CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

THIRD YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION SCIENCE

CHEM 313: COORDINATION CHEMISTRY

STREAMS: BSC & BED (SCI) **TIME: 2 HOURS**

DAY/DATE: MONDAY 06/04/2020 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS: Answer question ONE and any other TWO questions

QUESTION ONE (30 MARKS)

(a) (i) What are transition elements? [1 mark]

(ii) Explain why transition elements show tendency to form large number of complexes. [1.5 marks]

(iii) The ionic radii of M^{2+} transition metal ions in octahedral environment show a general decrease from left to right across the periodic table. However, there is a dip at vanadium and nickel. Explain this trend. [3 marks]

(b) (i) By giving reasons, write the expected and the observed electron configuration of copper $[z = 29]$ and chromium $[Z = 24]$ [3.5 marks]

(ii) Define the term exchange energy [1 mark]

(iii) The magnitude of exchange energy can be determined using the following equation

$$E^{x} = \sum_{2}^{N(N-1)} Kx$$

Define all the terms in this equation and calculate the relative exchange energy for Ni^{2+} and Cu^{2+} ions [6 marks]

(c) State the effective atomic number rule. How is it related to the eighteen electrons rule and what is its usefulness in coordination chemistry? [1.5 marks]

(d) For each of the following complexes

(i) $[Co(NH_3)_6]^{3+}$

(ii) $[MnCl_6]^{3-}$

Five the valence bond description of the bonding. Include orbital diagrams for the free metals ions and the metal ions in the complex. Indicate which hybrid orbitals the metals uses for bonding and specify the EAN number and unpaired electrons for the central metal. [5 marks]

(e) What is the difference between Werner's concept of a primary valence and a secondary valence and what terms do modern chemists use for these concepts? [2 marks]

(f) Distinguish between a Lewis base and a Lewis acid and explain why ammonia serves as a Lewis base but BH_3 molecule does not. [2 marks]

(g) Define any TWO of the following terms [2 marks]

(i) Constitutional isomers

(ii) Stereoisomers

(iii) Enantiomers

(iv) Racemic mixture

(h) Draw all the possible constitutional isomers for the compound $[\mathrm{Ru(NH_3)_5(NO_2)}]\mathrm{Cl}$. Label the isomers as linkage or ionization isomers [1.5 marks]

QUESTION TWO (20 MARKS]

(a) Name the following compounds [5 marks]

(i) $[\mathrm{Ni(NH_3)_6}]\mathrm{Br_2}$

(ii) $[\mathrm{Co(en)_2(H_2O)(CN)Cl_2}]$

(iii) $\mathrm{Na_2[MoOCl_4]}$

(iv) $\mathrm{(NH_4)_2[CuBr_4]}$

(v) $[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$

(b) Write the correct formula for each of the following compounds [5 marks]

(i) Hexaamminechromium(III) nitrate

(ii) Pentaaquabromomanganes(III) sulphate

(iii) Dichlorobis(ethylenedianine)platinum(iv)bromide

(iv) Bis (ethylenediamine) zinc(II)tetraiodomercurate (II)

(v) Potassium diaquatetrabromovanadate (III)

(c) Indicate the coordination number of the central metal, oxidation number of the metal, the number and the type of each donor atom in each of the following complexes. [10 marks]

(i) $K_3[V(C_2O_4)_3]$

(ii) $K_2[MoOCl_4]$

(iii) $[Mo(en)_2F_2]NO_3$

(iv) $[Pt(NH_3)Br_3]Br$

(v) $Na_2[CdCl_4]$

QUESTION THREE (20 MARKS)

(a) Polydentate ligands can vary in the number of coordination positions they occupy around a metal. In each of the following complexes, identify the polydentate ligand present and indicate the probable number of coordination position it occupies. Also name the ligand.

[7.5 marks]

(i) $[Co(NH_3)_4(o-phen)Cl_3]$

(ii) $[Cr(EDTA)H_2O]$

(iii) $[Hg(bipy)Br_2]$

(iv) $[Zn(en)_2](ClO_4)_2$

(v) $[Cr(C_2O_4)(H_2O)_4]Br$

(b) (i) What is meant by the term Chelate effect? [1 mark]

(ii) Explain thermodynamic factor that is responsible for the chelate effect [1 mark]

(iii) Why are polydentate ligands often called sequestering agents? [1 mark]

(c) Using a sketch, explain why the (dxy, dyz, dxz) and $(dx^2 - y^2, dz^2)$ groups of d orbitals have different energies in an octahedral complex. In your sketch show the definition of crystal field splitting energy and the barry centre. Which of the two groups has higher energy? [6 marks]

(d) (i) Weak field ligands tend to give high spin complexes but strong field ligands tend to give low spin complexes. Explain [1.5 marks]

(ii) The complex ion $[\mathrm{Fe(CN)_6}]^{3-}$ and $[\mathrm{Fe(NCN)_6}]^{3-}$ has one unpaired electron, whereas $[\mathrm{Fe(NCN)_6}]^{3}$ has five unpaired electrons. From these results, what can you conclude about whether each complex is high spin or low spin. Explain your answer. [2 marks]

QUESTION FOUR (20 MARKS)

(a) The complexes $[\mathrm{V(H_2O)_6}]^{3+}$ and $[\mathrm{VF_6}]^{3-}$ are both known

(i) Determine the electronic configuration of the central metal in both complexes [1 mark]

(ii) Draw the energy level diagram for V^{3+} octahedral complex and show the placement of electrons [2 marks]

(iii) Calculate in multiples of the CFSE of the central metal [1 mark]

(iv) Explain what gives rise to the colours of these complexes and by giving reasons indicate which of the above complexes would you expect to absorb light of higher energy. [3 marks]

(v) Discuss what properties of the ligand determine the size of splitting of the d and orbitals energies in an octahedral field such as those of the above complexes. [2 marks]

(d) For each of the following complexes, find the spin only magnetic moment and the ground state term symbol (indicating how they are affected by the ligand field) [9 marks]

(i) $[\mathrm{Cr(H_2O)_6}]^{3+}$

(ii) $[\mathrm{CoCl_4}]^{2-}$

(iii) $[Cu(H_2\,O)_6]^{2+}$

(c) What do you understand by the term nephelauxetic effect? Explain its effect on the racah parameter (B) in coordination compound [2 marks]
