^{-1}) or Hz

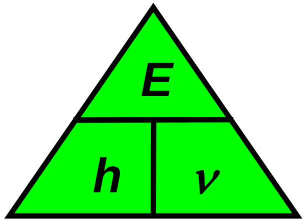


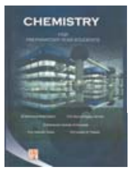
Particle-Like Behavior of Light and Planck's Equation

Light is composed of particles called photons.

The energy of this photon is equal to the frequency of the light times a constant and can be calculated using the formula:

$$E_{photon} = h\nu$$





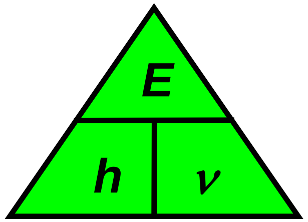
where E is the energy of the photon, ν is the frequency and h is called Plank's constant, h = 6.63 × 10^{-34} J s

What is the energy (in kilojoules) of photons of radar waves with a frequency equal 4.00×10^8 Hz?

Using the formula $E_{photon} = h\,\nu$

$E = (6.63 \times 10^{-34}\ \text{J s}) \times (4.00 \times 10^{8}\ \text{s}^{-1})$

$= 2.65 \times 10^{-25}\ \text{J} = 2.65 \times 10^{-28}\ \text{kJ}$

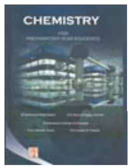


What is the wavelength, in nanometers, of light that has an energy content of 508 kJ/mol photons?

$$\text{Energy} = 508\ \text{kJ/mol photons} \times \left(\frac{1000\,\text{J}}{1\,\text{kJ}}\right) \times \left(\frac{1\,\text{mole photon}}{6.023 \times 10^{23}\ \text{photons}}\right) = 8.44 \times 10^{-19}\ \text{J/photon}$$

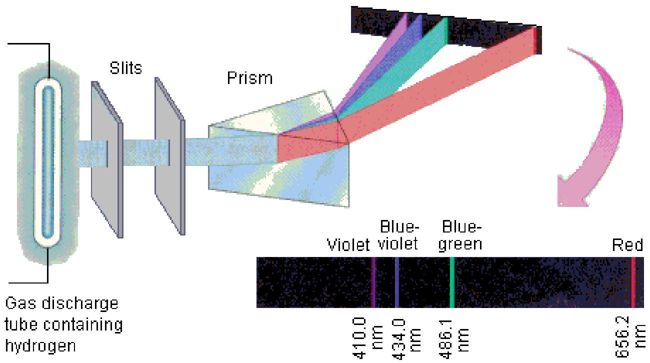
$$E = h\nu = h\,c/\lambda \qquad \lambda = hc/E \qquad \lambda = \left(\frac{(6.626 \times 10^{-34}\ \text{J} \bullet \text{s})(3.00 \times 10^{8}\ \frac{\text{m}}{\text{s}})}{8.44 \times 10^{-19}\ \text{J}}\right) = 236 \times 10^{-9}\ \text{m}$$

$$\lambda = 236 \times 10^{-9}\ \text{m} = 236 \times 10^{-9} \times 10^{9}\ \text{nm} = 236\ \text{nm}$$



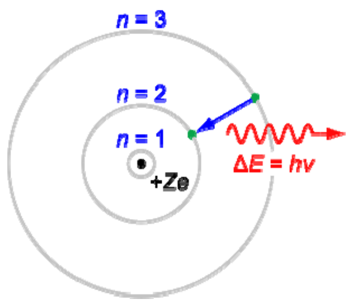
Development of Current Atomic Theory

- Atomic spectrum can be used as a "fingerprint" for an element and the scientists conclude that if atoms emit only discrete wavelengths, may be atoms can have only discrete energies.
- The discrete amounts of energy are absorbed or released (energy is said to be quantized).



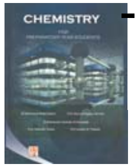
- Atoms absorb and emit electromagnetic radiation as the energies of their electrons change.

Bohr's Theory of the hydrogen atom



The Bohr model of the hydrogen atom uses the assumptions that:

- the light negatively charged electron circulates around the much heavier positively charged.
- the electron, although often acting like a particle, is actually a wave.
- the electron fits in a circular orbit around the proton.



In the case of hydrogen atom spectra, the energies that the electron can possess are given by:

$$E_n = -R_H\,(1/n^2)$$

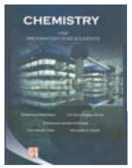
where R_H, the Rydberg constant, has the value 2.18 x 10^{-18} J. The number n is the integer called the principal quantum number; it has the values n = 1, 2, 3, 4,…

Example

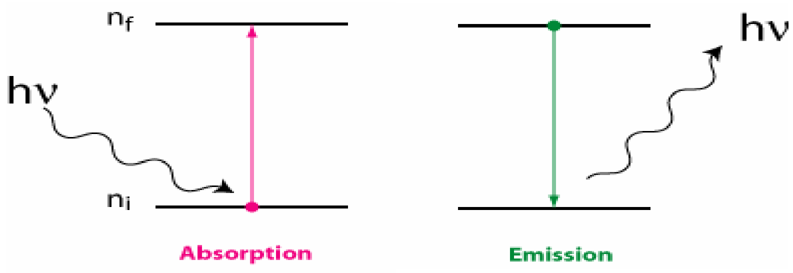
Calculate the value of the energy level (n = 3) of the hydrogen atom according to Bohr-Theory.

Answer

According to the equation: $E_n = -R_H\,(1/n^2)$

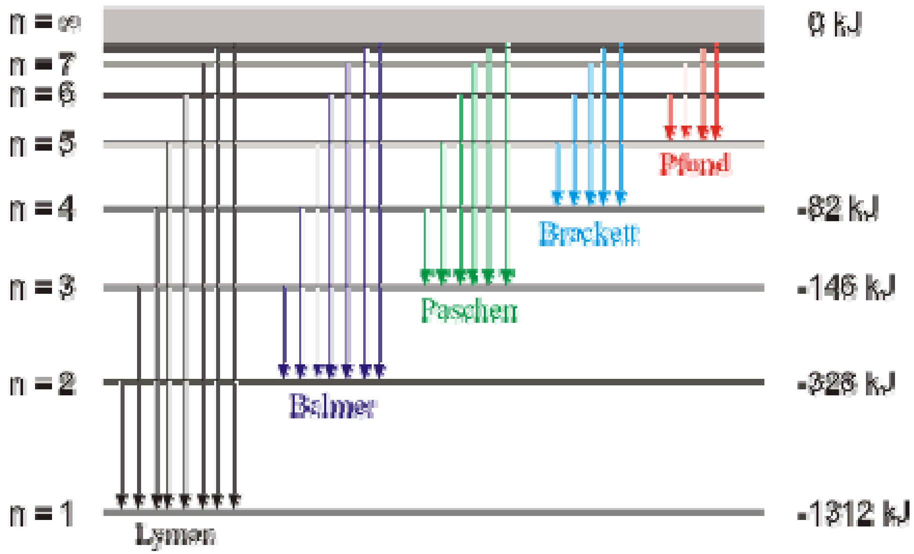


$$E_3 = -2.18 \times 10^{-18}\ \text{J}\ (1/3^2) = -2.42 \times 10^{-19}\ \text{J}$$



$$E_i = -R_H\ (1/n_i^2) \qquad E_f = -R_H\ (1/n_f^2)$$

$$\Delta E = h\nu = E_f - E_i = R_H\ (1/n_i^2 - 1/n_{f2})$$



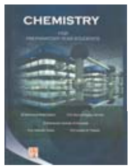
Lyman series is due to the transfer of electrons from excited state to ***n*** **=1**

Balmer series is due to the transfer of electrons from excited state to ***n*** **=2**

Paschen series is due to the transfer of electrons from excited state to ***n*** **=3**

Brackett series is due to the transfer of electrons from excited state to ***n*** **=4**

Pfund series is due to the transfer of electrons from excited state to ***n*** **=5**



What is the wavelength of a photon (in nanometers) emitted during a transition from the ni = 5 state to the nf = 1 state in the hydrogen atom?

Step 1: Calculate ΔE using the following equation:

$$\Delta E = h\nu = E_f - E_i = R_H\,(1/n_i^2 - 1/n_f^2)$$

$$= 2.18 \times 10^{-18}\ \text{J}\ (1/5^2\ -\ 1/1^2)$$

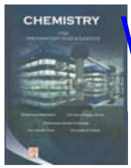
$$= -2.09 \times 10^{-18}\ \text{J}$$

The negative sign (-ve) indicates that this energy associated with an emission process.

Step 2: calculate the wavelength, (omit the –ve sign of ΔE).

$\Delta E = 2.09 \times 10^{-18}$ J $= h\nu = h \times c/\lambda$

$\lambda = c\,h/\Delta E = (3.00 \times 10^{8}\ \text{m/s})\ (6.63 \times 10^{-34}\ \text{J.s})\ /\ (2.09 \times 10^{-18}\ \text{J})$



Wavelength $\lambda = 9.52 \times 10^{-8}$ m $= 9.52 \times 10^{-8} \times 10^{9}$ nm $= 94.2$ nm

What is the wavelength of a photon (in nanometers) emitted during a transition from the $n_i = 5$ state to the $n_f = 1$ state in the hydrogen atom?

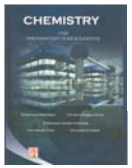
OR

in one step:

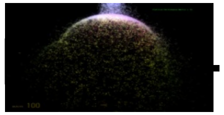
$$\lambda = \frac{9.12 \text{ x } 10^{-8}\, m}{\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)}$$

$$\lambda = \frac{9.12 \text{ x } 10^{-8}\, m}{\left(\frac{1}{5^2} - \frac{1}{1^2}\right)} = \frac{9.12 \text{ x } 10^{-8}\, m}{\left(\frac{1}{25} - \frac{1}{1}\right)} = \frac{9.12 \text{ x } 10^{-8}\, m}{-0.96}$$

Wavelength λ = 9.52 x 10^{-8} m = 9.52 x 10^{-8} x 10^{9} nm = 94.2 nm



Duality of the Electron

- Electron can be described as if it were a  and .
- Since waves are described by their wavelength λ and particles are described by their momentum, **p,**
- $E = h\nu = hc/\lambda$ (wave)
- $E = mc^2 = pc$ (particle)

The DeBroglie relationship:between **momentum** (a particle property) and **wavelength** (a wave property)

$$p = mc = h/\lambda \quad \text{or} \quad ms = h/\lambda$$

$$\mathbf{ms = h/\lambda}$$

(m is the mass in kg and s is the speed in m/s),

What is the DeBroglie wavelength (in meter) of an electron of a mass 9.11×10^{-31} kg and a speed of 2.2×10^{6} m/s. (Notice that: J.s = $kg.m^2.s^{-1}$)

- Using the formula:

$$m\,s = h/\lambda \text{ or } \lambda = h/ m\,s$$

$\lambda = h/ m\,s = (6.63 \times 10^{-34}\ kg.m^2.s^{-1})/(9.11 \times 10^{-31} \times 2.2 \times 10^{6}\ m\ s^{-1})$

$= 3.3 \times 10^{-10}$ m

Calculate the energy (in joules) of a photon with a wavelength of 6.00×10^{4} nm.

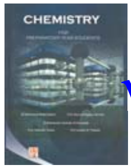
Using the following formula:

$E_{photon} = h\,\nu$ and $\nu = c/\lambda$

Wavelength (λ) = 6.00×10^{4} nm

$= 6.00 \times 10^{4} \times 10^{-9}$ m $= 6.00 \times 10^{-5}$ m,

Speed of light (c) = 3.00×10^{8} m/s, Planck's constant (h) = 6.63×10^{-34} J.s



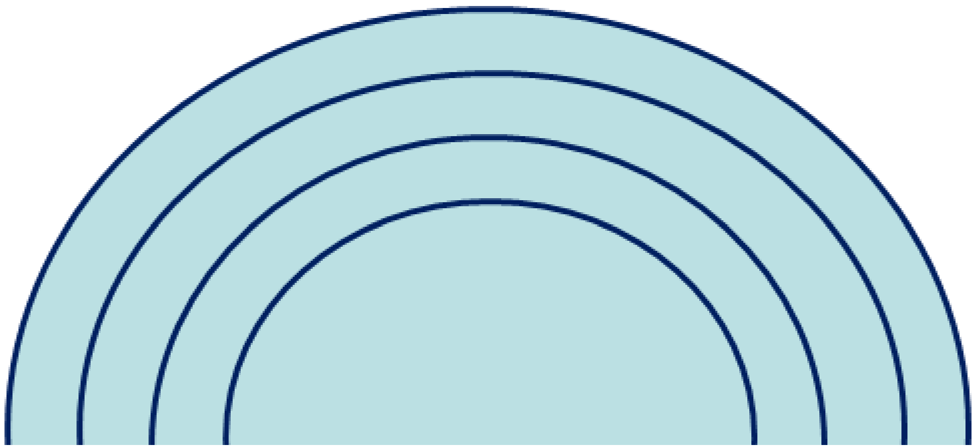
$\nu = 0.5 \times 10^{13}\ s^{-1}$ and $E_{photon} = 3.315 \times 10^{-21}$ J

Quantum Numbers and Atomic Orbitals

Each electron in an atom is described by **four different quantum numbers** **(n, *l*, m_l, & m_s)**

1.<u>Principal Quantum Number</u> (*n*):

Specifies the **energy** of an electron and the **size** of the orbital. All orbitals that have the same value of *n* are said to be in the same shell (level). ***n* takes the values of 1, 2, 3, …, ∞.**



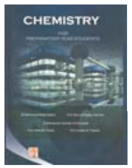
2. Angular Momentum (Secondary) Quantum Number (*l*)

Specifies the **shape** of an orbital with a particular principal quantum number. ***l takes the values of*** **0, 1, 2,..., *n*-1.**

The secondary quantum number divides the shells into smaller groups of orbitals called **subshells**.

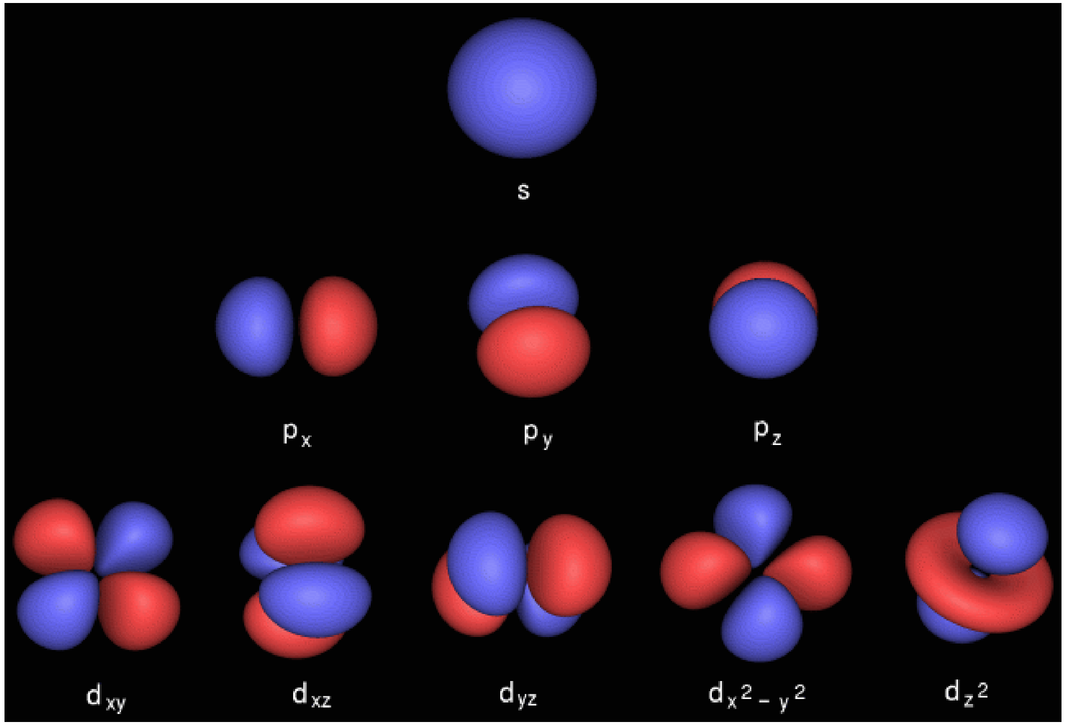
l	0	1	2	3	4	5	. . .
Letter	*s*	*p*	*d*	*f*	*g*	*h*	. . .

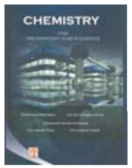
If n = 1	**, then *l* = 0**	***s* orbital**	**1*s***
If n = 2	**, then *l* = 0**	***s* orbital**	**2*s***
	and *l* = 1	***p* orbital**	**2*p***
If n = 3	**, then *l* = 0**	***s* orbital**	**3*s***
	and *l* = 1	***p* orbital**	**3*p***
	and *l* = 2	***d* orbital**	**3*d***



3. Magnetic Quantum Number (m_l):

Specifies the **orientation in space** of an orbital of a given energy (*n*) and shape (*l*).
m_l takes the values of -*l*, ..., 0, ..., +*l*.





4. Spin Quantum Number (m_s)

Specifies the **orientation of the spin axis** of an electron.

An electron can spin in only one of two directions:

$m_s = +\frac{1}{2}$ ↑ $m_s = -\frac{1}{2}$ ↓

The Pauli exclusion principle:

"No two electrons in the same atom can have identical values for all four of their quantum numbers".

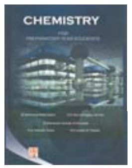
i.e.: no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**

Hund's rule

"When several orbitals of equal energy are available, electrons enter singly with parallel spins".

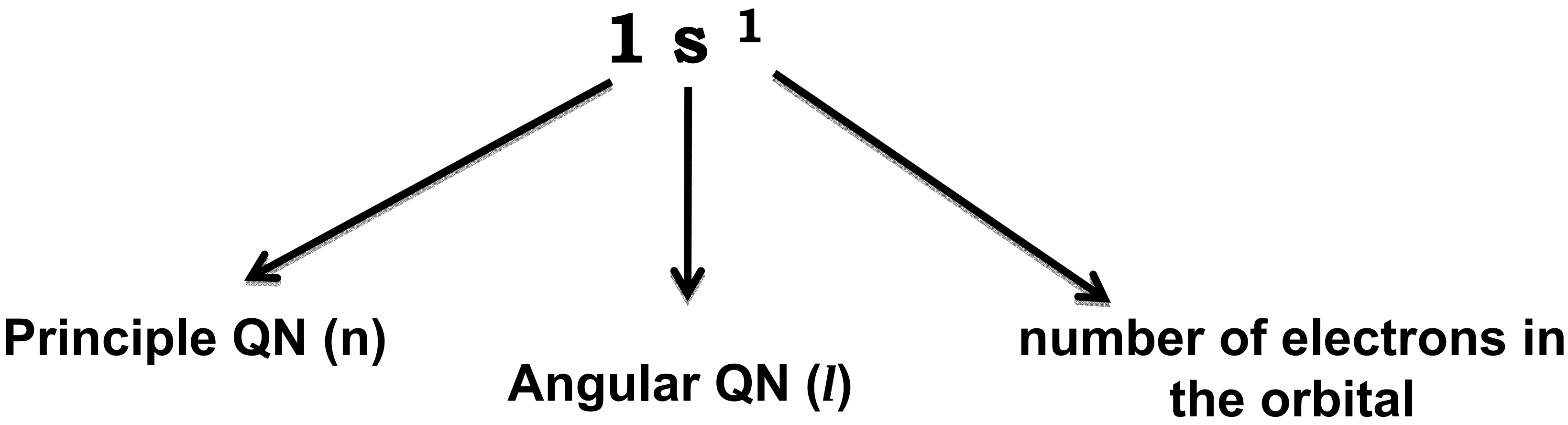
Magnetic properties:

- When electron spins, it creates a magnetic field, which can be oriented in one of two directions.
- When all the electrons of an atom are **paired**, these substances are not attracted to magnets and are said to be **diamagnetic**.
- When at least one electron of an atom is **unpaired**, these substances are attracted to magnets and are said to be **paramagnetic**.



n	l	m_l	Number of orbital	Orbital Name	Number of electrons
1	0	0	1	1*s*	2
2	0	0	1	2*s*	2
	1	-1, 0, +1	3	2*p*	6
3	0	0	1	3*s*	2
	1	-1, 0, +1	3	3*p*	6
	2	-2, -1, 0, +1, +2	5	3*d*	10
4	0	0	1	4*s*	2
	1	-1, 0, +1	3	4*p*	6
	2	-2, -1, 0, +1, +2	5	4*d*	10
	3	-3, -2, -1, 0, +1, +2,+3	7	4*f*	14

For an orbital:

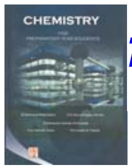


Write the four quantum numbers for an electron in a 5p orbital

n **= 5,**

l **= 1 (for p),**

m_l **= -1, 0, or +1,**

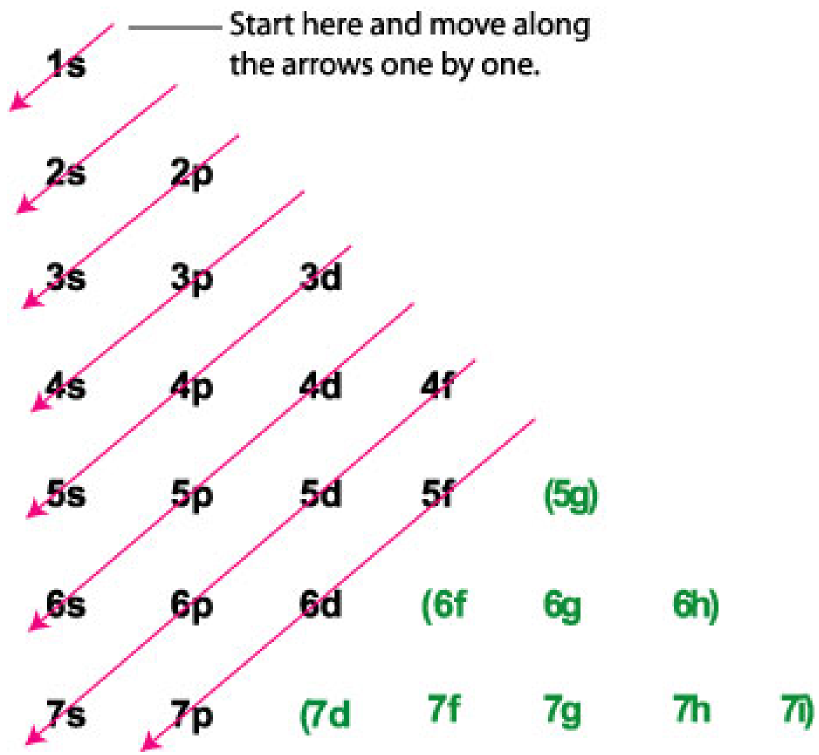


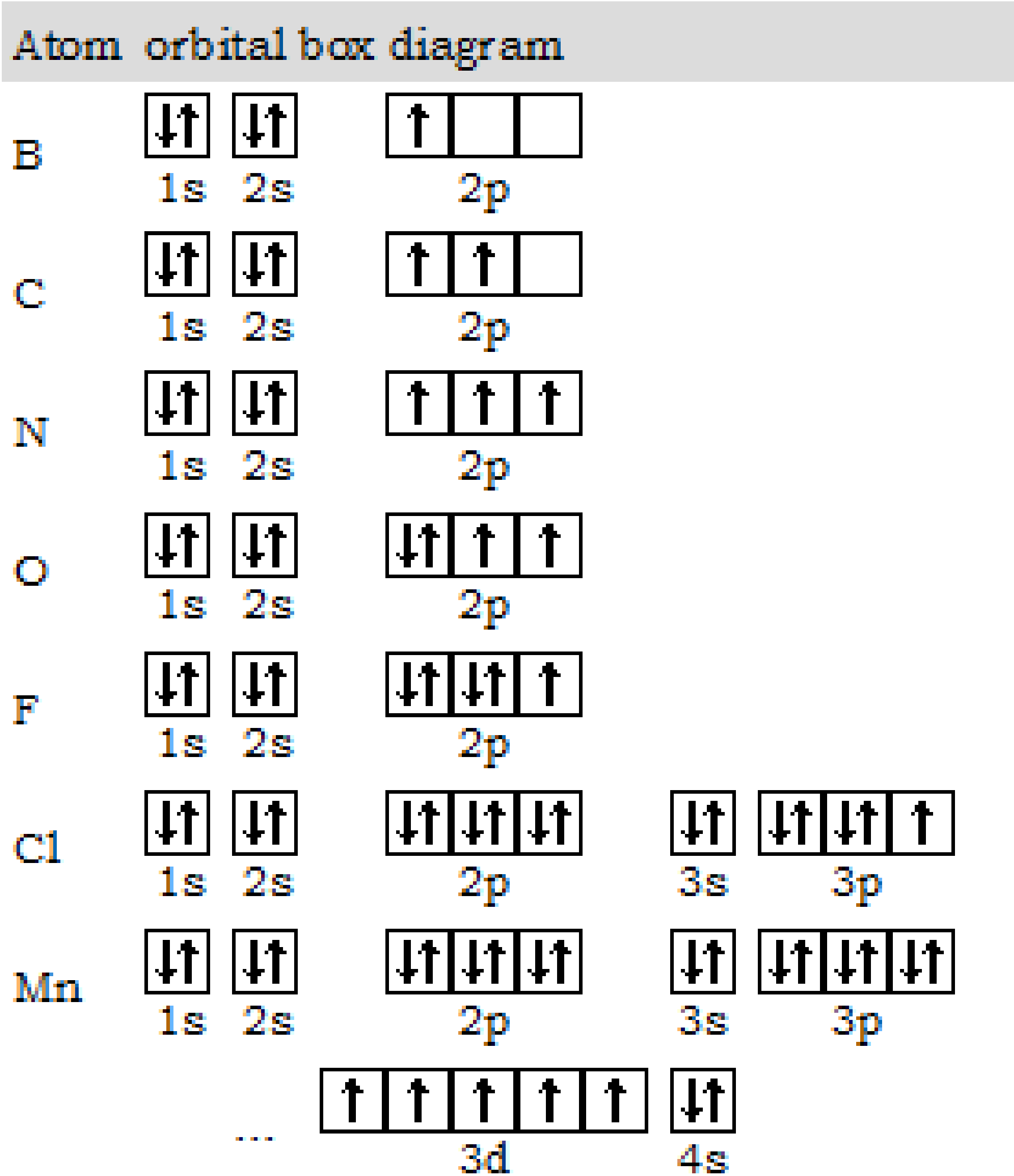
m_s **could be +1/2 (upward) or -1/2 (downwards).**

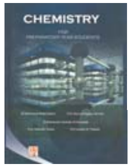
Writing Electron Configurations

- The electrons are filled in according to a scheme known as the **Aufbau principle** ("building-up"), which corresponds (for the most part) to increasing energy of the subshells:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p,……etc.




Atom orbital box diagram
B
1s 2s 2p
C
1s 2s 2p
N
1s 2s 2p
O
1s 2s 2p
F
1s 2s 2p
Cl
1s 2s 2p 3s 3p
Mn
1s 2s 2p 3s 3p
...
3d 4s



Show the electronic configuration, magnetic properties, and the four quantum numbers for the last electron for **Phosphorus** ($_{15}P$) and **Chromium ($_{24}Cr$)**.

Phosphorus ($_{15}P$)

$1s^2 2s^2 2p^6 3s^2 3p^3$

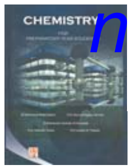
paramagnetic (unpaired electrons)

n = 3, l = 1 (p orbital), m_l = +1, m_s = +1/2

Chromium ($_{24}Cr$)

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

paramagnetic (unpaired electrons)



n = 3, l = 2 (d orbital), m_l = +2, m_s = +1/2

- **What is the orbital diagram for the $_{29}Cu$, $_{24}Cr$, and $_{30}Zn$ atoms?**

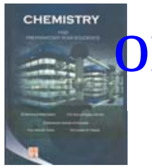
Write the electronic configuration of $_{22}Ca$, $_{11}Na$, $_{51}Sb$ and $_{82}Pb$

$_{20}$**Ca** is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^2$
or [Ar] $4s^2$

$_{11}$**Na** is $1s^2\ 2s^2\ 2p^6\ 3s^1$
or [Ne] $3s^1$

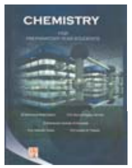
$_{51}$**Sb** is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^3$
or [[Kr] $4d^{10}\ 5s^2\ 5p^3$

$_{82}$**Pb** is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^{10}$, $6p^2$
or [Xe] $6s^2$, $4f^{14}$, $5d^{10}$, $6p^2$



- Write the electronic configuration of antimony ($_{51}Sb$) and answer the following questions:
- Write the sets of the four quantum numbers for the 38th electron in ($_{51}Sb$).
- How many electrons are in the orbitals with the value (l = 1) of $_{51}Sb$?
- How many unpaired electrons are in $_{51}Sb$?
- How many electrons are in the orbitals with the value (m_l = +1) of $_{51}Sb$?

- **Write the four quantum numbers for the differentiating electron in the atoms $_{9}F$ and $_{48}Cd$**



Ionization of the atom

The atom can be ionized by messing one or more of electrons from the outermost shell

$${}_{11}Na:\ 1s^2\ 2s^2\ 2p^6\ 3s^1 \longrightarrow Na^+:\ 1s^2\ 2s^2\ p^6$$

Na atom → Na^+ ion

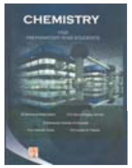
Write the electronic configuration of Fe^{2+} and Fe^{3+}

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

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

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

What is the electronic configuration for the ${}_{29}Cu^{+1}$ and ${}_{29}Cu^{+2}$?



The Periodic Table

- The modern periodic table (PT) represents the arrangements of elements according to the building up (**Aufbau principle**), where each element has one electron more than the previous element.
- The periodic table can be classified in many different ways:

➢ **Metallic character:**

metals, nonmetals, and metalloids.

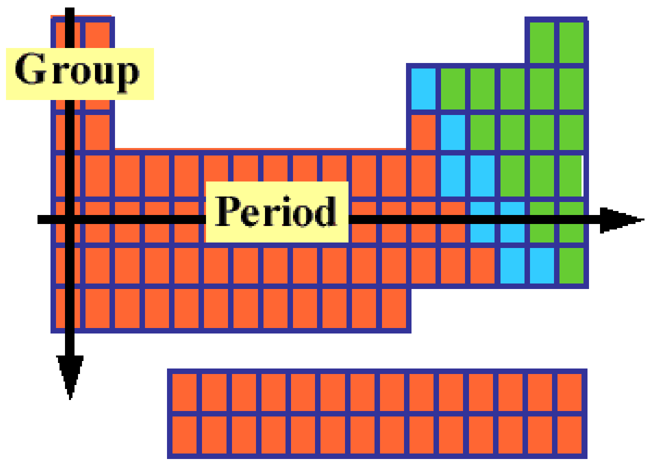
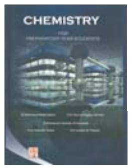


Fig. 5.1 The periodic table classification

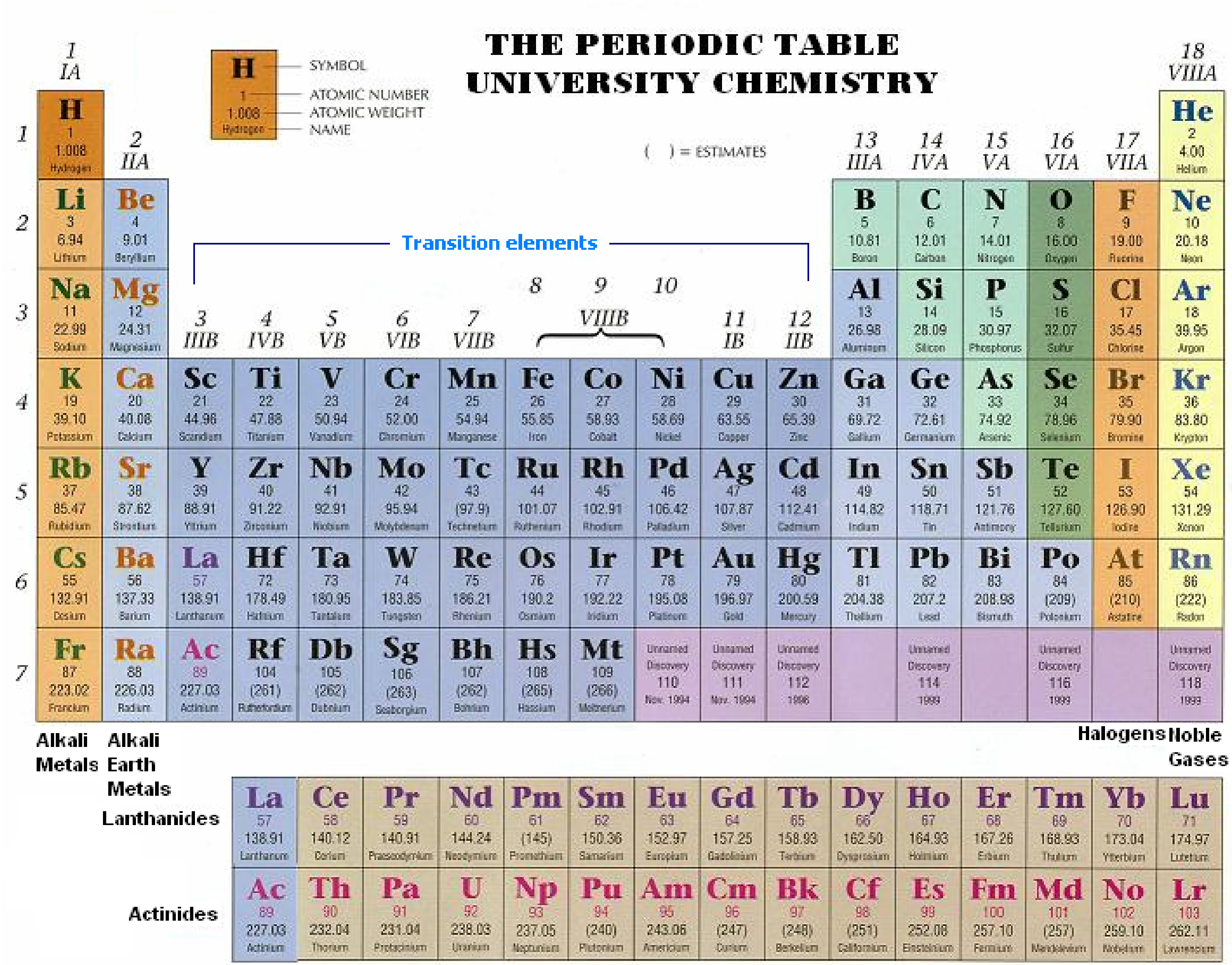
➢ **Position in the periodic table:**

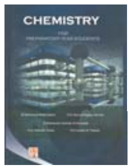
horizontal rows (**Periods**)

vertical columns (**Groups**)



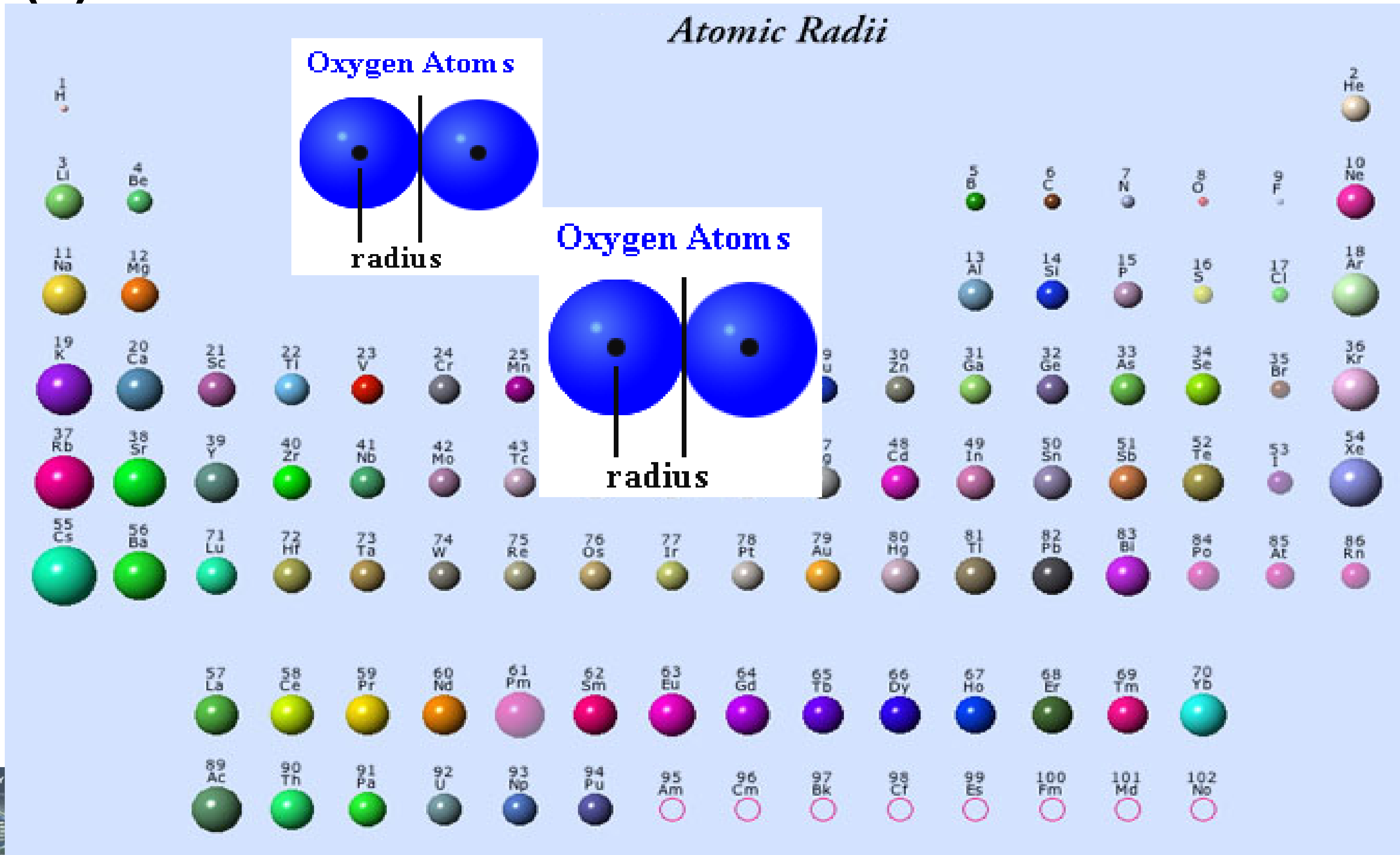
The periodic table contains the following important groups:





Periodic properties of elements

(1) Atomic radius:



Periodic properties of elements

(2) Ionization energy (IE)

The energy required to remove the most loosely held electron from an isolated gaseous atom in its ground state.

$$A(g) \rightarrow A^{+}(g) + e^{-}$$

• Atoms of metals with low IE because tend to lose electrons and become positive ions in chemical reactions.

• Atoms of non-metals with high IE because tend to accept electrons.

• The IE of noble gases atoms is high and they are stable.

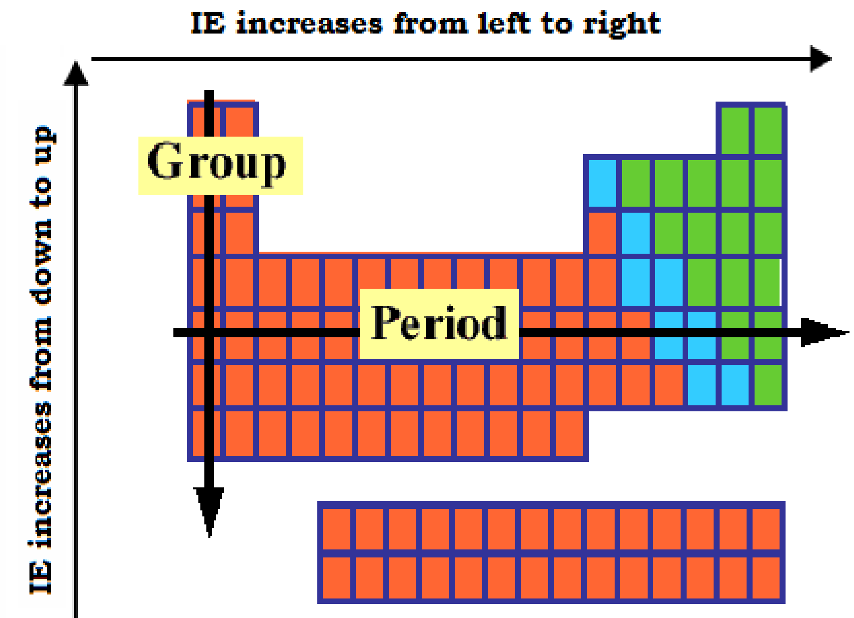
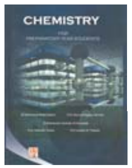


Fig. 4.10 Trends in the ionization energy within the Periodic Table.



- The second IE for an atom is higher than the first one because of increasing of the attraction of electrons by higher positive charge of the nucleus.
- For example, Mg

$$Mg\,(g) \rightarrow Mg^{+}(g) + e^{-},\ IE_{1st} = +738\,kJ/mol$$

$$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-},\ IE_{2nd} = +1450\,kJ/mol$$

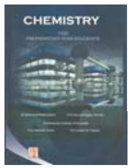
$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-},\ IE_{3rd} = +7731\,kJ/mol$$

Arrange the following elements according to their (a) atomic radius and (b) IE: P, N, O, F.

(a) according to the atomic radius, F< O < N < P

(b) according to the IE, F> N> O> P

There is exception between O and N, because higher energy is required to remove an electron from the half-filled p orbital in nitrogen atom



Periodic properties of elements

(3) Electron affinity (EA)

The energy associated with the process in which an electron is added to an atom in its ground state.

Energy is usually evolved in these processes (negative signs)

•Few elements have electron affinity

•EA Increases (the negative value) from the left to right across a period.

* EA increases from down to up in a group.

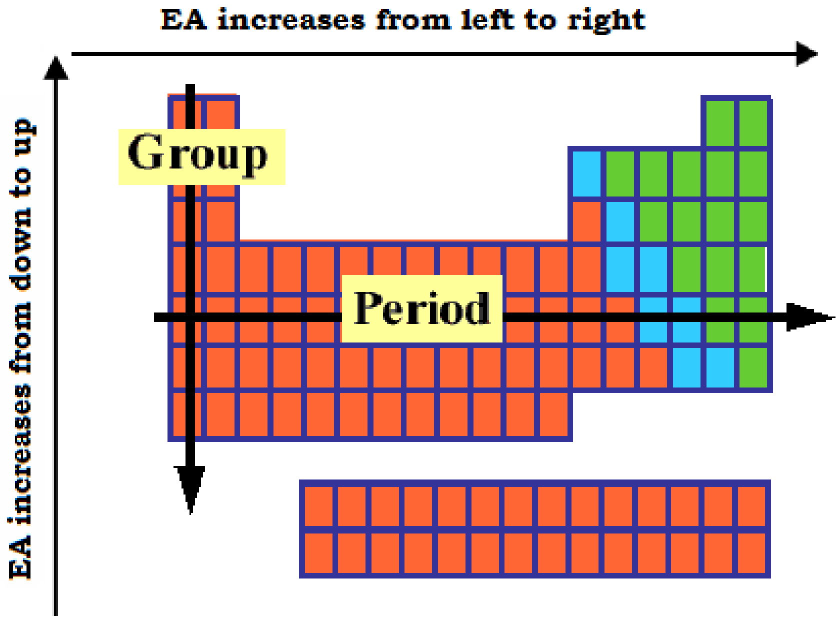
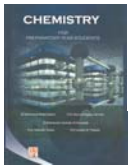


Fig.4.11 Trends in the electron affinity within the Periodic Table.



Periodic properties of elements

(4) Electronegativity (EN)

- The ability of an atom to attract electrons in a molecule

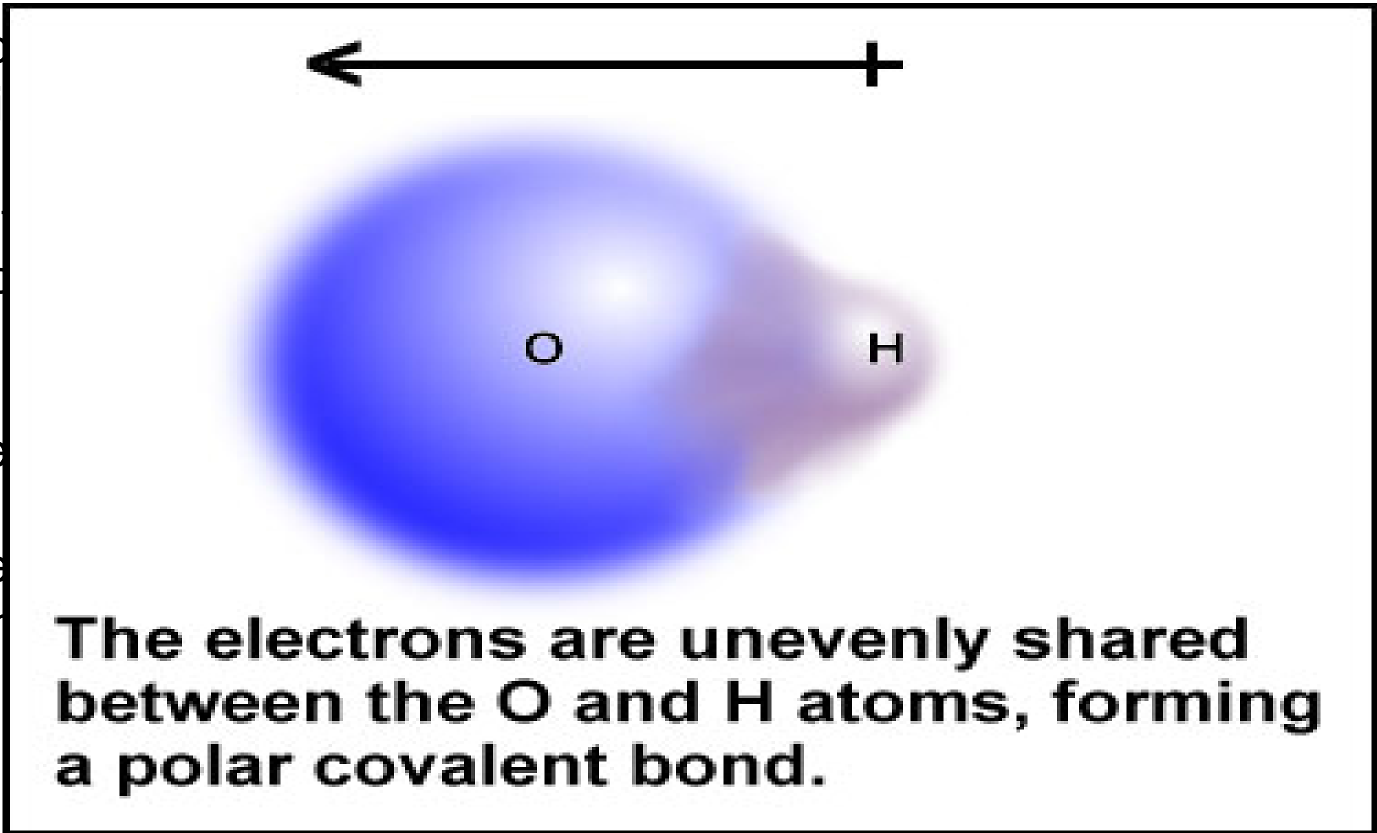
Energy is usually evolved in these processes (negative signs)

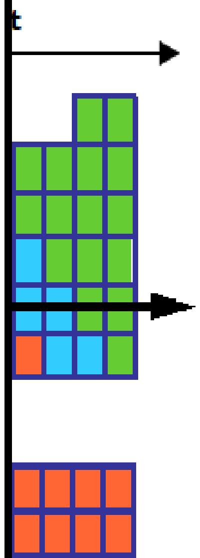
•EN ac
left to ri

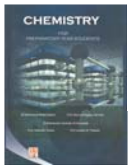
•EN wi
down to

•EN for
non-me

* The
electron
oxygen







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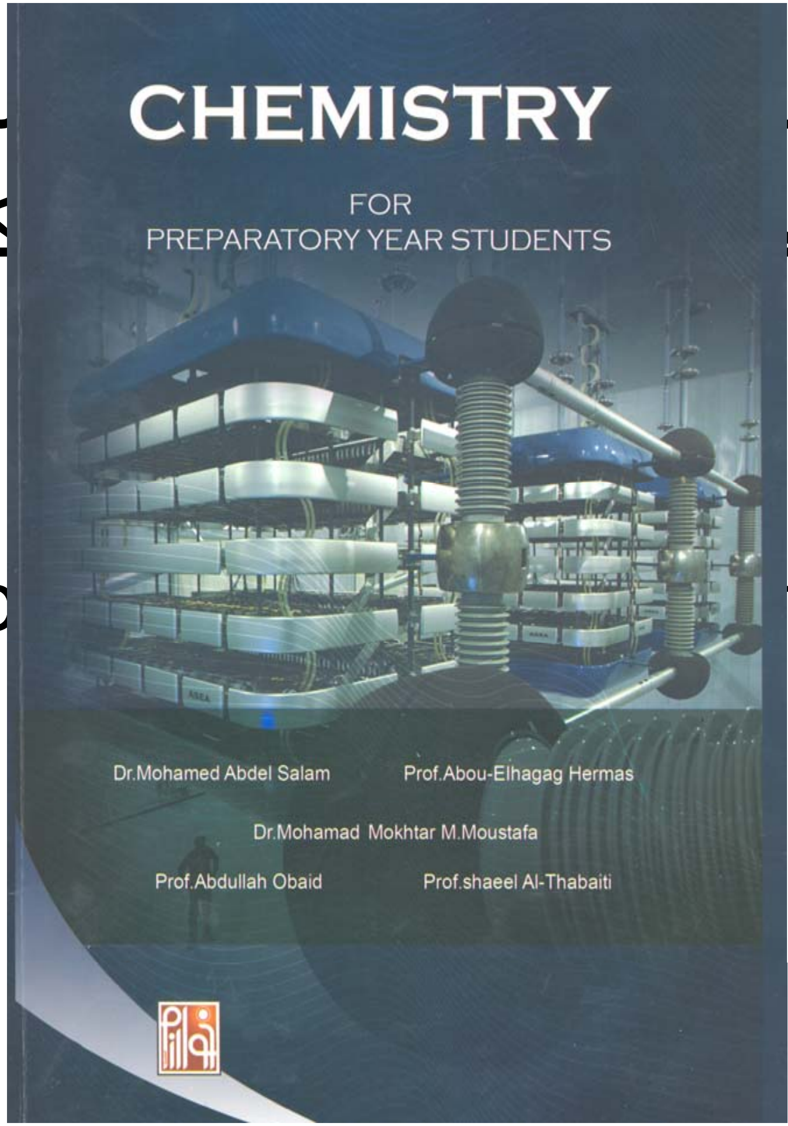

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