PART II.b – Inorganic chemistry

Problem 1

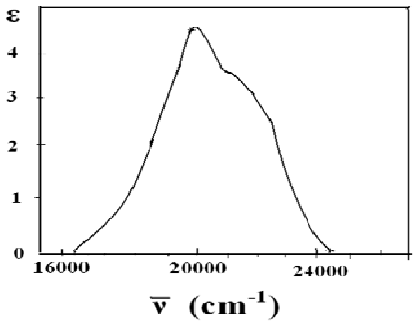
Given the imbalanced chemical equation summarizing the experimentally observed facts for the production of perchloric acid:

$NH_4ClO_4 + HNO_3 + HCl \rightarrow HClO_4 \cdot 2H_2O + N_2O + NO + NO_2 + Cl_2 + H_2O$

a) Balance the equation in such a way, that the sum of positive, integer coefficients would be minimal, i.e. with smallest possible whole number (including zero) coefficients.

b) Balance the equation in such a way, that it would satisfy experimentally estimated $HClO_4 \cdot 2H_2O$ to Cl_2 ratio of 9:1.

Problem 2



Complex compounds

This is an UV/VIS absorption spectra of $Co(H_2O)_6]^{2+}$ complex.

1. What color would you expect this complex to be? Why?
2. The peak in the spectra and the color are both caused by electronic transition between two 3d orbitals. From which d orbitals to which does the transition happen?
3. How would the answer to question 2 be different if the complex would be tetrahedral containing only four water molecules as ligands?
4. Why is there an energy difference in 3d orbital energies at all, although they all have the same energy in atomic Co.
5. As you can see in the spectra there is not a single peak but there are actually 2 peaks overlapping. Why is that so?

Problem 3

Crystal structure

The existence of element **X** was predicted D.I. Mendeleev. Under normal conditions element X is a soft silvery-white metal, which has a density of 9.196 g/cm^3 and metallic radius is 1,68 Å. In air it oxidized forming a yellow oxide **X**O_n, which has a density of 8.96 g/cm^3. When the structure of the metal and the oxide were examined using X-ray diffraction (Cu-K_α, λ = 154 pm) it appeared, that in both metal and oxide the atoms of **X** are arranged in one of the cubic packages. In case of the oxide the first lowest-angle reflection is observed at 2θ = 27.36°.

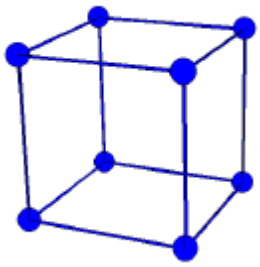
Hint: according to the Bragg's law:

$$n\lambda = 2d_{hkl}\sin\theta_{hkl},$$

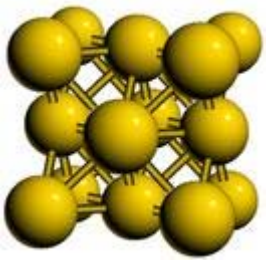
where $d_{hkl} = a/\sqrt{h^2+k^2+l^2}$.

For primitive cubic package all combinations of integers *h*, *k*, *l* are allowed. However for other packages, due to destructive interference taking place, only the combinations, in which all *h*, *k*, *l are either even, or odd (for body centered cubic package) or the sum of* *h*, *k*, *l* is an odd number (for face centered cubic package) lead to diffraction maxima.

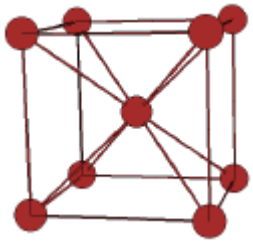
Calculate the molar mass of element **X** using for your calculations given crystal structures for the metal and its oxide.



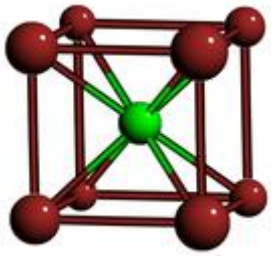
PC



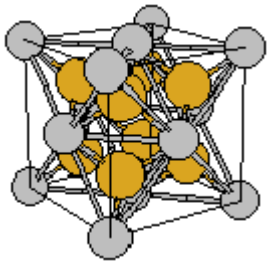
FCC



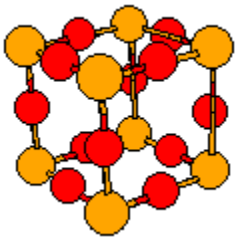
BCC



XO



XO_2



XO_3

Problem authors:

Vladislav Ivaništšev (4th year PhD student, University of Tartu, Institute of Chemistry)
Roberts Bluķis (2nd year BSc student, Cambridge University)
Vladislav Ivaništšev (4th year PhD student, University of Tartu, Institute of Chemistry)