Chem ch-5 alag - Chem ch-5

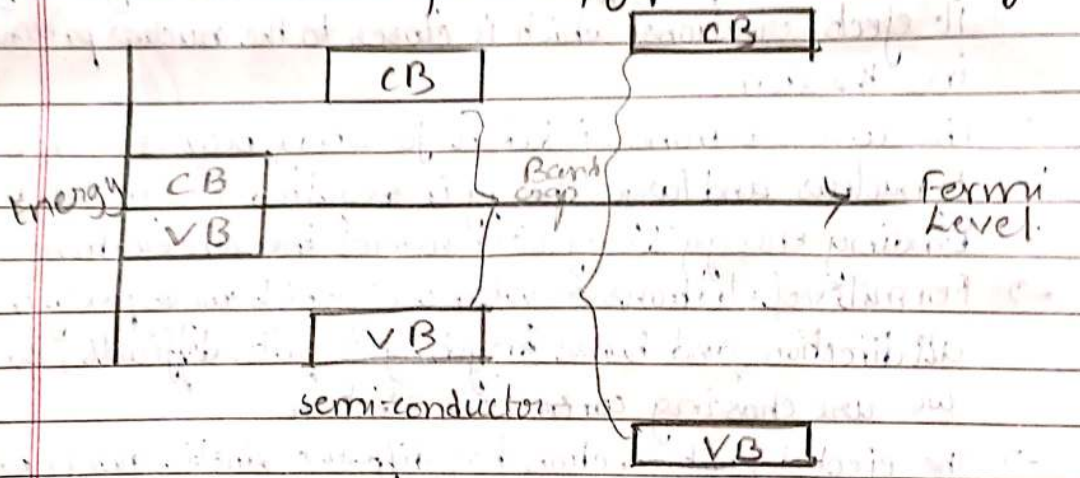
Chemistry (SRM Institute of Science and Technology)

1/12/22

UNIT-5

VVIP * XPS (or) ESCA

XPS - X-ray Photoelectron Spectroscopy. (or)
ESCA - Electron spectroscopy for chemical analysis.



Valence Band :-
in solid-state physics, the outermost orbital of an atom is filled with electrons is called valence band.

Conduction Band (CB) :-
The region where the orbitals are unoccupied of electrons can jump from the valence band.

Band Gap :-
The energy difference between highest occupied energy state (valence band) and lowest occupied energy state (conduction band)

Fermi Level :-
It is the highest energy state occupied by electron in a material at absolute 0° Kelvin (hypothetical situation)

* XPS

→ XPS is surface characterisation technique that can analyze a sample to the depth of 2 to 5 nm

→ Using the x-ray source, photoe⁻s are generated and to produce the spectra. i.e. Intensity Vs binding energy

principle

→ XPS is based on photoelectron effect

→ When the surface of the sample is irradiated by x-ray it ejects electrons which is closer to the nucleus present in the atom

→ The core electrons, is taken for study bcoz it is closer to nucleus and larger energy is required i.e greater than binding energy to eject (remove) the core electron.

→ Fermi level electrons or valance e⁻ which move freely in all direction and hence targeting is quite difficult; so we are chosing core electron.

→ The ejected photoelectron has different kinetic energy but maximum and comes out of the fermi-level and reaches the conduction band.

→ In order to calculate the KE of ejected photoelectron the following relation is used

$$KE = h\nu - BE - \phi_{spec}$$

where BE → binding energy of e⁻ closer to nucleus

ν → frequency of photon

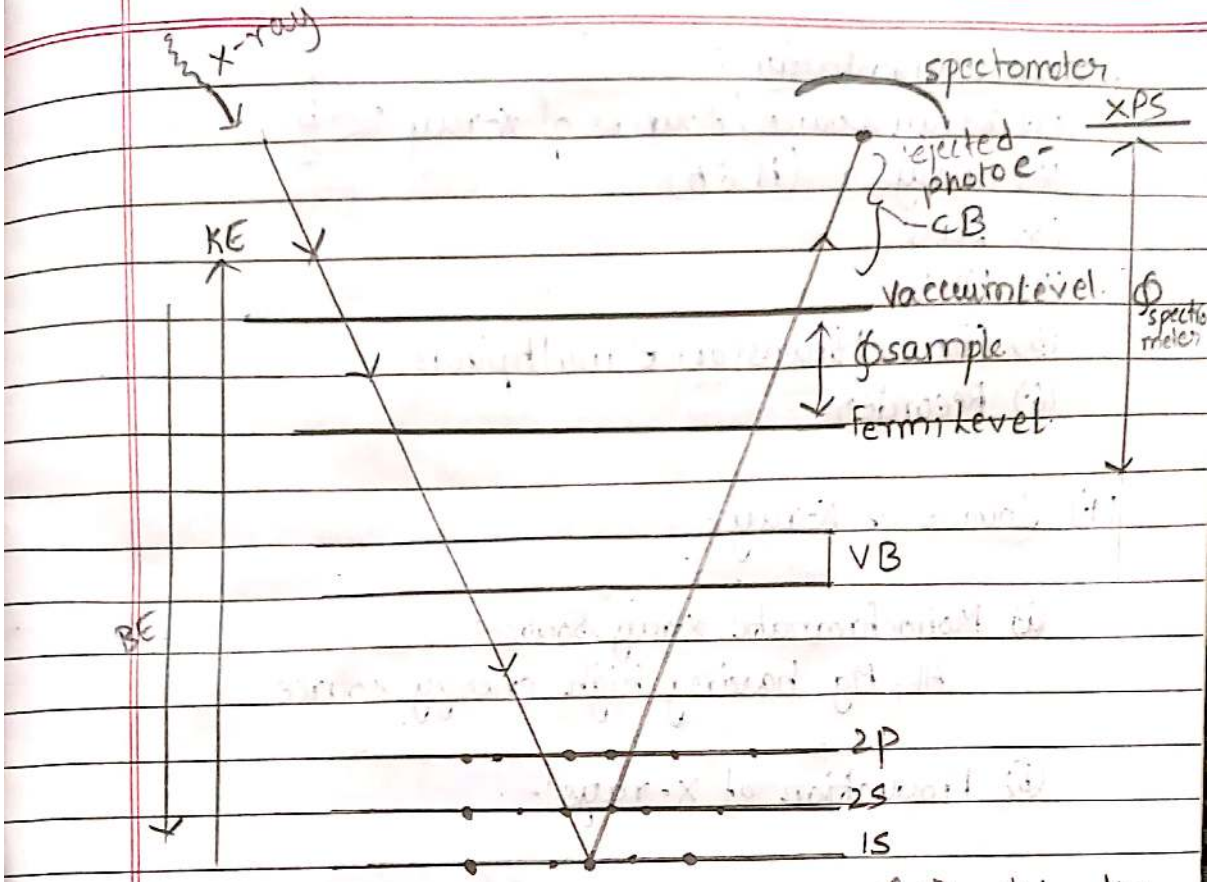
h → plancks' constant

ϕ_{spec} → work function of spectrometer

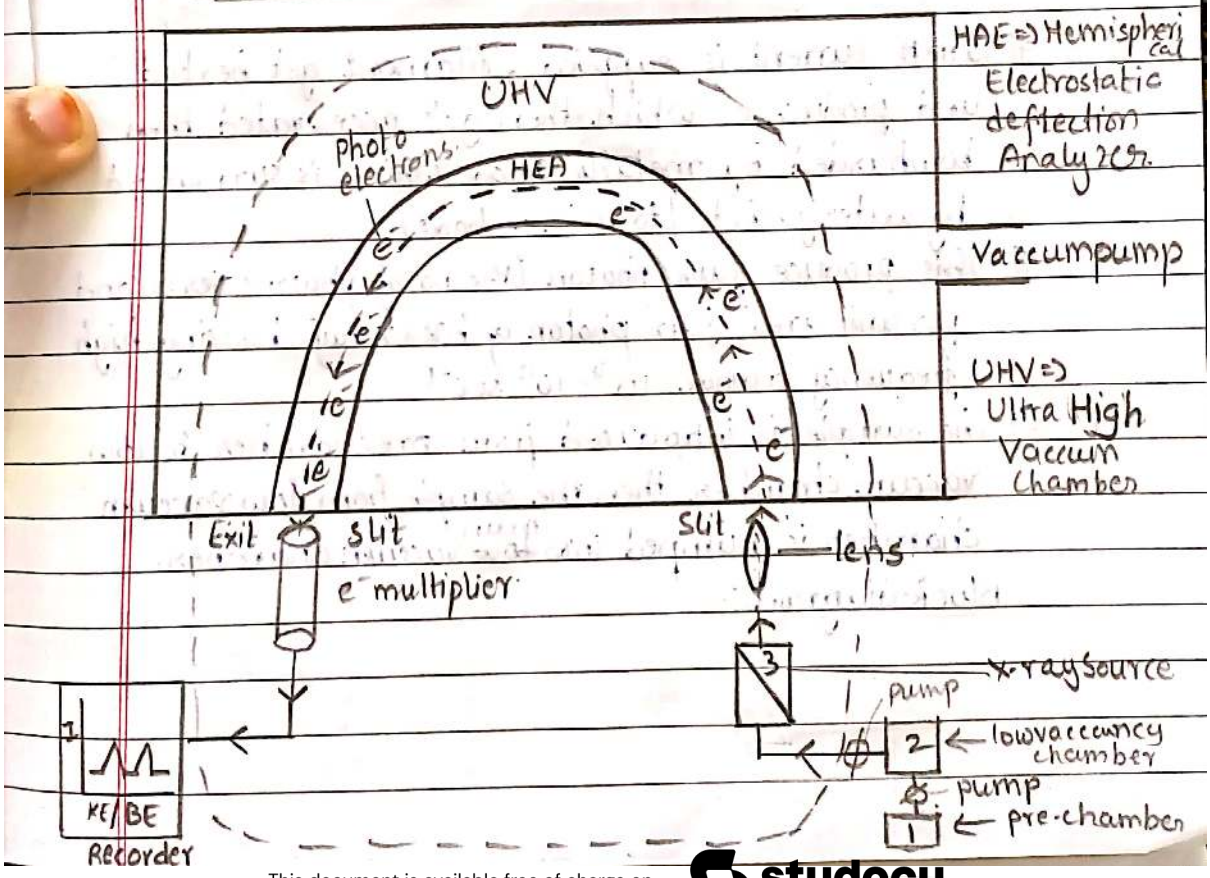
KE → kinetic energy

→ Augere⁻:-

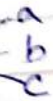
X-ray source falls down e⁻ eject out, now if vacancy is created then higher level electrons falls down to the lower level and releasing certain amount of energy. This energy use little bit of KE and this e⁻ is called augere⁻



Instrumentation:



→ Instrumentation:-

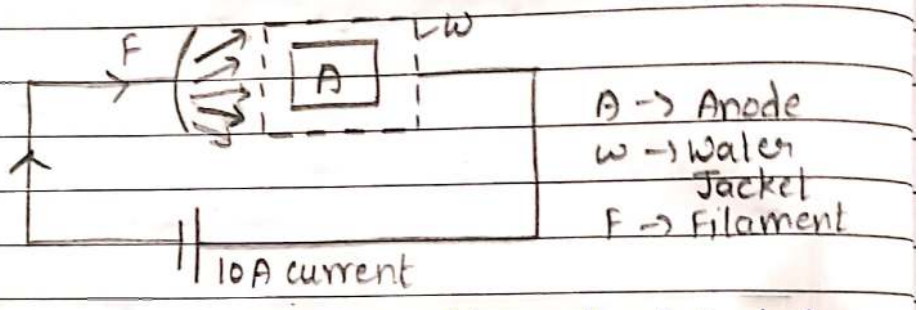
(1) X-ray Source / Sources of X-ray 

(2) Analyzer (HEA)
(3) Lens
(4) UHV
(5) Channeltrans(or) e^- multipliers
(6) Recorder

(1.) Source of X-ray:-

(a.) Monochromatic X-ray Source:-
Al, Mg having high energy source

(b.) Production of X-rays:-

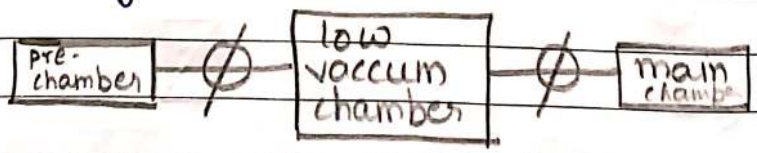


10mA current is supplied, filament get heated and produce e^- which then get accelerated then bombarded by metallic anode which is surrounded by water jacket (to reduce heat)

This produce flux photon (the no. of photons per second per unit area) flux photon of $h\nu$ (x-ray) having high frequency range 10^{10} - 10^{12} sec^{-1}

(c.) The sample is introduced from prechamber to low vaccum chamber then the sample from low vaccum chamber is pumped into ~~low~~ main vaccum chamber.

Block diagram:-



(2) Analyzer:

→ In order to measure KE of various ejected photone an analyzer is required other than source.
→ Name of analyzer is Hemispherical Electrostatic deflection Analyzer
→ In the presence of Electricfield the ejected photo e⁻ having different KE (velocity) take different paths or pathways inside the analyzer.
→ The resolution is directly propotional to intensity of peak obtained in the spectrum.
→ Hence for good resolution the moveing rate of e⁻ must be slowed doiwn.
→ The electrons are decelarated then we can get a good resolution and high intense peak is obtained is spectrum.
→ The energy required to slow down the movement of electrons is known as pass energy.
→ The analyzer is hemispherical in shape.

(3) Lens:-

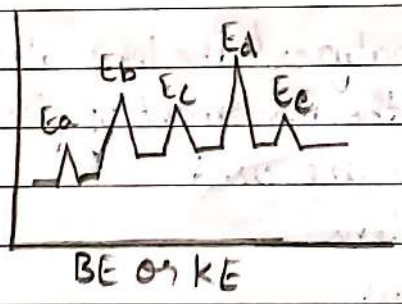
→ Apart from analyzer the lens also deaccelerate or accelerate the movement of ejected photoe⁻
→ Two types of lens are used
(1) Electrostatic Lens
(2) Magnetic lens

(a) Electrostatic Lens:- retard the movement of electrons if it is fast moving.
(b) Magnetic Lens: focus the electrons which have been slowed down, into the analyzer.

(4) UHV :- (Ultra High Vaccum)
In this chamber the vaccum environment is maintained to reduce or eliminate the surface contamination of sample

(5) Channeltrons / Electron multiplier:-
→ It is hallow tube which detect different electrons with different KE
→ By applying external potential (volt) multiplies the incident electrons as shower of electron
→ The KE of diff e⁻ are calculated by using that equation $KE = h\nu - BE - \phi_{spect}$

(6) Recorder :-
→ It records the signal as peaks in the spectra i.e. taken KE Vs intensity
→ The position of the peaks gives an idea about the type of core electron (1s/2s/2p) and also specifies the element taken for study.



the area of the peaks gives idea about conc of elements under study

→ Applications:

1. To identify the elements at the surface level itself (1-nm)
2. To analyse the contamination in the surface (1-2 nm)
3. To find the emperical formula of material
4. To analyze combine state of element
5. To find BE of e⁻
6. To analyze thickness of material
7. To differentiate the chemical state b/w the sample

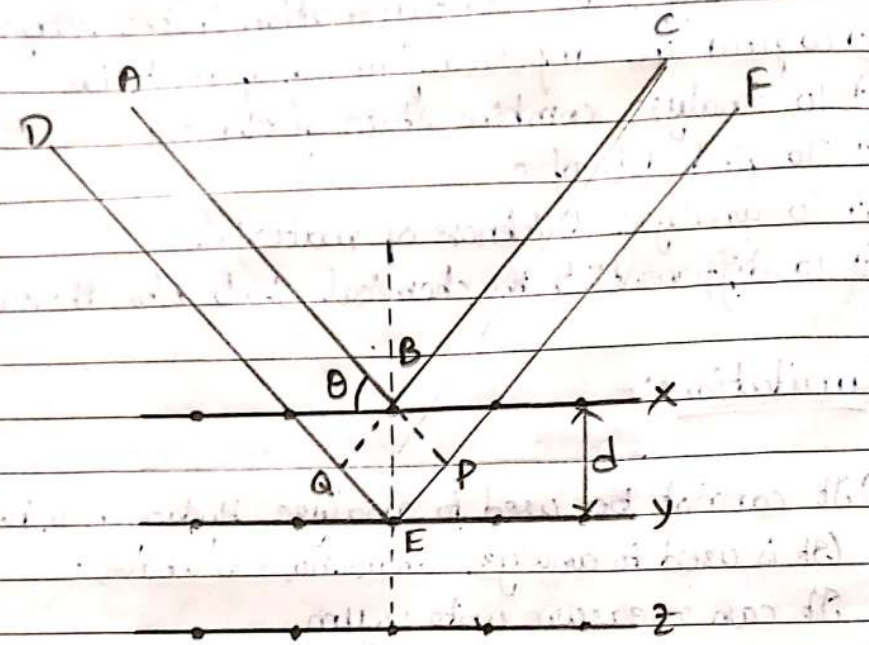
→ Limitations:

1. It cannot be used to analyze Hydrogen & Helium atoms (It is used to analyee atomic no 3 & above).
   It can measure upto 10 μm
2. It is a time consuming process
3. It is very expensive.
4. High vaccum is required.

* XRD :- (X-RAY DIFFRACTION)

→ It is a technique to understand the molecular and physical structure of crystal.
→ In crystallography we use only crystals
→ Regular arrangements of atoms in a molecule is called as as "crystal"
→ Diffraction is bending of wave or light at the sharp edge of obstacle.

(Q) Investigate of "crystal structure of solid" by using "Bragg's Law"



AB & DE → Incident rays
BC & EF → Reflected rays
d → interplanar space
θ → glancing angle
BQ & BP → are propotionally draw from B on DE & EF respectively

{ William Hendry Bragg
William Lawrence Bragg } - studied bragg's law in 1915

→ Bragg's Law

The relationship between X-ray light incident into and its reflection of from crystal surface.

→ Consider a set of parallel and equidistance planes XYZ in the crystal seperated by a distance 'd' (interplanar surface)
→ Suppose a beam of X-ray 'i' is incident on crystal at an angle θ (Glancing angle).
→ Some of the rays are reflected from the upper and successive lattice plane (reflected rays - BC & EF)

→ Draw the line BQ & BP perpendicular to the beam so these are drawn from B on DE & EF respectively.

→ The path difference b/w the two waves ABC & BEF is PE + EQ.

consider, ΔPBE

$$\Rightarrow \sin\theta = \frac{PE}{BE} \rightarrow (1)$$

$$\Rightarrow PE = BE \sin\theta$$

$$\Rightarrow PE = d\sin\theta \rightarrow (2) \quad (\because BE = d)$$

Now, consider ΔQBE

$$\Rightarrow \sin\theta = \frac{EQ}{BE}$$

$$\Rightarrow EQ = BE\sin\theta$$

$$\Rightarrow EQ = d\sin\theta \rightarrow (3) \quad (\because BE = d)$$

∴ from (2) & (3)

the path difference = PE + EQ

$$= d\sin\theta + d\sin\theta$$

$$= 2d\sin\theta \rightarrow (4)$$

$$\therefore \boxed{n\lambda = 2d\sin\theta} \text{ - Bragg's law}$$

→ If this path difference $2d\sin\theta$ is equal to the integral multiple of 'λ' of the x-rays i.e. '$n\lambda$' then the constructive interference will occour between the reflected beam and they will reinforce with eachother.

→ Hence the intensity of reflected beam is maximum

→ The two waves are travelled in the same distance and the extra distance travelled can be calculated from bragg's law i.e. $n\lambda = 2d\sin\theta$

where n →

λ → wavelength of incident ray

d → interplanar surface

θ → glancing angle

Applications:

To find out atomic structure of the crystal like the table salt (NaCl), $ZnSO_4$, graphite etc...

X —— CT3 —— X

CT-3 syllabus