

I-E of Chemistry

15,75

ex. I

- 1) For Al: $Z = 13$, 13th group and 3rd period
 For In: $Z = 49$, 13th group and 5th period
 For Tl: $Z = 81$, 13th group and 6th period

- 2) They belong to the "p" block, and they are all metallic elements.
 They are ordered by increasing radius like this:

$$r_B < r_{Al} < r_{Ga} < r_{In} < r_{Tl}$$

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

It possesses 3 valence electrons.

4) a) $\bar{V} = 2 \times 0,35 + 8 \times 0,85 + 2 \times 1 = 9,5$
 $Z_4^* = 13 - 9,5 = 3,5$

- b) Al^{+} has one electron less on its valence shell than Al, hence:

$$\bar{V} = 0,35 + 8 \times 0,85 + 2 = 9,15$$

$$Z^* = 13 - 9,15 = 3,85$$

5) $E(Al)_{3p} = -13,6 \times \frac{Z_{4p}^*}{n^2} = -13,6 \times \frac{(3,5)^2}{3^2} = -18,5 \text{ eV}$

$$E(Al^{+})_{3s} = -13,6 \times \frac{Z^*}{n^2} = -13,6 \times \frac{3,85^2}{3^2} = -22,4 \text{ eV}$$

$$E_{i,1} = 3 \times E(AI)_{\text{ex}} - 2E(AI)_{\text{ex}} = \underset{\substack{\uparrow \\ 18,5}}{3} - \underset{\substack{\uparrow \\ 22,4}}{2} = \underset{10,7}{3,1} \text{ eV}$$

6) The value we obtained is ~~3,1~~ 56% higher than the experimental one, hence there must be a problem either in the calculations or in the experiment?

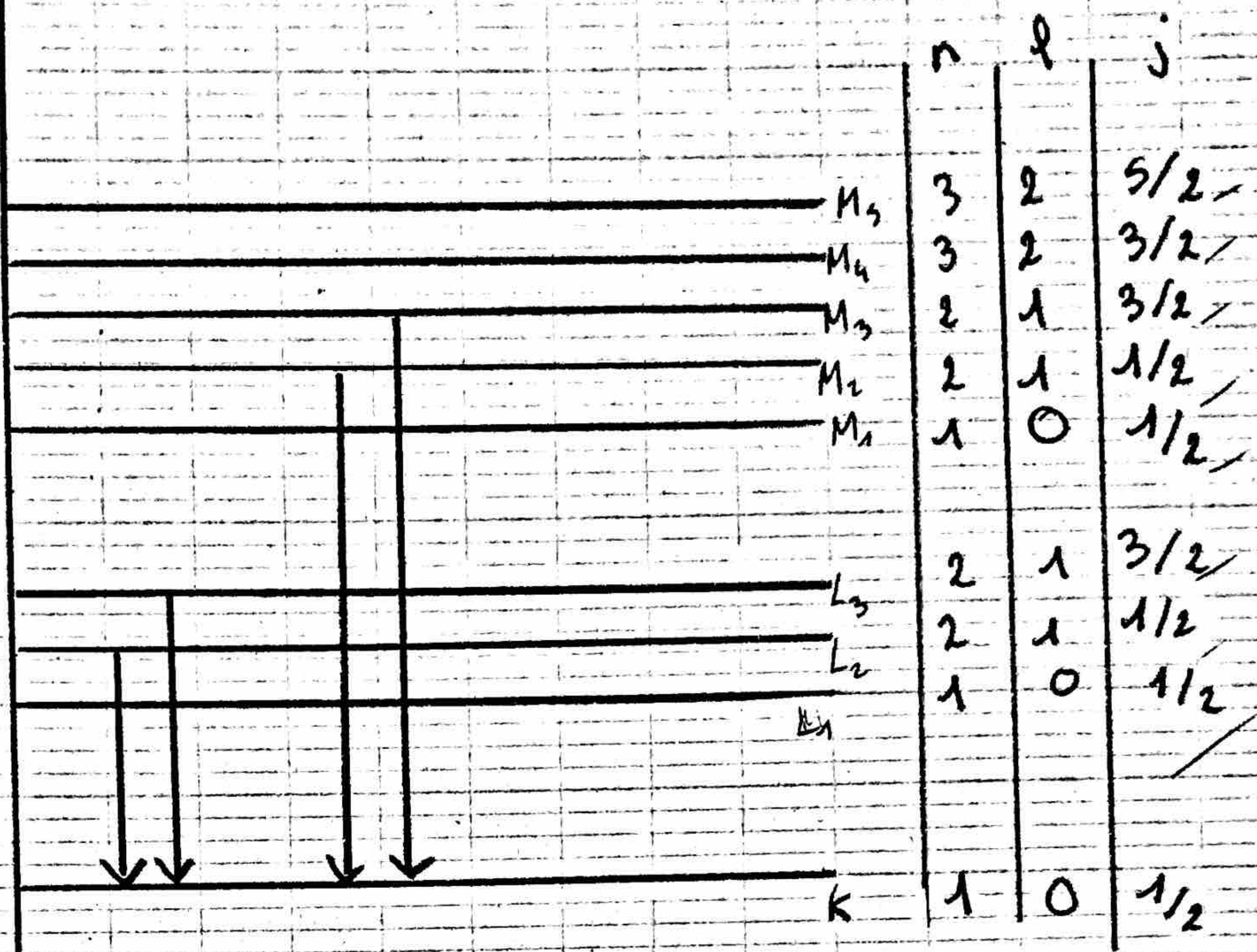
7) The fact that the 3rd and 4th ionization energies are very different is ~~caused~~ because for the 4th ionization energy, an electron from the 2p⁶ subshell is extracted, and this ~~subshell~~ shell is saturated, hence more energy is required. While for the 3rd ionization energy, an electron from 3s¹ is extracted, which requires less energy.

~~ex. IP~~

ex III

A) 1)

E



↓: possible transitions ($\Delta l = \pm 1$ $\Delta j = 0$ or $\pm 1/2$)

For Cr:

~~Ala~~ $E_k = 12400$ $E_{k-L_2} = E_k - E_{L_2} = 5989 - 583,8 = 5405,2 \text{ eV}$

$$\lambda_{k-L_2} = \frac{12400}{5405,2} = 2,2941 \text{ \AA}$$

$$E_{k-L_3} = 5989 - E_{L_3} = 5989 - 574,1 = 5414,9 \text{ eV}$$

$$\lambda_{k-L_3} = \frac{12400}{E_{k-L_3}} = \frac{12400}{5414,9} = 2,2899 \text{ \AA}$$

$$\lambda_{k-L_{2,3}} = \frac{(\lambda_{k-L_2} + \lambda_{k-L_3})}{2} = \frac{2,2941 + 2,2899}{2} = 2,292 \text{ \AA}$$

For Co

$$E_{k-L_2} = E_k - E_{L_2} = 7709 - 793,2 = 6915,8 \text{ eV}$$

$$\lambda_{k-L_2} = \frac{12400}{6915,8} = 1,7930 \text{ \AA}$$

$$E_{K-L_3} = E_K - E_{L_3} = 7709 - 778,1 = 6930,9 \text{ eV}$$

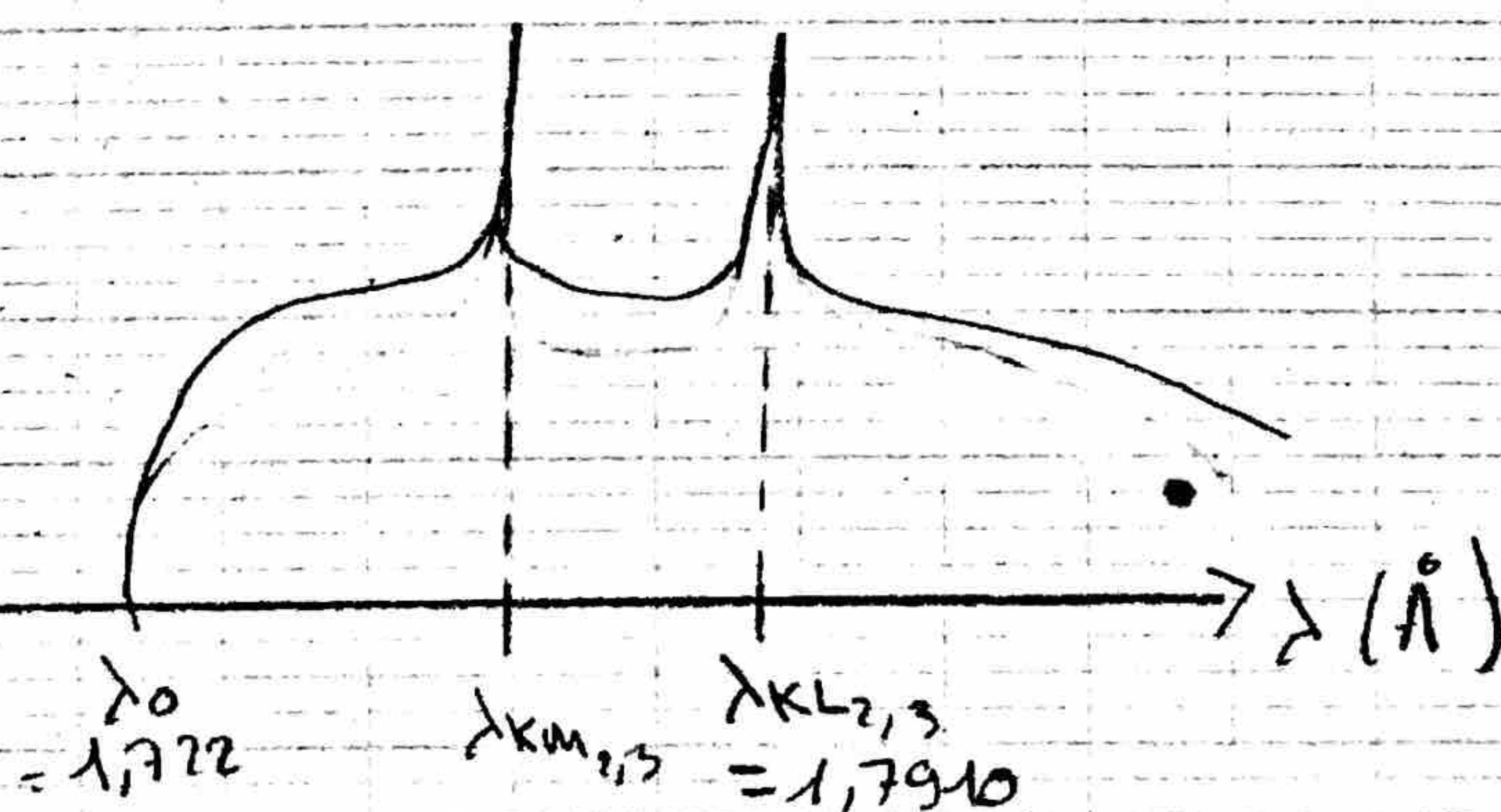
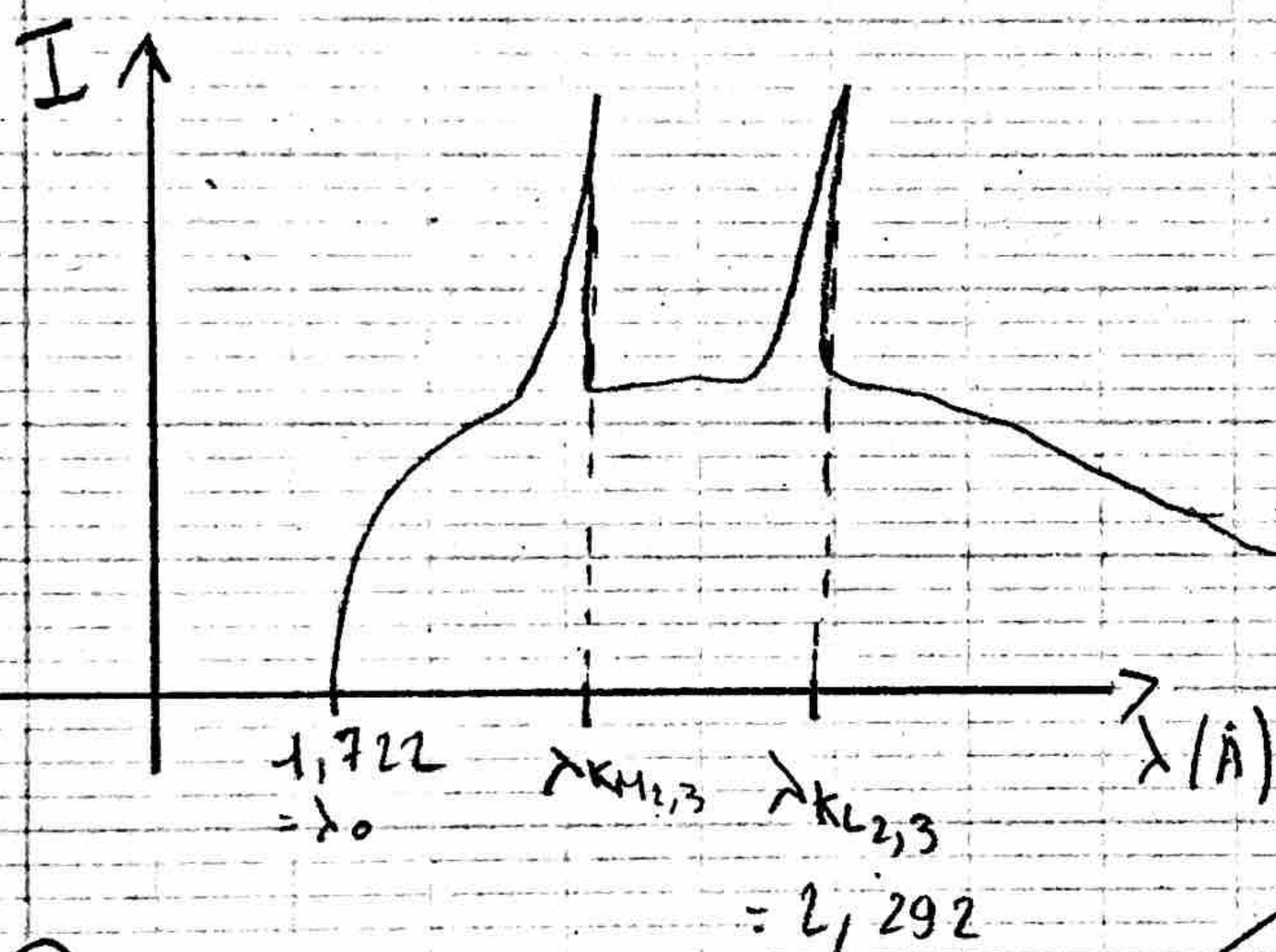
$$\lambda_{K-L_3} = \frac{12400}{6930,9} = 1,7891 \text{ \AA}$$

$$\lambda_{K-L_{2,3}} = \frac{\lambda_{K-L_2} + \lambda_{K-L_3}}{2} = \frac{1,7891 + 1,7930}{2} = 1,7910 \text{ \AA}$$

$$2) \lambda_0 = \frac{12400}{7200} = 1,722 \text{ \AA}$$

$$\text{since } \lambda \gg \frac{hc}{eU}$$

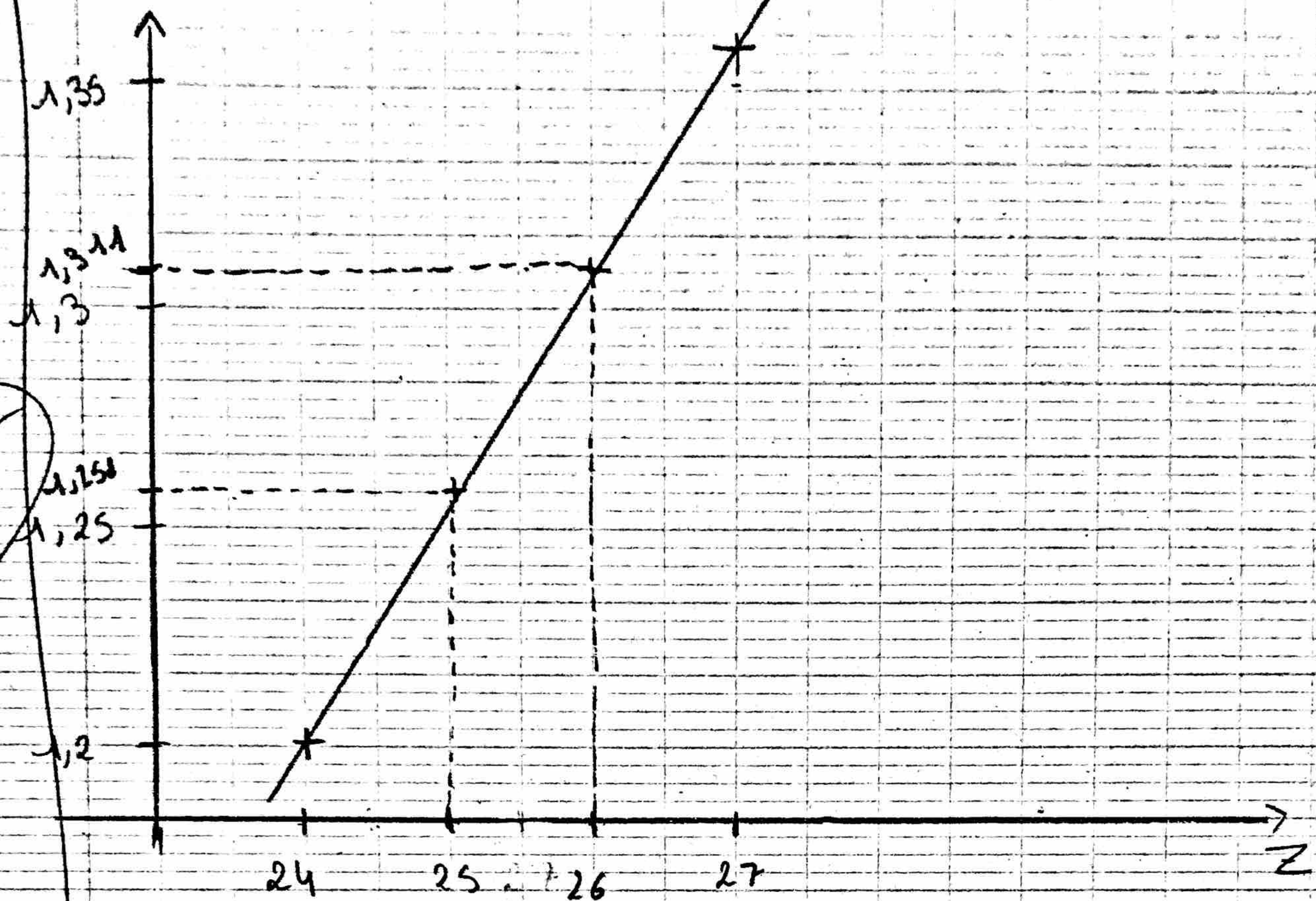
For Cu:



The continuous background that we can see on these spectra is the ~~excess~~ x-rays emitted by the incoming electrons when they are slowed down & when approaching the anticathode.

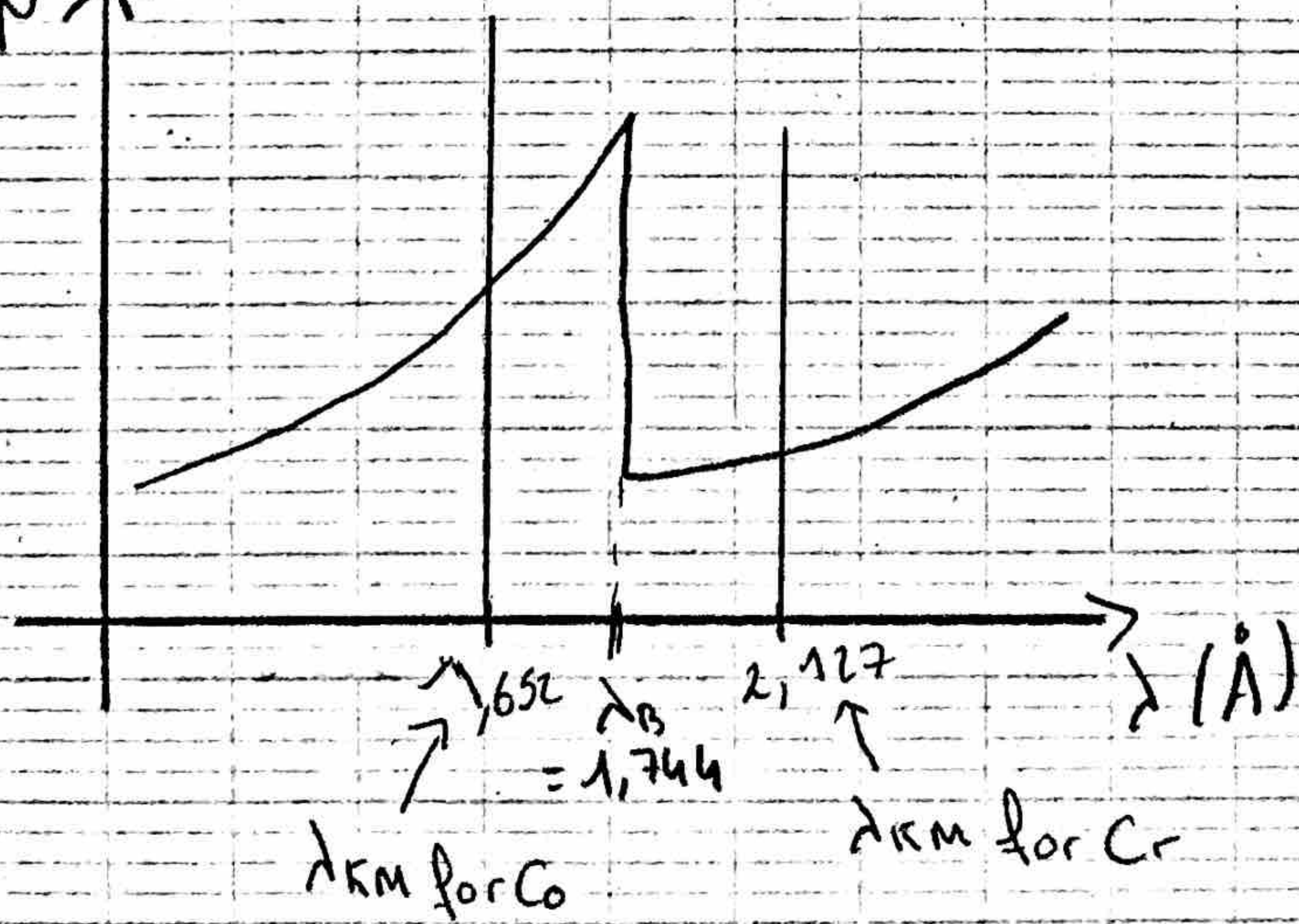
The two characteristic lines that we see correspond to

$\sqrt{D} (10^3 \text{ H})$



hence $Z_A = 25$ and $Z_B = 26$

d) N



We can see that λ_{KM} for Co is in the β part of the graph with the highest absorption, hence β this ray will be removed by filter B. However λ_{KM} for Cr is after the absorption drop, hence B cannot be used as a filter for the λ_{KM} ray of Cr.

ex. II

1) Each isotope's nucleus has the same composition, which is 17 protons and 17 neutrons.

3) $1s^2 2s^2 2p^6 3s^2 3p^5$

It belongs to the 17th group (halogens).

a) ~~Al~~ Al: 3 valence electrons $\rightarrow \cdot \text{Al} \cdot$

Cl: 7 valence electrons $\rightarrow \overline{\text{Cl}}$

AlCl_3 :



Lewis structure

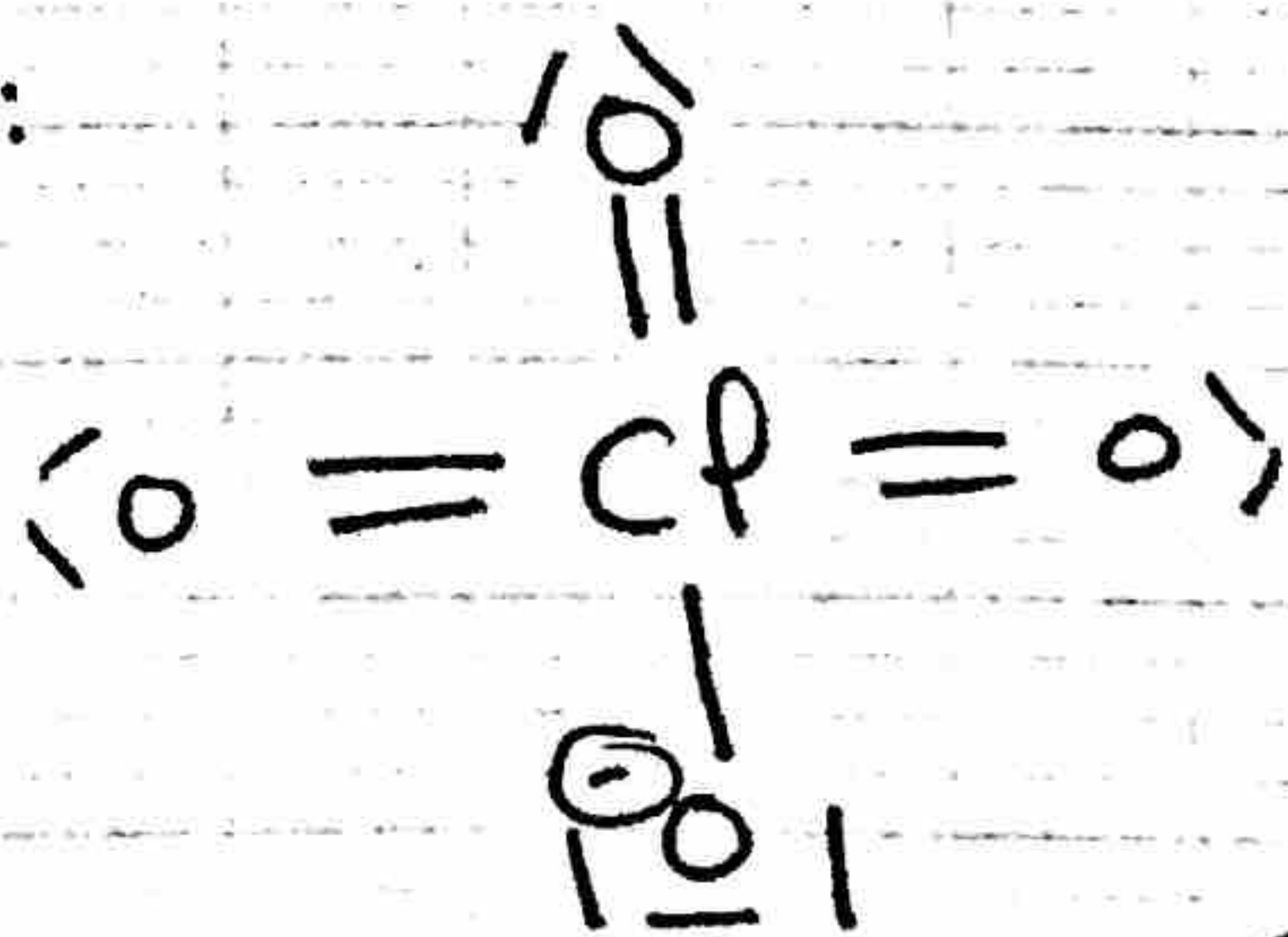
VSEPR theory: AX_3

hence AlCl_3 has a ~~pyramidal~~ structure and the angles between the Cl atoms are the same (120°).

b) In this molecule the Al will ~~complete~~ ^(3 of them) the octet rule with the electrons from the Cl atoms, otherwise the Al atom himself doesn't verify the octet rule.

5) a) O: $1s^2 2s^2 2p^4 \rightarrow \cdot \ddot{\text{O}} \cdot$

Lewis formula:



0,5

the internal transitions (from level L to level K and from level M to level K).

3) a) For Cu

$$E_{L-M} = E_{L_1} - E_M = \frac{12400}{23,10} = 536,8 \text{ eV}$$

hence $E_{L_1} - E_M = 536,8 \text{ eV}$

$$E_M = E_{L_1} - 536,8 = 159,2 \text{ eV}$$

$$E_{K-M} = E_K - E_M = 5989 - 159,2 = \cancel{5829,8} \text{ eV} \quad \underline{5830 \text{ eV}}$$

1,5

For Co

$$E_{L_1-M} = E_{L_1} - E_M = \frac{12400}{17,13} = 723,9 \text{ eV}$$

hence $E_M = E_{L_1} - 723,9 = 929,1 - 723,9 = 204,2 \text{ eV}$

$$E_{K-M} = 7709 - 204,2 = \underline{7508 \text{ eV}}$$

b) For Cr $\lambda_{K-M} = \frac{12400}{E_{K-M}} = \frac{12400}{5830} = 2,127 \text{ \AA}$

For Co $\lambda_{K-M} = \frac{12400}{7508} = 1,652 \text{ \AA}$

B) 4) a)
$$\begin{aligned} \frac{I_{K-L}}{I_{K-M}} &= \frac{I_{0KL} \times \exp(-\mu_{KL} \times 0,20)}{I_{0KM} \times \exp(-\mu_{KM} \times 0,20)} \\ &= \frac{7,4 I_{0KM} \times \exp(-1,870 \times 0,20)}{I_{0KM} \times \exp(-1,430 \times 0,20)} \\ &= \frac{7,4 \times \exp(-0,374)}{\exp(-0,286)} \\ &= \cancel{7,4} \quad 6,78 \end{aligned}$$

0,5

hence $\frac{I_{K-L}}{I_{K-M}} = 6,78$

b) $I = I_0 \exp(-\mu X)$

hence $X = \frac{\ln(I/I_0)}{-\mu}$

if $I = 0,98 I_0$ then $\frac{I}{I_0} = 0,98$

hence $X = \frac{\ln 0,98}{-1,870} \approx 0,0104 \text{ cm}$

$= 0,01080 \text{ cm} = 108,0 \mu\text{m}$

the maximum thickness of the window is $108,0 \mu\text{m}$.

c) s) a) The discontinuity corresponds to the drop in absorption of the metal, it corresponds to the λ_K of the metal.

b)

c) ~~To~~ To compute the atomic number of A and B we use Moseley's law.

We first compute $\sqrt{U}$ for the K levels of these metals:

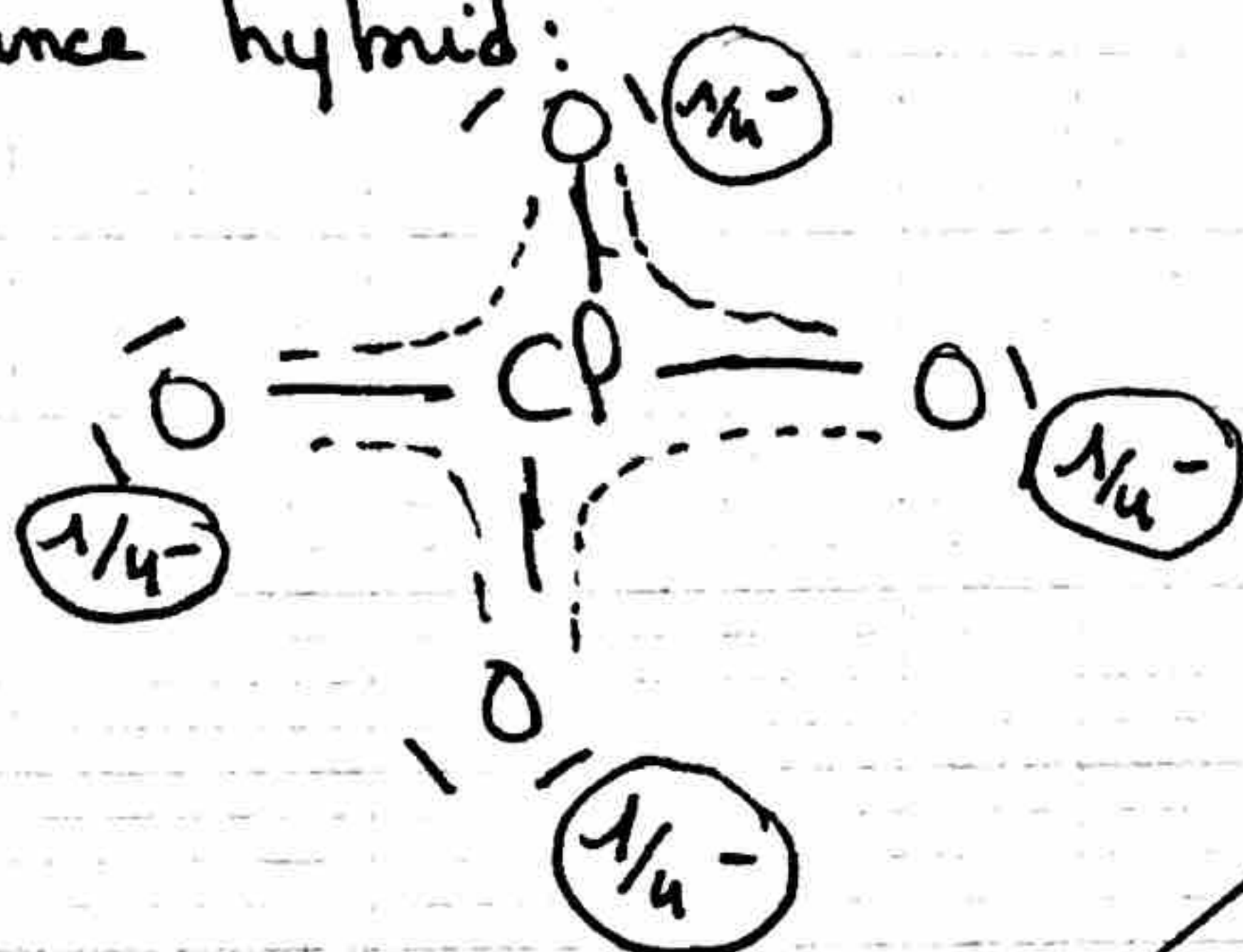
$U = \frac{c}{\lambda_K}$

Z	Cr: 24	Co: 27	A: ?	B: ?
$\lambda_K (\text{\AA})$	2,070	1,608	1,896	1,744
$U (\text{eV})$	$1,449 \cdot 10^{18}$	$1,866 \cdot 10^{18}$	$1,582 \cdot 10^{18}$	$1,720 \cdot 10^{18}$
$\sqrt{U}$	$1,204 \cdot 10^9$	$1,366 \cdot 10^9$	$1,258 \cdot 10^9$	$1,311 \cdot 10^9$

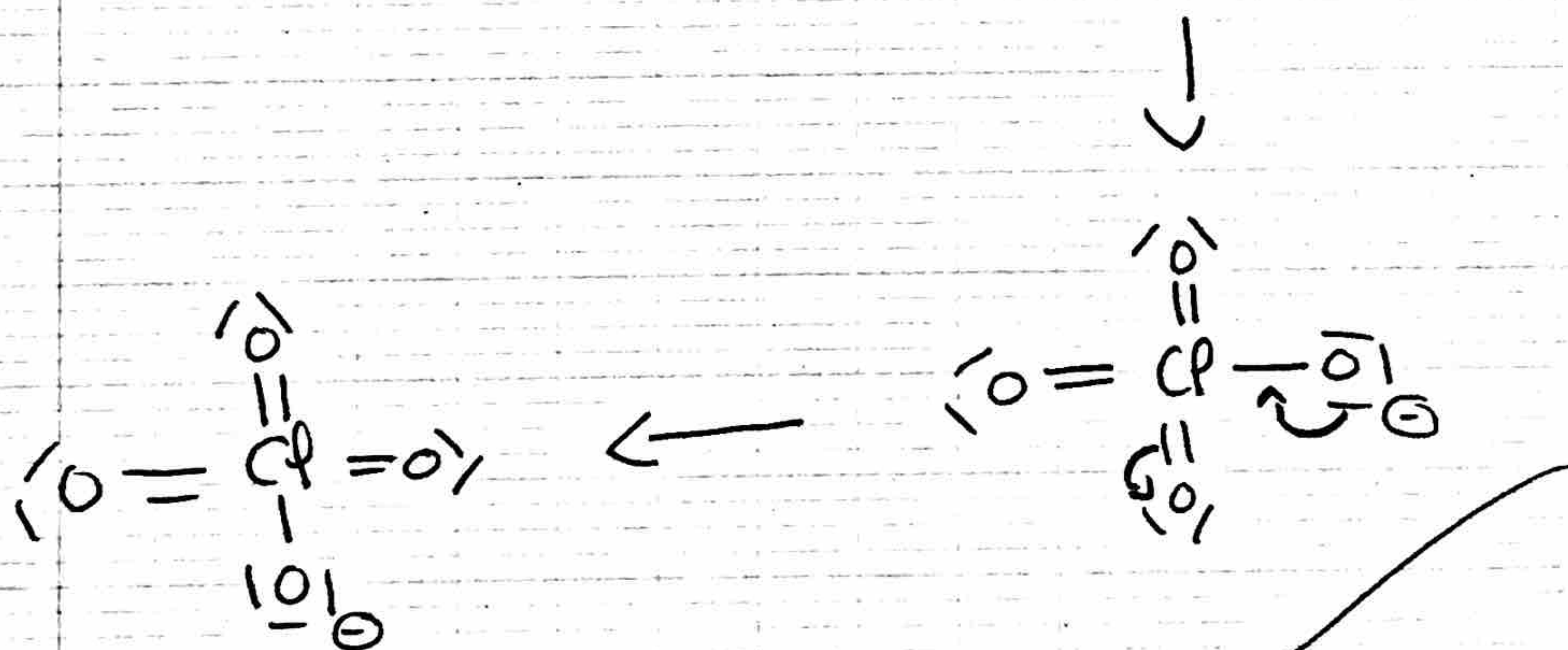
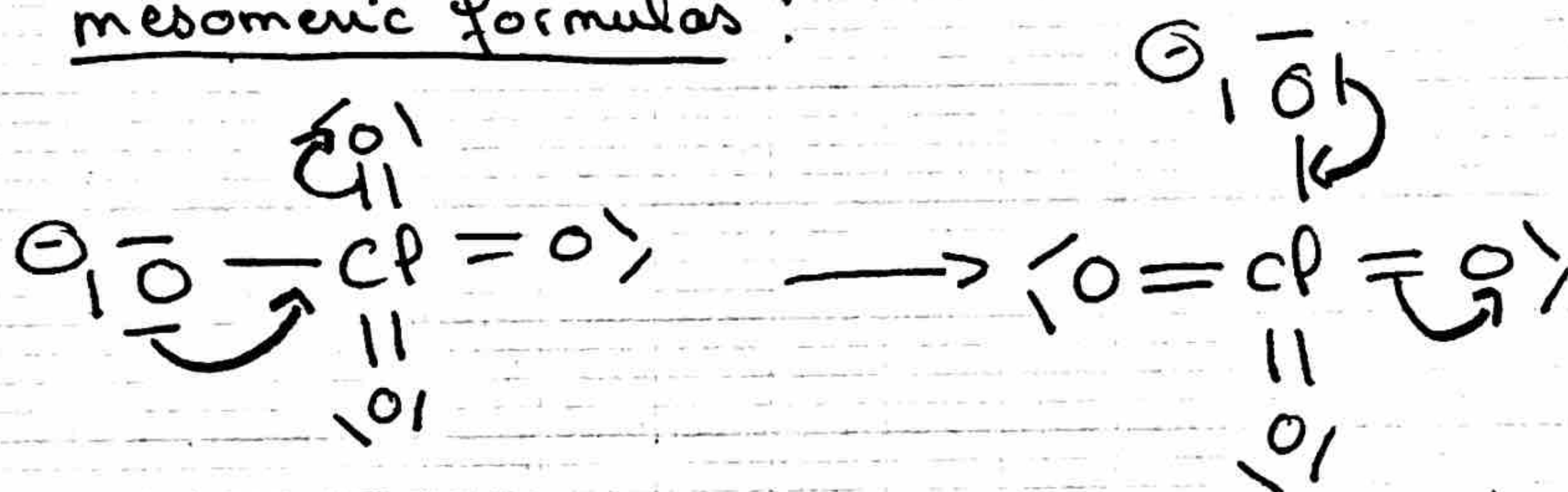
$\lambda_K = \frac{12600}{E_K}$

$U = \frac{c}{\lambda_K \text{ in meters}}$

resonance hybrid:



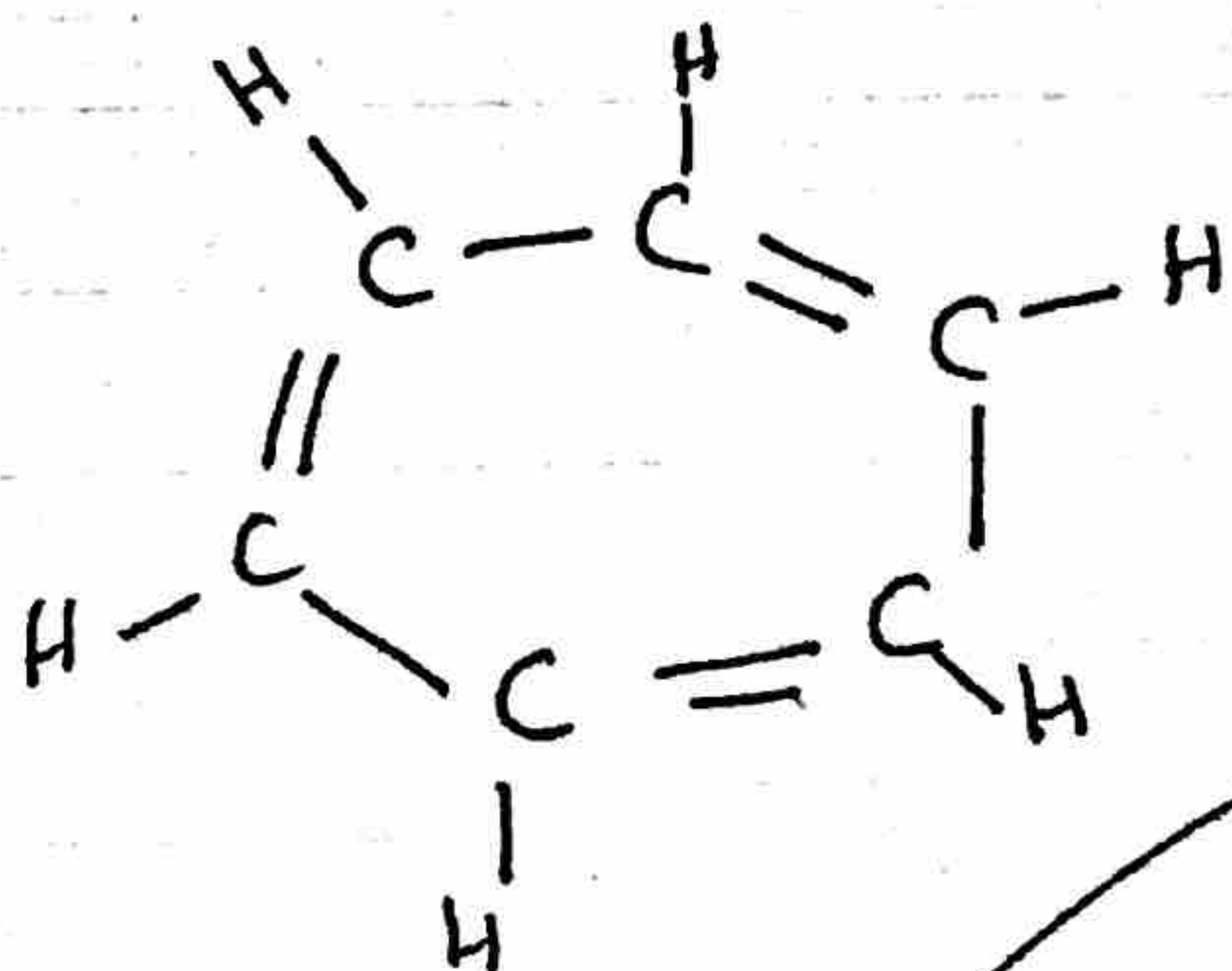
mesomeric formulas:

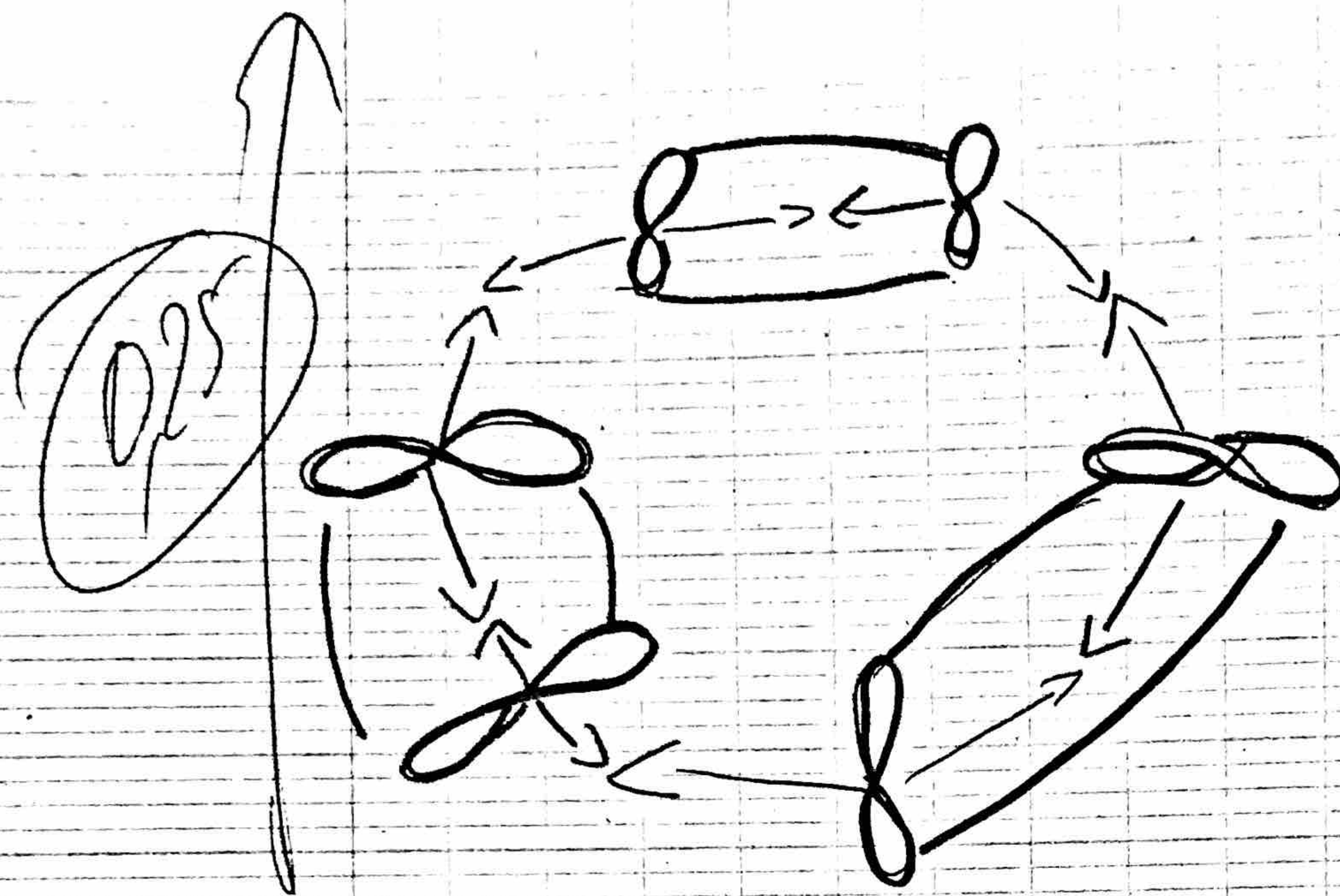


b) $AX_4 \rightarrow$ tetrahedral shape

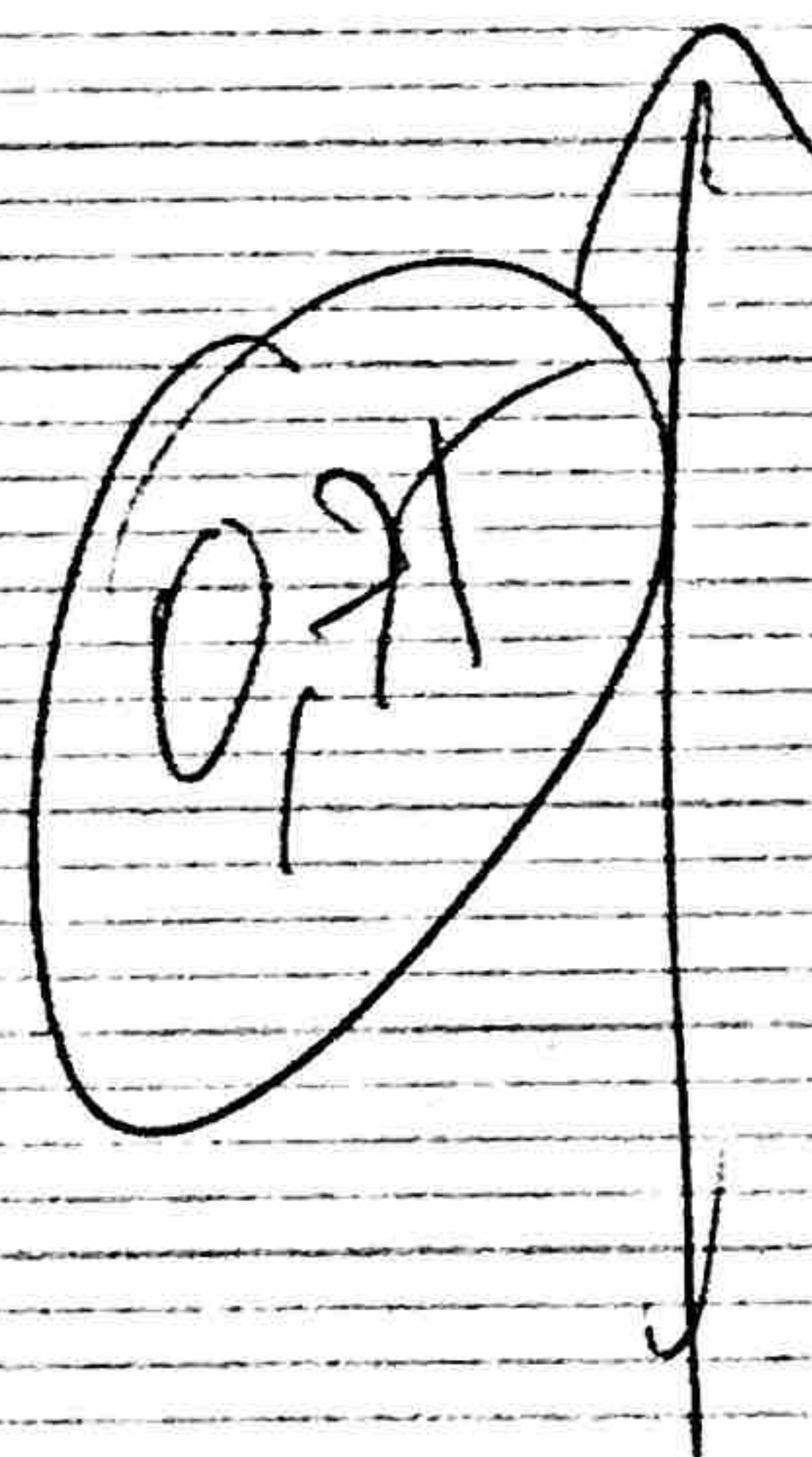
1 bonding angle will be bigger than the others, around the single bond with one O atom.

6) a) The hybridization state of carbon atoms in benzene is sp^2





in red : π bonds
in grey ($\rightarrow\leftarrow$) : σ bonds



b) σ and π bond (because double bond) but the π bond has a π characteristic

a) σ bond (because the carbon has a sp^3 hybridization state).

orbitals used: ~~2s~~ 2s and 2p ~~2p~~ ~~2p~~ ~~2p~~