**--- PROPOSED QUESTIONS FOR EXAM ---**

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1. **Explain the difference between XPS and AES along with kinetic energy calculations for each.**

Auger Electron Spectroscopy, AES, uses a beam of primary electrons to knock out an electron from a low energy level in an atom on the sample's surface. The radiation energy produced by the electron that falls from a higher energy level to fill the hole left behind by the initially ejected electron is used to emit an Auger electron. X-ray Photoelectron Spectroscopy, XPS, uses either monochromatic Aluminum Kα or non-monochromatic Magnesium Kα x-rays to eject a photoelectron from an atom at the sample's surface. An electron from a higher energy level then falls to fill the hole left behind and its emitted radiation energy is used to eject an Auger electron. Thus, XPS emits both photoelectrons and Auger electrons which can be seen in the spectrum. In addition, the penetration depth for AES is much smaller compared to XPS; 0.5-3 nm and 1-12 nm respectively.

AES
$KE=E_K-E_{L2}-E_{L3}-\Phi$

XPS
$KE=hv-BE-\Phi$

$\Phi$=work function
hv=E=Planck relation (h= Planck's constant, v=wave frequency)
BE=binding energy

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2. **Explain how the Cylindrical Mirror Analyzer (CMA) works in Auger Spectroscopy. Is there a CMA in XPS? If so, how does it differ?**

A high vacuum chamber encloses the CMA and also shields it from any external magnetic fields. The CMA has an outer and inner cylinder in which the former has a negative charge relative to the latter. The electrons scattered from the sample flow through the space between the inner and outer cylinder. The negative potential between the two cylinders bends the electrons, which have the right velocity, toward the center axis of the CMA where they are sent through two apertures and into the electron multiplier. The XPS does have a CMA and it is operated at a different voltage than the AES. A double pass CMA can be used in XPS, where two cylindrical mirror analyzers are in series.

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3. **Which method, AES or XPS, is better for resolving chemical shifts and why? Which direction would a peak in a given spectrum move if an atom loses a valence charge? What if the atom gains a valence charge?**

XPS is better for resolving chemical shifts since it has a better resolution which results in finer peak widths than AES. This better resolution stems from the use of monochromatic Al Kα x-rays and the fact that XPS is a single electron process. If an atom loses valence charge, the peak shifts to the left since the Binding Energy increases. The peak will shift right if an atom gains valence charge since the Binding Energy decreases.

4. **Why is the AES uses dN/dE instead of N(E) directly?**

5. **Does the Auger sensitivity depend on the electron beam energy?**

6. **Is the kinetic energy of the photoelectron dependent on the X-ray beam energy?**

7. **Meaning of transition nomenclature, eg. what is a KLL transition?**

Secondary electrons with discrete kinetic energy are produced from substances by the multistage Auger process. The initial step is the transfer of energy to a core electron shell of an atom (K or L), and ejection of an electron. Next (a) an electron from a shell beyond the core shell falls into the hole that has been formed and (b) another electron called the Auger electron is ejected with characteristic kinetic energy. Three electrons in total have been involved in the process and the atom has been left in a doubly ionized state figure 1.

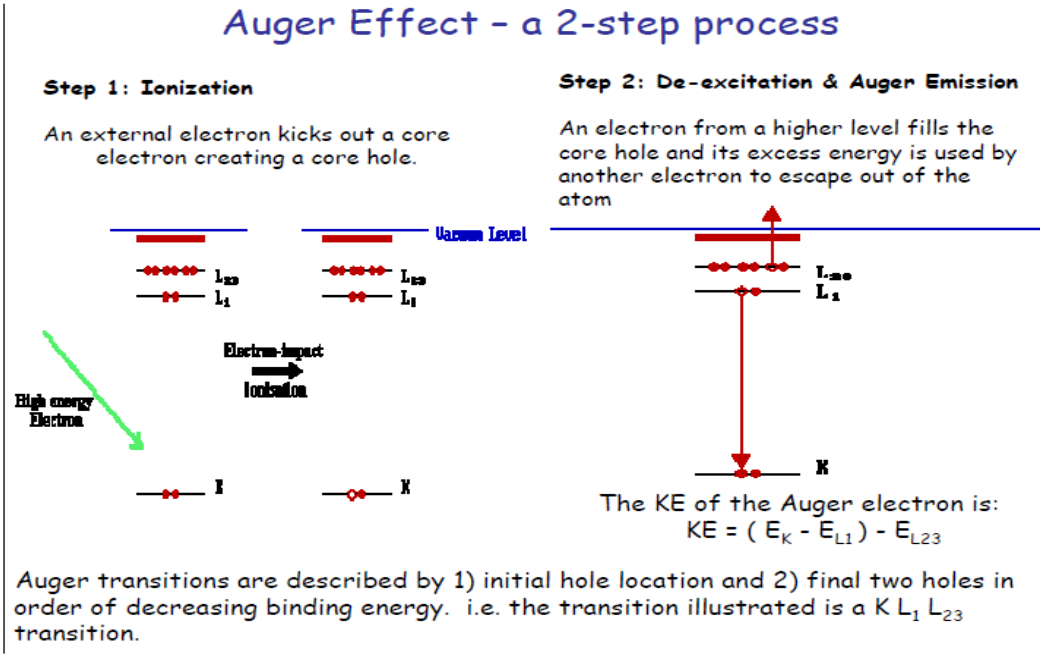



figure 1.

8. **What is the maximum depth of AES?**

The maximum depth is 2nm

9. **Can Auger electrons be non-core electrons?**

   Core holes can be created in all levels (not only K levels)

10. **Why is AES a more qualitative than quantitative technique?**

    AES is a more qualitative than quantitative technique because the AES peaks can be measured with somewhat higher sensitivity. For this purpose the most intense Auger transitions, those whose final state fall in the families, KLL, LMM, MNN should be used.
    It is found that Auger KLL spectra are readily obtained for lighter elements (Atomic number less than 35) and that LMM transitions are easily observed for all the elements that five Auger spectra. Peak overlap is occasionally a problem since natural peaks widths are only of the order of about 3-10 eV.

11. **What pressure is best when performing an AES measurement?**
    10E-8 to 10E-9 Torr

12. **Can the Auger electron emission process be initiated with x-rays?**
    Electron emission process can just be initiated with high energy electrons.

13. **Besides the beam electrons, how many electrons are involved in AES?**
    There are three more electrons involved in the Auger process.
    1. The electron leaving the K level
    2. The electron from the $L_1$ level moving to the K lever (filling the K electron vacancy)
    3. The Electron leaving the $L_{23}$ level with the energy gained from the transition of the $L_1$ electron to the K electron vacancy.

14. **Can x-rays eject non-core electrons?**
    Yes it can eject also noncore elelctrons

15. **What is the maximum depth of XPS?**
    The maximum depth of XPS is 2.5 nm for metals and metal oxides. And 10nm for organic substances and polymers.

16. **Why is XPS a more qualitative than quantitative technique?**
    XPS is a more qualitative technique because the spectral interfaces are minimal since XPS peaks for the core electrons tend to be fairly widely separated. XPS elemental analysis is based on core electron peaks usually straightforward. Further, because peaks undergo chemical shifts, qualitative analysis leading to identification of compounds and of oxidation of states of elements (separation) is often possible.

17. **How many electrons are involved in XPS?**
    There is just one electron is involved in the XPS process.

18. **What pressure is best when performing an XPS measurement?**
Ultra High Vacuum from 10E-8 to 10E-9 Torr

19. **Is the kinetic energy of the photoelectron dependent on the X-ray beam energy?**
Yes the photoelectron kinetic energies depend on photon energy while the Auger electron kinetics does not depend on the photon energy.

20. **Determine the Auger Electron in the following Titanium Auger process.**

**Fermi Level _____ 0**

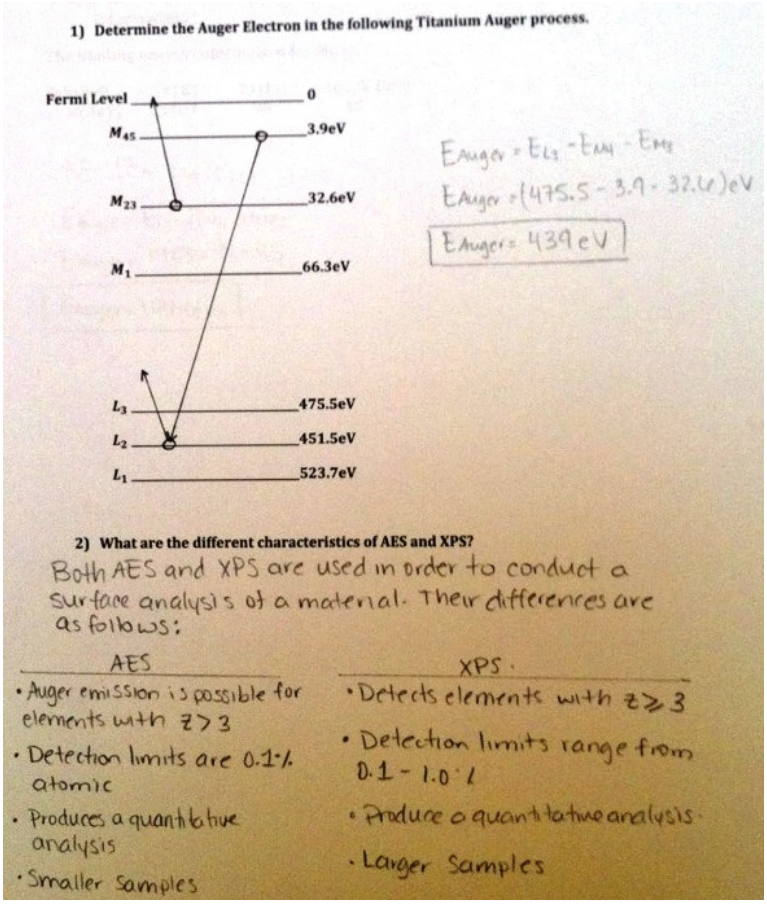
**$M_{45}$ _____3.9eV**

**$M_{23}$ _____32.6eV**

**$M_1$ _____66.3eV**

**$L_3$ _____475.5eV**
**$L_2$ _____451.5eV**
**$L_1$ _____523.7eV**

**Solution:**



1) Determine the Auger Electron in the following Titanium Auger process.



$E_{Auger} = E_{L_2} - E_{M_4} - E_{M_5}$

$E_{Auger} = (475.5 - 3.9 - 32.6)eV$

$E_{Auger} = 439\,eV$

2) What are the different characteristics of AES and XPS?

Both AES and XPS are used in order to conduct a surface analysis of a material. Their differences are as follows:

| AES | XPS |
|---|---|
| • Auger emission is possible for elements with $Z > 3$ | • Detects elements with $Z \geq 3$ |
| • Detection limits are 0.1% atomic | • Detection limits range from 0.1 - 1.0 % |
| • Produces a quantitative analysis | • Produce a quantitative analysis |
| • Smaller samples | • Larger samples |

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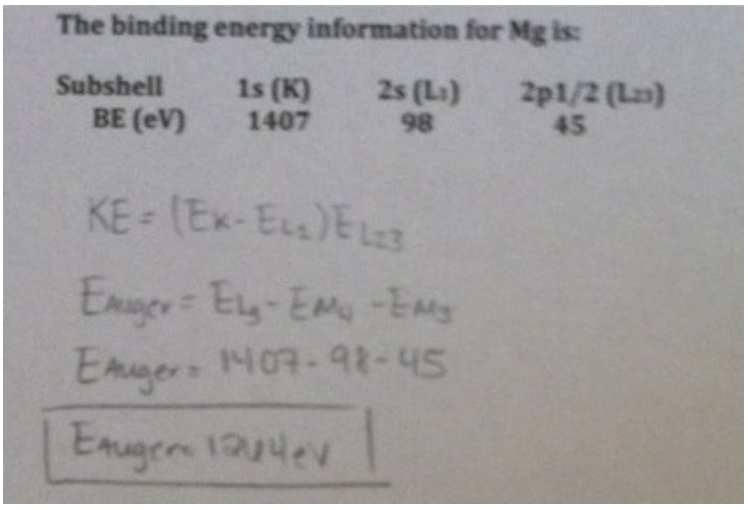
**21. Determine the Auger transitions that produced electrons with the provided information.**

**The binding energy information for Mg is:**

| Subshell | 1s (K) | 2s (L1) | 2p1/2 (L23) |
|---|---|---|---|
| BE (eV) | 1407 | 98 | 45 |

**Solution:**



The binding energy information for Mg is:

| Subshell | 1s (K) | 2s ($L_1$) | 2p1/2 ($L_{23}$) |
|---|---|---|---|
| BE (eV) | 1407 | 98 | 45 |

$KE = (E_K - E_{L_2})E_{L_{23}}$

$E_{Auger} = E_{L_3} - E_{M_4} - E_{M_5}$

$E_{Auger} = 1407 - 98 - 45$

$E_{Auger} = 1264\,eV$

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22. **Compare seven main characteristics of XPS and AES?**

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23. **How can we deduce atomic concentration from AES peaks?**

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24. **What are the three type of observed peaks originating in photo emission in XPS?**

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25. **What are the two main types of detectors used in AES and XPS systems? Explain how CMA works?**

- The two main types of detectors are the Cylindrical Mirror Analyzer (CMA) and the Hemispherical Sector Analyzer (HSA).

- The electrons ejected from the sample, after exposure to an x-ray beam, will pass through a CMA. The CMA has two concentric metal cylinders at different voltages. One of the metal cylinders will have a positive voltage and the other will have a zero voltage. As a result, it will create an electric field between the two cylinders. When the electrons pass through the metal cylinders, they will collide with one of the cylinders or they will just pass through them. If the velocity of the electron is too high it will collide with the outer cylinder. If the velocity is too slow it will collide with the inner cylinder. Only the electrons with the right velocity will go through the cylinders to reach the detector. By changing the cylinder voltage, the acceptable kinetic energy will change and then you can count how many electrons have that KE to reach the detector.

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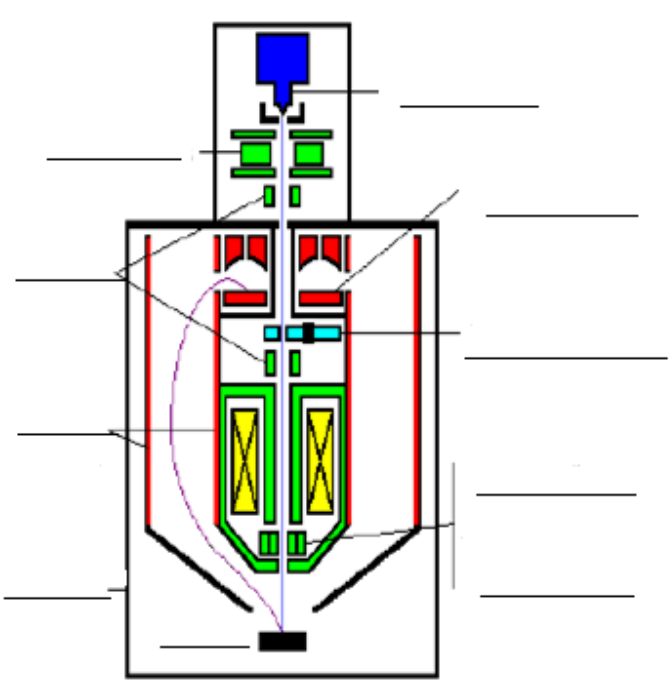
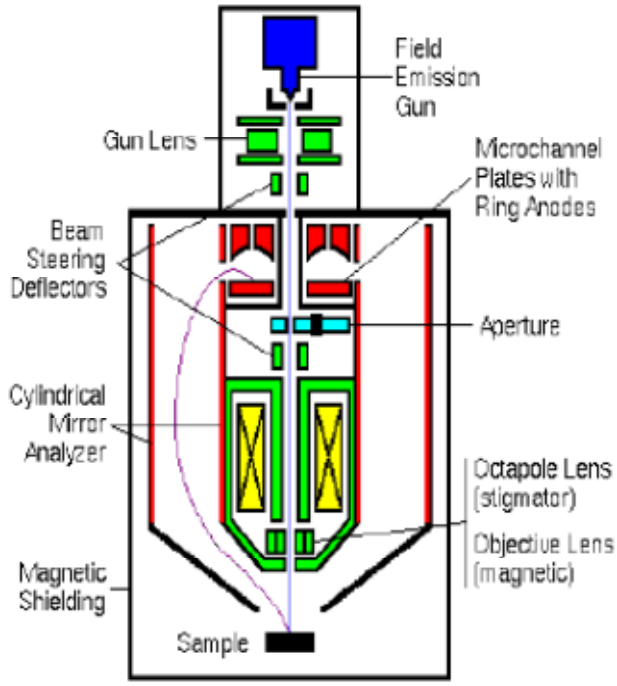
26. **Label the different parts of the instrumentation.**





**27. List the similarities and differences of XPS and AES.**

Similarities

- Use electron energy as the analyzed beam
- Their area of analysis is 10 μm
- They can analyze all elements except for H and He
- It's not possible to do molecular identification
- Their depth of profiling is elemental and chemical
- They both are non-destructive analyzers

Differences

- XPS uses X-rays as their primary beam, while AES uses electrons
- XPS can analyze all types of samples but charging is possible on the surface, while AES only analyses conductive samples.
- The nature of chemical bonding for XPS is due to shifts and straightforward, while for AES it's due to shifts and shapes.
- AES has a better imaging of the analyzed data; it can measure better distribution of elements and chemical states over the surface.

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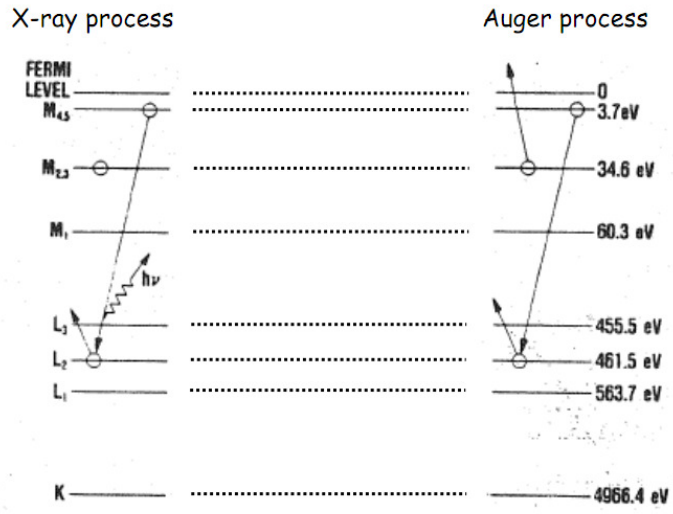
**28. What is the difference between Auger electrons and x-ray electrons?**

i) Auger emissions are independent of how the initial ionization is produced and the energy levels used to calculate the kinetic energy should be those of ionized atoms not the normal atoms. Auger can be described as the initial hole location and the final two holes in order of decreasing binding energy

ii) On the other hand x-ray electrons scatter inelastically with the atoms and bounce back producing a high background (secondary electrons).

iii)




$h\nu = E_{L_2} - E_{M_4} = 457.8\,\text{eV}$ $\quad E_{Auger} = E_{L_3} - E_{M_4} - E_{M_3} = 423\,\text{eV}$

$\lambda = 27.1\,\text{Å}$

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**29. What does CMA stand for and what does it measure?**

i) CMA- Cylindrical Mirror Analyzer

ii) The CMA measures the number of Auger electrons as a function of electron energy

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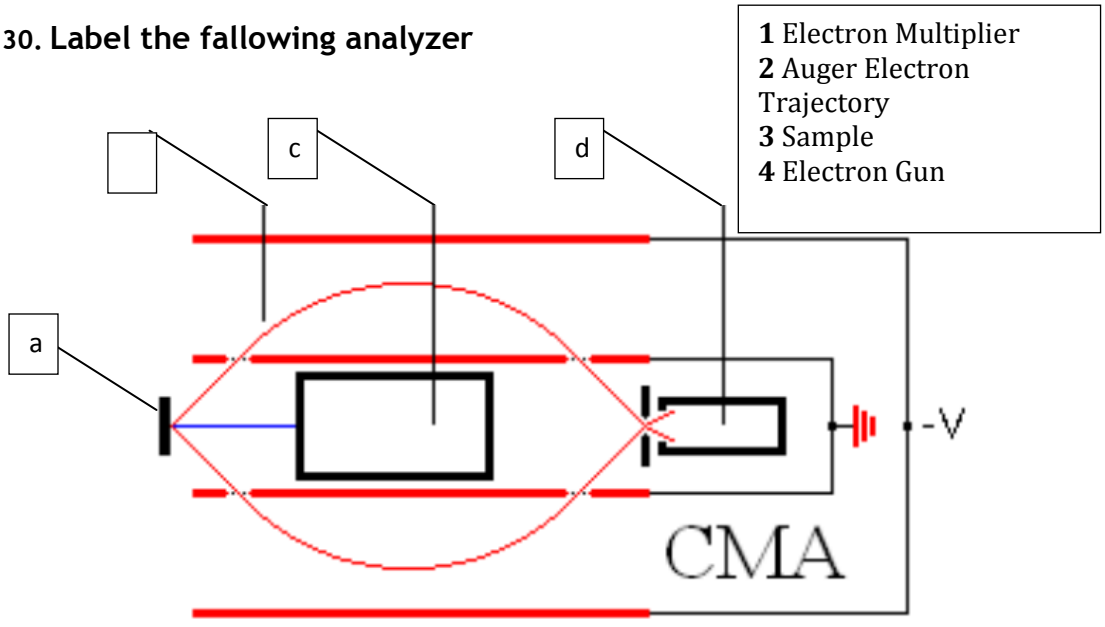
**30. Label the fallowing analyzer**

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**31. What are the three steps of Auger Spectroscopy**

1) Atom is ionized by removing a core electron,
2) Upper level electron falls to lower level,
3) Third electron (Auger electron) is excited by the energy given off in step 2 and detected.

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**32. Why is an Auger spectrum presented as a derivative plot?**

When a solid is probed with high energy electrons, not only Auger electrons are ejected from the solid. A plot of number of emitted electrons from the solid with a given kinetic energy would display only a small peak against large background at a particular Auger electron transition energy

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33. **What is the advantage of using Auger for elemental analysis relative to other techniques?** Auger has the following advantages:

It is sensitive for low atomic number atoms which XPS cannot detect effectively especially atomic numbers below 7; minimal effect on matrix; high spatial resolution which allows detailed examination of solid surfaces.

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**34. What is the difference between X-rays and e- Beam?**

X-Rays can hit all sample area simultaneously permitting data acquisition that will give an idea of the average composition of the whole surface.
Electron Beam can be focused on a particular area of the sample to determine the composition of selected areas of the sample surface.

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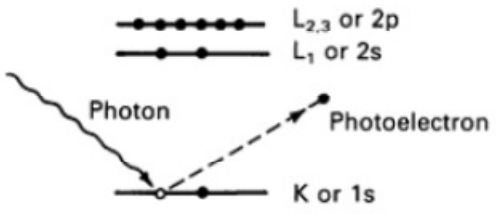
**35. What is the sampling depth of XPS?**

Sampling Depth is defined as the depth from which 95% of all photoelectrons are scattered
by the time they reach the surface ( 3λ ). Most λ‘s are in the range of 1 – 3.5 nm for AlKα radiation, So the sampling depth (3λ) for XPS under these conditions is 3-10 nm

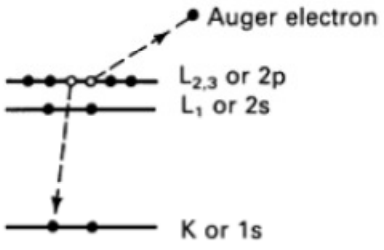
**36.**

1. Draw the energy level diagram and write down the kinetic energy equations for Auger Electron Spectroscopy.

Energy Level Diagram:




**(a)**




**(b)**

Energy-level diagrams of (a) photoelectron and (b) Auger electron excitation.

Kinetic Energy equations for the Auger Electron is, $E_{ke} = E_K - 2E_{L2,3} - \phi$

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**37.**

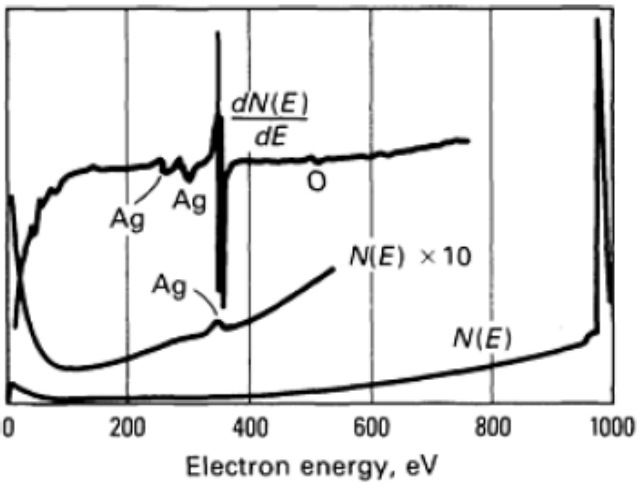
2. $I_1$, $I_2$, $I_3$, $I_4$, $I_5$ are the measured intensities and $S_1$, $S_2$, $S_3$, $S_4$ and $S_5$ are the corresponding sensitivity in an XPS spectra. Determine the concentration of element 3.

Concentration of element 3, $C_3 = \dfrac{\frac{I_3}{S_3}}{\frac{I_1}{S_1} + \frac{I_2}{S_2} + \frac{I_3}{S_4} + \frac{I_4}{S_4} + \frac{I_5}{S_5}}$

**38.**

3. How the problem of low signal in Auger spectrum is minimized?

As only 0.1% of the total current is contained in Auger peaks, the peaks are relatively small. Therefore, the signal is relatively small over a large background. But by taking derivative dN(E)/dE of the spectrum the problem is minimized as shown in the figure below-




**39. What are the most common notation designated in Auger electrons and what each letter corresponds to in terms of location?**

Most common: KLL, LMM, MNN
First Letter: initial core location
Second Letter: initial location of relaxing electron
Third Letter: location of second hole (initial location of Auger electron)

| KL1L2,3 = | K | L1 | L2,3 |
|---|---|---|---|
| | (1s) | (2s) | (2p) |
| | Location of core hole | origin of relaxing electron | Auger electron (electron that leaves ion) |

**40. How charging can be resuced almost completely?**

An oxygen atmosphere, at 5 x 10-9 Torr reduces charging almost completely. Higher pressure, about 2 x 10-8 Torr, can prevent charging for 2 days, allowing an increase of about 35 eV at most.

**41. How is the excitation energy affects the KE of Auger and how in XPS?**

While KE of Auger electron is independent of excitation energy, apparent BE will change depending upon x-ray hn in XPS.

42. **How it is called the separation between the two peaks in XPS and how different the values are of spin orbital splitting of a core level of an element in different compounds?**

The separation between the two peaks are named spin orbital splitting. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same. The peak area ratios of a core level of an element in different compounds are also nearly the same.

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43. **Find the volume in (cubic meters) of a total mass of helium of 1 kg contained in a vessel pressurized at 1 MPa and at 27 degree Celsius?**

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44. **a) Calculate the resulting kinetic energy of an electron ejected by bombarding a sample with Mg Kalpha rays with energy of 1253.6 eV if the binding energy exhibited by the peak in the spectrum is 910 eV. Assume that the work function of the device is 0.5% of the impinging energy source.**

**b) Judging by the 910 eV peak in the spectrum, what is the most probable element detected in this sample by XPS?**

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45. **By looking at the chart of required energy VS atomic number, what would be the minimum energy required to allow emission of Auger electrons following the LMM transition from Zirconium?**