JARAMOGI OGINGA ODINGA UNIVERSITY OF SCIENCE AND TECHNOLOGY
SCHOOL OF BIOLOGICAL AND PHYSICAL SCIENCES
UNIVERSITY EXAMINATION FOR THE DEGREE OF BACHELOR OF EDUCATION (SCIENCE)
4TH YEAR 1ST SEMESTER 2018/2019 ACADEMIC YEAR
MAIN
REGULAR

COURSE CODE: SCH 402

COURSE TITLE: INORGANIC REACTION MECHANISMS

EXAM VENUE: **STREAM: EDUCATION**

DATE: **EXAM SESSION:**

TIME: 2:00 HRS

Instructions:

1. **Answer question 1 (Compulsory) and ANY other 2 questions.**
2. **Candidates are advised not to write on the question paper.**
3. **Candidates must hand in their answer booklets to the invigilator while in the examination room.**

QUESTION ONE (30 MARKS) COMPULSORY

a) Determine the electronic configurations of the following transition elements and hence their ions. V(23); Cr (24); Fe (26); Cu (29) [10 mrks]

I) V^{4+}
II) Cr^{3+}
III) Fe^{+}
IV) Fe^{3+}
V) Cu^{+}

b) Distinguish between crystal-field theory and ligand-field theory as models of the electronic structure of the d-metal complexes. [4mks]

c) Determine the ligand -field stabilization energies of the following;

a) d^3 b) high-spin d^5 (c) high-spin d^6 (d) low-spin d^6 (e) d^9 [10mks]

d) a) The magnetic moment of a certain octahedral Co (II) complex is 4.0 μ_B. Determine is its d-electron configuration? [3mks]

b) the magnetic moment of the complex $[Mn(NCS)_6]^{4-}$ is 6.06 μ_B. determine its electronic configuration [3mks]

QUESTION TWO (20 MARKS)

a) i) Distinguish between a π-donor ligand and a π – acceptor ligand [2mks]

ii) By use of an illustration using π orbitals of ligand, describe the effect of a π-donor ligand and a π – acceptor ligand. [6mks]

b) The second-order rate constant for the reaction of I^- with trans-$[Pt(CH_3)Cl(PEt_3)_2]$ in methanol at 30 $^{\circ}C$ is 40 $dm^3\ mol^{-1}s^{-1}$. The corresponding reaction with N_3^- has k_2 = 7.0 $dm^3mol^{-1}s^{-1}$. Estimate S and C for the reaction given the n_{Pt} values of 5.42 and 3.58, respectively, for the two nucleophiles. [4mks]

c) The second-order rate constants for formation of $[VX(OH_2)_5]^+$ from $[V(OH_2)_6]^{2+}$ and X^- for X^- = Cl^-, NCS^-, and N_3^- are in the ratio 1:2:10. What do the data suggest about the rate determining step for the substitution reaction? [4mks]

d) The rate constants for the formation of $[CoX(NH_3)_5]^{2+}$ from $[Co(NH_3)_5OH_2]^{3+}$ for X=Cl^-, Br^-, N_3^-, and SCN^- differ by no more than a factor of two. Determine the mechanism of the substitution. [4mks]

QUESTION THREE (20 MARKS)

a) If a substitution process is associative, give a reason why it may be difficult to characterize an aqua ion as labile or inert? [2mks]

b) i) Distinguish between associative mechanism and dissociative mechanism in relation to substitution reaction. [2mks]

ii) the reaction s of $Ni(CO)_4$ in which phosphines or phosphites replace CO to give $Ni(CO)_3L$ all occur at the same rate regardless of which phosphine or phosphite is being used. With reason state whether the reaction is associative or dissociative. [2mks]

c) Predict the products of the following reactions;

a) $[Pt(PR_3)_4]^{2+} + 2Cl^-$ [2mks]
b) $PtCl_4]^{2-} + 2PR_3$ [2mks]
c) *cis*- $[Pt(NH_3)_2(py)_2]^{2+} + 2Cl^-$ [2mks]

d) a) Write out the inner-and outer-sphere pathways for reduction of azidopentaamminecobalt(III) ion with V^{3+} (aq) [4mks]

b) Based on the two pathways above, explain the experimental data that can be used to distinguish between them.
[4mks]

QUESTION 4 (20 MARKS)

a) How does each of the following modifications affect the rate of a square-planar complex substitution reaction?

i) Changing a *trans* ligand from H to Cl. [3mks]
ii) Changing the leaving group from Cl to I. [3mks]
iii) Adding a bulky substituent to a *cis* ligand [3mks]
iv) Increasing a positive charge on the complex. [3mks]

b) Octahedral complexes of metal centers with high oxidation numbers or of d metals of the second and third series are less labile than those of low oxidation number and d metals of the first series of the block. Explain this observation on the basis of a dissociative rate determining step.
[5mks]

c) The rate of loss of chlorobenzene, PhCl, from $[WCO)_4L(PhCl)]$ increases with increase with increase in the cone angle of L. how does this observation suggest about the mechanism? [3mks]