THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 4
FINAL EXAMINATION – 2013/2014
INORGANIC CHEMISTRY CMU2122/CME4122 AND CHU2123/CHE4123

17th June 2014 (Tuesday) Time Duration = 2 hours 1.00 p.m. – 3.00 p.m.

Avogadro constant, L	$= 6.023 \times 10^{23}$ mol^{-1}
Gas constant, R	$= 8.314$ J K^{-1} mol^{-1}
Planck's constant, h	$= 6.63 \times 10^{-34}$ J s
Velocity of light, c	$= 3 \times 10^{8}$ m s^{-1}
Mass of an electron	= 0.0005 a.m.u
Mass of a proton	= 1.0073 a.m.u.
Mass of a neutron	= 1.0089 a.m.u.
1 a.m.u.	$= 1.661 \times 10^{-27}$ kg
1 MeV	$= 1.6021 \times 10^{-13}$ J

Answer the COMPULSORY Question 1 (200 marks) AND three other Questions (100 marks each)

1.(a) Consider the complex $[FeCl_2(gly)(en)]$ (**A**).
(Atomic number of Fe is 26, $gly^- = H_2NCH_2COO^-$ and $en = H_2NCH_2CH_2NH_2$)
(i) What is the oxidation number of Fe in (**A**)?
(ii) What is the coordination number of Fe in (**A**)?
(iii) Determine the Effective Atomic Number (EAN) of Fe in (**A**).
(iv) Does it obey the EAN rule?
(v) Give the IUPAC name of (**A**).
(vi) Draw the three **geometrical** isomers of (**A**). (40 marks)

(b) A mole of *cis*-$[PtCl_2(NH_3)_2]$ reacts with one mole of sodium oxalate ($Na_2C_2O_4$) to give a **neutral square planar** complex (**B**). Draw the structure of (**B**). (10 marks)

(c) Complete the following nuclear equations:
(i) $^{210}_{84}Po \rightarrow {}^{206}_{82}Pb + ?$ (ii) $^{87}_{36}Kr \rightarrow {}^{87}_{37}Rb + ?$
(iii) $^{19}_{10}Ne \rightarrow {}^{19}_{9}F + ?$ (iv) $^{7}_{4}Be + ? \rightarrow {}^{7}_{3}Li$ (20 marks)

(d) Complete the following notations:

(i) ${}^{32}_{16}S(n,p)$? (ii) ${}^{11}_{5}B(?,n){}^{11}_{6}C$ (iii) ${}^{6}_{3}Li\ (n,?\ ){}^{3}_{1}H$

(15 marks)

(e) ${}^{131}I$ ($t_{1/2}$ = 8.1 days) is used in the treatment of thyroid disease. If a dose of NaI containing 10 μg of ${}^{131}I$ is administered to a patient, how long will it take for the amount of ${}^{131}I$ to decrease to 0.1 μg? (15 marks)

(f) Define a unit cell of a crystal and sketch the three types of cubic unit cells. (15 marks)

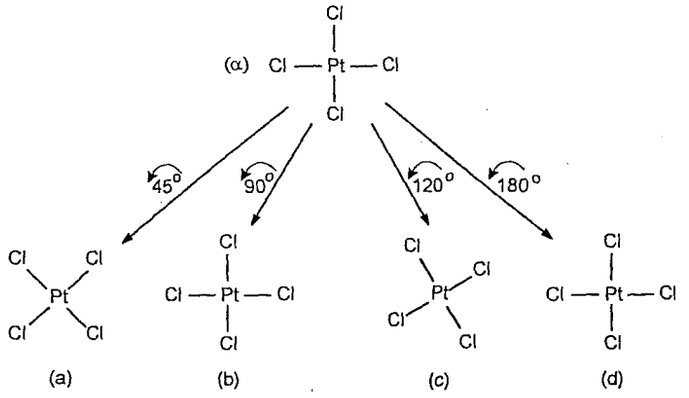
(g) A cubic unit cell contains a cobalt ion in the centre, potassium ions at the corners of the cell and fluoride ions in the centre of each face.

(i) What is the empirical formula of this compound?

(ii) What is the possible oxidation number of the cobalt ion? (15 marks)

(h) Write down the Bragg equation and identify all terms.
Calculate the wave-length of X-rays that would give a second order reflection from a crystal with an angle of 20.40^0 from the plane, with a spacing of 4.00 Å. Express your answer in nanometers. Is it possible to get a second order reflection with visible light? Explain your answer. (20 marks)

(i) $PtCl_4^{2-}$ is a square planar ion. Following figure indicates the resultant configurations when the $PtCl_4^{2-}$ ion in configuration (α) is rotated, counter clockwise, by 45^o, 90^o, 120^o and 180^o about the axis that passes through the Pt nucleus and perpendicular to the paper.



(i) Giving reasons identify configuration/s, out of (a), (b), (c) and (d), which is/are equivalent to the configuration (α). (12 marks)

(ii) Explain why the axis mentioned above is a symmetry axis (of rotation) of $PtCl_4^{2-}$. (12 marks)

(iii) Determine the order of the above mentioned axis of rotation. (10 marks)

(iv) Indicate the locations of the four vertical planes (of symmetry) of $PtCl_4^{2-}$. (12 marks)

(v) Indicate the location of the horizontal plane (of symmetry) of $PtCl_4^{2-}$. (04 marks)

2. (a) (i) Write the molecular formula of the salt pentaamminenitrochrominum(II) bromide (**C**).
(ii) Draw the structure of the **linkage** isomer of (**C**).
(iii) Draw the structure of the **ionization** isomer of (**C**). (20 marks)

(b) An **octahedral** complex (**D**) with the empirical formula $CoBr_3 \cdot 4NH_3 \cdot 2H_2O$ shows a molar conductivity typical for a 1:1 electrolyte (100 $m^2\Omega^{-1}mol^{-1}$).

(i) What is the molecular formula of (**D**)?

(ii) Draw the structures of the two isomers of (**D**). (20 marks)

(c) (i) State three assumptions of the Crystal Field Theory (CFT).
(ii) According to CFT what is the d-electron configuration

(number of t_{2g} and e_g electrons) of Fe in $[Fe(py)_6]^{3+}$?

(Assume pyridine (py) as a **strong neutral** ligand, Group number of Fe is 8).

(iii) Calculate the Crystal Field Stabilization Energy (**CFSE**) in kJ mol^{-1}

if $\Delta_o = 200$ kJ mol^{-1}.

(iv) Calculate the Total Stabilisation Energy (**TSE**) in kJ mol^{-1} if Pairing Energy = 100 kJ mol^{-1}.

(v) Arrange the following ligands (H_2O, Cl^-, CN^-, NH_3) in the order of increasing crystal field strength. (35 marks)

(d) Draw all **geometrical (03)** and **optical (02)** isomers of $[NiCl(CN)(H_2O)(NH_3)]$. (25 marks)

3. Answer **any two** Parts from **Parts A, B and C**.

Part A

(a) A **neutral mononuclear** 18e-complex (**X**), containing **zerovalent** nickel and CO, is formed when a nickel salt is reduced with carbon monoxide.

The Group number of Ni is 10.

(i) What is the molecular formula of (**X**)?

(ii) Predict the geometry of (**X**) and draw the structure of (**X**).

(iii) (**X**) is a diamagnetic compound. Using Valence Bond Theory, determine the hybridization of nickel in (**X**). (30 marks)

(b) (i) What is meant by "trans effect"?
(ii) Identify (**Y**) and (**Z**) if the *trans*-effect order is $CO > Br^- > H_2O$.
(α) The mono-substitution reaction of *trans*-$[NiBr_2(H_2O)_2]$ with CO gives (**Y**).

(β) The mono-substitution reaction of *cis*-$[Ni(H_2O)_2(CO)_2]^{2+}$ with Br^- gives (**Z**).

Note: indicate *cis-trans* isomerism and the charge of (**Y**) and (**Z**), if any. (20 marks)

Part B

(c) (i) What is the d-electron distribution (number of t_{2g} and e_g electrons) of an octahedral d^9 metal centre?

(ii) If it forms two elongated axial bonds, how many d-electrons are there in d_z^2 and $d_{x^2-y^2}$ orbitals?

(iii) Calculate the spin only magnetic moment (μ_s) in BM of this metal centre. (20 marks)

(d) Identify (**P**), (**Q**) and (**R**).

(i) $PdCl_2$ undergoes an **associative** reaction with **two** moles of NaCl to give a **square planar** complex anion (**P**).

(ii) $[HRh(CO)_4]$ undergoes an **dissociative** reaction to give a **neutral square planar** Rh(I) complex (**Q**) and a toxic gas molecule (**R**). (15 marks)

(e) Using Crystal Field Theory and spin rule, explain why $[Mn(H_2O)_6]^{2+}$ is off-white. Group number of Mn is 7. (15 marks)

Part C

(f) Account for the following observations in terms of atomic structure, intermolecular forces/ intramolecular forces.

(i) The melting points of the Group I elements decrease with increasing atomic number (Li to Cs) whereas the melting points of the Group 17 elements increase with increasing atomic number (F to I).

(ii) Germanium, tin, and lead form stable chlorides in which they exhibit oxidation states of +2 and +4 but the +4 state decreases in stability relative to the +2 state with increasing atomic number. (20 marks)

(g) A 0.800 g sample of a bronze medal was dissolved in hot concentrated nitric acid. After cooling and dilution, an excess of potassium iodide solution was added and the solution was made up to 250.0 cm^3. A 25.00 cm^3 portion of this solution required 12.20 cm^3 of 0.100 $moldm^{-3}$ sodium thiosulfate solution in the presence of starch indicator.

Write relevant balanced chemical equations for the processes.

Calculate the percentage by mass of copper in the bronze medal.

(Molar mass of Cu = 63.55 g mol^{-1}) (30 marks)

4. Answer **Parts A and B (CMU2122 students)** or **Parts A and C (CHU2123 students).**

Part A (common to all students)

(a)(i) What do you mean by 'nuclear fission'?

(ii) Calculate the energy released in MeV in the nuclear fission, $^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{143}_{60}Nd + {}^{90}_{40}Zr + 3{}^{1}_{0}n$, given the masses (amu or u) of $^{235}_{92}U$, $^{143}_{60}Nd$ and $^{90}_{40}Zr$ as 235.043915, 142.909779 and 89.904700 respectively. (20 marks)

(b)(i) $^{238}_{92}U$ decays by α and β emissions to finally give $^{206}_{82}Pb$. Calculate the number of α and β particles emitted.

(ii) A rock contains 0.257 mg of lead-206 for every milligram of uranium-238. The half-life for the decay of uranium-238 to lead-206 is 4.5×10^9 yr. How old is the rock? (30 marks)

Part B - for CMU2122 students only

(c)(i) Define the term 'activity' of a radionuclide.

(ii) Calculate the activity of 1 mg of pure cobalt-60 in Becquerel (Bq). The half- life of cobalt-60 is 5.27 years. (20 marks)

(d) Indicate, giving reasons, whether each of the following nuclides will be expected to be stable or not.

(i) ${}^{11}_{6}C$ (ii) ${}^{20}_{9}F$ (iii) ${}^{20}_{10}Ne$ (15 marks)

(e) Predict the mode of decay of the following radionuclides. Write nuclear equations for such decay processes.

(i) ${}^{15}_{8}O$ (ii) ${}^{23}_{10}Ne$ (15 marks)

Part C- for CHU2123 students only

(f) Calculate the average binding energy in MeV of ${}^{21}_{10}Ne$ which has a mass of 20.99384 amu. (20 marks)

(g) Briefly explain the method of radiocarbon dating. (20 marks)

(h) Benzoic acid is a strong acid in liquid ammonia. Explain. (10 marks)

5. (a).A solid A^+B^- has NaCl type close packed structure.

(i) If the anion has a radius of 250 pm, what would be the ideal radius for the cation?

(ii) Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^-?

Give reasons for your answer.

(Hint: The limiting radius ratio for an octahedral site is 0.414 whereas for a tetrahedral site it is 0.225). (30 marks)

(b). MnO has either NaCl type structure or the CsCl type structure. The length of a side of the MnO unit cell is 4.47×10^{-8} cm and the density of MnO is 5.28 g cm^{-3}.

Does MnO crystallize in the NaCl or the CsCl type structure?

(Atomic mass: Mn = 55, O = 16)

(40 marks)

(c) Identify the difference(s) between the following in relation to crystal defects.

(i) Interstitial impurity (ii) Substitutional impurity

In what way do the above mentioned defects differ from a self-interstitial defect?

In each case, comment on the size of the impurity atom.

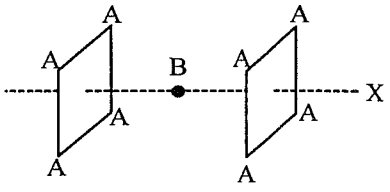
(30 marks)

6. Answer **any two** Parts from **Parts A, B and C.**

Part A

(a) Define the following as applied in studying symmetry of molecules.
(i) Vertical plane
(ii) Dihedral plane.
(iii) Improper axis of rotation (15 Marks)

(b) A student prepared an exotic ion BA_8^{n-}, where A and B are non-metallic and metallic atoms respectively. B is sandwiched in between the two square planar, A_4 rings, The confirmation of BA_8^{n-} in the eclipsed configuration is shown in the figure to the right. Axis X passes through the centres of the two A_4 rings and is perpendicular to the plane of each ring. B is on X, in the midpoint between the rings.



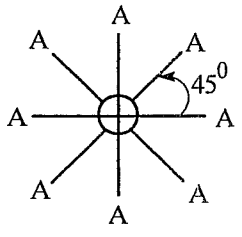
(i) Indicating the order, state where the principal axis of BA_8^{n-} is located.

(ii) How many C_2 axes does BA_8^{n-} has in its eclipsed confirmation?

(iii) Indicate the locations of all the above mentioned C_2 axes. (35 Marks)

Part B

(c) Newman projection formula of BA_8^{n-} described in Part A (b) above in its staggered confirmation is shown in the figure to the right.

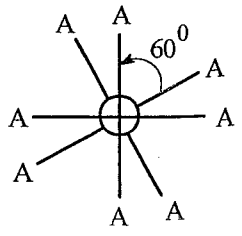


(i) Identify an improper axis of rotation of BA_8^{n-} in its staggered confirmation and deduce its order.

(ii) How many C_2 axes does BA_8^{n-} has in its staggered confirmation?

(iii) Indicate the locations of all the above mentioned C_2 axes. [You may copy the above Newman projection formula on to your answer script, draw the C_2 axes and describe their locations] (25 Marks)

(d) Newman projection formula of BA_8^{n-} in a neither eclipsed nor staggered confirmation is shown in the figure to the right.



(i) Is the axis identified as an improper axis in part (c)(i) above an improper axis of rotation of BA_8^{n-} in this neither eclipsed nor staggered confirmation shown in the figure?

(ii) How many C_2 axes does BA_8^{n-} has in this neither eclipsed nor staggered confirmation shown in the figure?

(iii) Indicate the locations of all the above mentioned C_2 axes. [You may copy the above Newman projection formula on to your answer script, draw the C_2 axes and describe their locations] (25 Marks)

Part C

(e) With clear diagrams explain the bonding in B_2H_6. Why is it referred to as an electron deficient compound? (15 marks)

(f) What is meant by the term "disproportionation"? Use standard electrode potentials for reactions to show that it is possible for $Cu^+(aq)$ to disproportionate in aqueous medium

$Cu^{2+}(aq) + e \rightarrow Cu^+(aq)$; $E^0 = +0.15$ V and

$Cu^+(aq) + e \rightarrow Cu(s)$; $E^0 = +0.52$ V (15 marks)

(g) Explain why

(i) It is difficult to separate Lanthanides from each other.

(ii) Graphite conducts electricity whereas diamond does not.

(20 marks)
