Chemistry Unit 5 XPS - Unit 5 study notes

Chemistry (SRM Institute of Science and Technology)

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Unit - 5

XPS :- [Photoelectron Spectroscopy)

ESCA - Electron Spectroscopy for chemical Analysis.

XPS is used for analysing the structure of the atoms and also gives the information about the IE of particular electron in an atom. In recent years a no. of methods have been developed for surface characterization.

Surface Spectroscopic method now provide useful info about the chemical nature of surface. These methods provide both qualitative and quantitative about the chemical nature, composition and surface layer of the solids.

Principle:

It is a surface sensitive Spectroscopic technique that measures the elemental composition, emprical formual, chemical, electronic state of the element.

It is obtained by irradiating the material with a beam of x-ray and simultaneously measuring the KE the no. of electrons that escapes from 0 to 10 nm of the we analysed.

The peneteration depth of these photons in solids is lin to few microns.

Thus, interactions takes place between the incident photo and the atoms in the surface leading to the emission of $e^{\ominus}$s. From the KE of emitted electrons the B.E is calculated.

$$E_{Binding} = E_{photon} - (E_{K.E} + \phi)$$

$$BE = h\nu - (E_{KE} + \phi)$$

$E_{Binding}$ = Binding energy of photons.

ϕ = work Function depends upon spectrometer and material.

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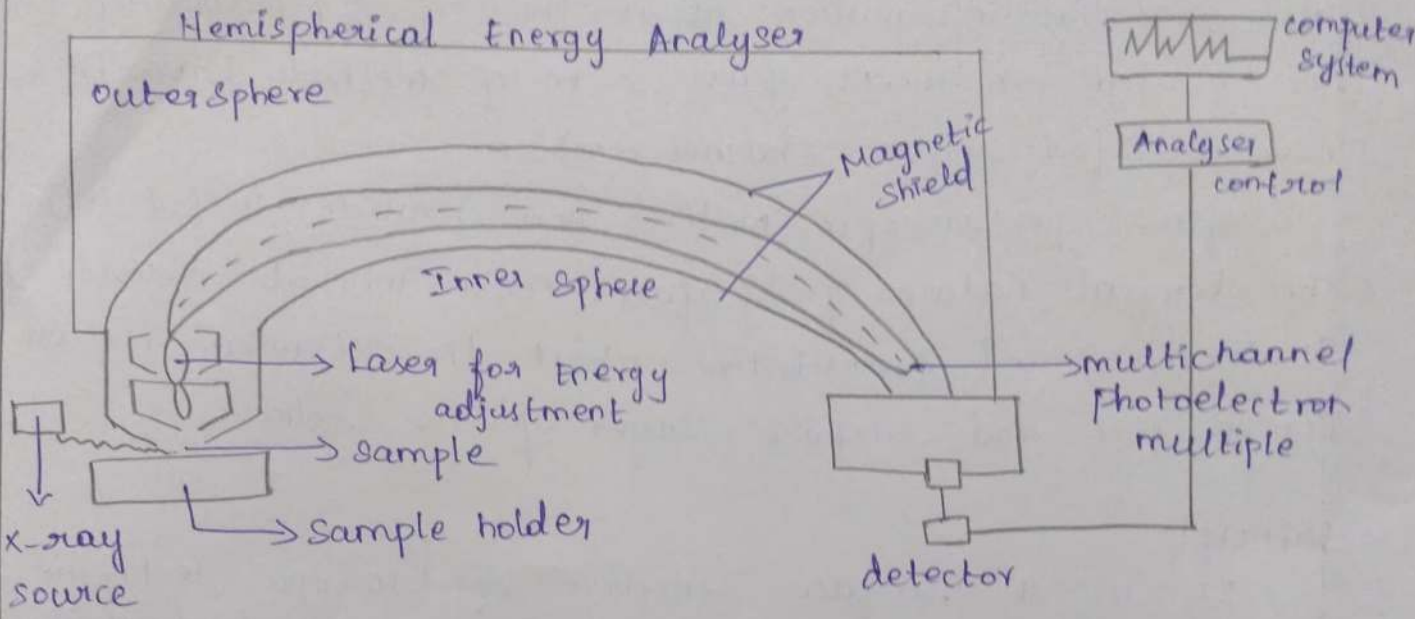
Instrumentation :-

1) Source
2) Sample holder
3) Energy analyser
4) Detector
5) Ultra-high vaccum.



Source - He(I), He(II) - singly and doubly ionised He for removing Valanced $e^{\ominus}$ to produced ions.

Yttrium (m) zeta x-rays can cause the ejection of outercore $e^{\ominus}$ (Just inside the Valence shell)

AlK_{α} or CrK_{α} or MgK_{α} - most energetic radiations reach the inner shell causing ionisation.

The simplest x-ray source for xps or x-ray tubes equipped with Mg, Al targets and suitable filter. Al and Mg target tubes are generally used because of high intensity and narrow wavelength bands of K_{α} light narrow bands are desirable because they give rise to high resolution.

Sample holder - Solid samples are mounted in a fixed position as close to photon or electron source and the entrance slit of the spectrometer as possible.

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Energy Analyser [Monochromator] :- The energy analyser is placed between the sample and the detector. It should be sensitive to identify the $e^{\ominus}$ beam. i.e coming out of the sample most of the Spectrometers are in hemispherical type in which the electron beam is deflected by an electrostatic magnetic field in such a manner that the $e^{\ominus}$ travel in the curve path.

It has two concentric metal cylinders at different voltage. One of the metal cylinder will have the positive voltage and the other will have 0 voltage this will create an electric field between the two cylinders when the $e^{\ominus}$ pass through the cylinders they will collide with one of the cylinder or they will just pass through,

1) If the electrons velocity is too high it will collide with the outer cylinder.

2) If the velocity is very low it will collide with inner cylinder.

3) only the $e^{\ominus}$ with right velocity will go to cylinder to reach the detector.

Detector - The $e^{\ominus}$ multiplier is usually employed as a det because of its sensitivity and convinience.

Ultra-high Vaccum - This ultra high vaccum environment will p... the contamination of the surface and provide an accurate analysis of the sample it will allow the photo $e^{\ominus}$ the sample to the detector without any interference.

Working - When the sample kept in UHV is illuminated by the photons of energy hν the sample surface emits the core $e^{\ominus}$ called photoelectrons. These $e^{\ominus}$ when they leave from the atom some energy of the $e^{\ominus}$ is consumed in overcoming the

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columbic attraction of the nucleus thereby decreasing KE at this time the outer orbitals read and deliver extra energy to the outgoing $e^{\ominus}$.

The XPS is obtained by determining the KE and the no. of $e^{\ominus}$ escaping from the surface of the sample under investigation.

Applications:-

→ It is useful in the qualitative determination such as chemical state, surface adsorption, chemical structure, bonding.

→ It is useful in the quantitative determination of elemental composition of various organic and inorganic material.

→ It is useful in the identification of elements in the periodic table.

→ It is also used in the determination of O.S of the element as well as the type of the species to which it is bonded.

X-ray diffraction - Bragg's Equation:

Bragg pointed out that scattering of x-rays by crystal can be considered as reflection from successive planes of atoms in the crystal.

However, unlike reflection of ordinary light the reflection of x-rays can take place only at certain angle which are determined by the wavelength of x-rays and the distance of plane inside the crystal.

The fundamental equation that gives relation between the wavelength of x-rays and interplanar angle between planes and the angle of reflection is known as Bragg's equation.

$$n\lambda = 2d\sin\theta$$

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consider the above diagram the horizontal line represents Parallel planes in the crystal structure seperated from one-another by a distance. Suppose a beam of x-rays fall on the crystal at an angle (θ). Some of the x-rays will be reflected from the upper plane at the same angle θ while some other rays absorbed and get reflected from the successive layers as shown.

Let ABC and DEF are incident, reflected rays respectiv the reflected rays from the layers will coincide with one another only if the path length of rays is equal to the integral no. of wavelengths. Drawing OL, OM Perpendicular to the incident, reflected beams the difference in path length (Δ) of the ways reflected from the successive layers is given by LN + LM this should be equal to the whole no. multiple wavelength.

$$\Delta = LN + LM$$

$$LN + NM = n\lambda$$

Since, the triangles OLN, OMN are congruent hence

$$LN = Nm$$

$$2LN = n\lambda$$

$$\boxed{n\lambda = 2d \sin\theta}$$

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Elastic limit :-

The maximum stress upto which a body exihibits the property of elasticity is called elastic limit.

Hook's Law :-

It states that within the elastic limit stress in a body is directly proportional to strain produced on it.

$$\text{Stress} \propto \text{strain}$$

$$\text{Stress} = \text{constant } (E) \times \text{Strain}$$

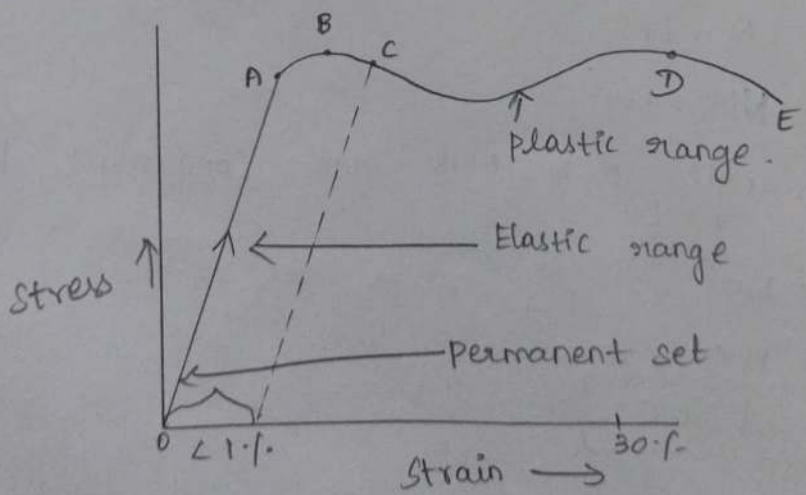
$$E = \frac{\text{stress}}{\text{strain}}$$

E = modulus of elasticity (or) co-efficient of elasticity.

Stress - Strain diagram and its uses :-

Consider a wire which is rigidly fixed at one end it is loaded at the other end the strain produced for different loads are noated untill the wire breaks down.

A graph is drawn between strain along X-axis and stress along Y-axis this graph is known as stress - strain graph. From this graph we get useful informations regarding the behaviour of solid materials.



A - Proportional limit
B - Elastic limit
C - Yield point
D - Breaking point (tensile strength)
E - Practure point.

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Hook's Law :- The portion of OA curve is a straight line in this region stress is directly proportional to strain.

This means that upto OA to the material obeys hook's law. The wire is perfectly elastic. The point A is called as the limit of proportnality.

Elastic limit :- The stress is further increased till point B. The Point B lying near to A denotes the elastic limit. upto this point the wire regain its original length if the stress is removed if the wire is loaded beyond this limit then it will not restore its original length.

Yield point : On further Increasing the stress beyond the elastic limits the curve bends and points C reached. In this region slight increase in stress produce large strain in the material. This point is called the Yield point.

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