THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 4
FINAL EXAMINATION – 2011/2012
INORGANIC CHEMISTRY CMU2122/CME4122 & CHU2123/CHE4123

31st December 2011 (Saturday) Time Duration = 2 hours 1.00 – 3.00 p.m.

Avogadro constant, L	$= 6.023 \times 10^{23}$ mol^{-1}
Gas constant, R	$= 8.314$ 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) (i) Give the IUPAC name of $[Co(CN)Cl_2(CO)(H_2O)_2]$ (**A**).
(ii) Determine the Effective Atomic Number of Co in (**A**).
(Atomic number of Co = 27) (14 marks)

(b) Draw the three **geometrical** isomers of $[RuCl_2(NH_3)_2(en)]$.
(en = ethylenediammine) (18 marks)

(c) The substance with the composition $CrCl_3 \cdot 6H_2O$ shows hydrate **isomerism**.
(i) Give the chemical formulae of the **three** salts.
(ii) State a **chemical test** to distinguish these isomers. (18 marks)

(d) A part of the (4n+1) decay series is given below:

$$^{237}_{93}Np \xrightarrow{-\alpha} X \xrightarrow{x} {}^{233}_{92}U \xrightarrow{-\alpha} Y \xrightarrow{y} {}^{225}_{88}Ra \xrightarrow{-\beta^-} Z$$

Identify x, y and the atomic numbers and mass numbers of X, Y and Z.
(15 marks)

(e) Write complete nuclear equation for each of the following notations:

(i) ${}^{242}_{96}Cm(\alpha, n)$ (ii) ${}^{18}_{8}O(n, \beta^-)$ (iii) ${}^{96}_{42}Mo(\ , n)\ {}^{97}_{43}Tc$ (15 marks)

(f) Write balanced equations for the nuclear reactions described below:

(i) α decay by ${}^{235}_{92}U$

(ii) β^- decay by ${}^{234}_{91}Pa$

(iii) Electron capture by ${}^{40}_{19}K$

(iv) Positron emission by ${}^{11}_{6}C$ (20 marks)

(g) Ammonium salts are widely used as fertilizers. One standard method for the analysis of ammonium salts (except the chloride) is to react them in a solution with methanal, HCHO. This forms a neutral organic compound together with an acid which can be titrated with standard alkali. For ammonium nitrate the equation for this reaction is,

$$4\ NH_4NO_3 + 6\ HCHO \rightarrow (CH_2)_6N_4 + 4\ HNO_3 + 6\ H_2O$$

15.0 g of a fertiliser containing ammonium nitrate as the only ammonium salt was dissolved in water and the solution made up to 1.00 dm3 with pure water. 25.0 cm^3 portions of this solution were treated with saturated aqueous methanol and allowed to stand for a few minutes. The liberated nitric acid was then titrated with 0.100 mol dm^{-3} NaOH solution. The volume of NaOH solution used was 22.30 cm^3.

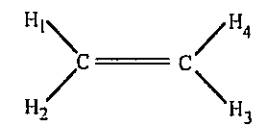
What percentage by mass of the fertilizer was ammonium nitrate? Show all steps in your calculation. (Relative atomic mass: N = 14 H = 1, O = 16) (30 marks)

(h) Explain how the ozone balance in the stratosphere may get disturbed by the presence of Chlorofluorocarbons in the atmosphere. What effects does it have on the environment? (20 marks)

(i) Copy the following configuration of an ethylene molecule on to your answer script and then draw

(i) an *identical* configuration to it.

(ii) an *equivalent* but <u>not</u> identical configuration to it.



(16 marks)

(j) Write down, in standard notation, all the distinct symmetry operation about the following symmetry elements in a molecule.

(i) C_5 (ii) S_5 (20 marks)

(k) Define a symmetry plane of a molecule. (14 marks)

2. (a) (i) What is the **molecular formula** of the **binuclear** compound diamminedichloro-μ-dichlorodiplatinum(II) (**B**).

(ii) (**B**) is a symmetrical molecule without a metal-metal bond. Draw the **structures** of the two isomers (*cis*- and *trans*-forms) of (**B**).

(iii) What is the coordination Number of each Pt in (**B**). (25 marks)

(b) (i) What is meant by "trans effect"?

(ii) Identity (**P**) and (**Q**) if the *trans*-effect order is $CO > Cl^- > NH_3$.

(α) The reaction of *cis*-$[PtCl_2(CO)_2]$ with NH_3 gives the complex (**P**).

(β) The reaction of *trans*-$[NiCl_2(NH_3)_2]$ with CO gives the complex (**Q**). (20 marks)

(c) (i) According to the **Crystal Field Theory** what is the d-electron configuration (number of t_{2g} and e_g electrons) of iron in $[FeBr_4]^{2-}$?

Br^- is a weak field ligand. (Group number of Fe is 8).

(ii) Calculate the Crystal Field Stabilization Energy (**CFSE**) in kJ mol^{-1} if $\Delta_t = 200$ kJ mol^{-1}.

(iii) Calculate the spin only magnetic moment (μ_s) of $[FeBr_4]^{2-}$? .

(iv) What is the hybridization of iron in $[FeBr_4]^{2-}$ according to the **valence bond theory**?

(40 marks)

(d) Two moles of the bidentate ligand, $H_2NCH_2CH_2NH_2$, (en) reacts with one mole of $PtCl_2$ to give a **square planar** salt (**R**) with a molar conductivity of 250 $m^2ohm^{-1}mol^{-1}$. Draw the structure of (**R**). (15 marks)

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

Part A

(a) A **neutral, four-coordinate, mononuclear** complex (**X**) of platinum(II) contains only NH_3 and chloride ligands. The Group number of Pt is 10.

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

(ii) **Draw** and **identify** the two isomers of (**X**).

(iii) (**X**) is a diamagnetic compound. According to VBT, what is the hybridization of platinum in (**X**)?

(iv) Give three **polymerization isomers** of (**X**). (50 marks)

Part B

(b) (i) What is meant by "chelate effect"?

(ii) The logβ values of $[Cu(NH_3)_4]^{2+}$ and $[Cu(en)_2]^{2+}$ are 12.7 and 19.7, respectively. Comment on the stability of above complexes. (20 marks)

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

(i) Electron deficient BH_3 undergoes an addition reaction with NaH to give the salt (**P**).

(ii) *fac*-$[RhMe_3(PPh_3)_3]$ undergoes an reductive elimination reaction to give an alkane (**Q**) and a **square planar** Rh(I) complex (**R**). (20 marks)

(d) An **octahedral** complex (**Z**) with the empirical formula $CrBr_3 \cdot 3H_2O \cdot 3NH_3$ shows a molar conductivity of 420 $m^2\ \Omega^{-1}\ mol^{-1}$. What is the molecular formula of (**Z**)? (10 marks)

Part C

(e) A 1.100 g sample of copper ore is dissolved and the Cu^{2+} (aq) is treated with excess KI. The liberated iodine requires 11.24 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ for its titration. What is the percent copper by mass in the ore? (20 marks)

(f) (i) What is the most notable change in the chemical character of elements down the group headed by carbon in the Periodic Table? Explain your answer by comparing the types of compounds formed by the first and the last member of the group.
(ii) Explain what is meant by "catenation" and "inert pair effect" by selecting appropriate elements in the carbon group. (30 marks)

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

Part A (common to all students)

(a) Calculate the energy released in MeV per fusion in the process,
$^2_1D + {}^1_1H \rightarrow {}^3_2He$, given that the atomic masses (a.m.u.) ^2_1D : 2.01410,

^1_1H : 1.007825 and ^3_2He : 3.01603. (25 marks)

(b) Radiocarbon dating makes use of the decay of carbon-14 which is a β-emitter ($t_{1/2}$ = 5730 year). Every gram of carbon in living tissue has a constant β-ray activity of 15.3 disintegrations per minute. If a piece of charcoal from a prehistoric campsite is found to emit 3.85 β- particles per minute per gram of carbon, estimate the age of the campsite. (25 marks)

Part B - for CMU2122 students only

(c) (i) Derive the relationship between the half- life, $t_{1/2}$ and decay constant, λ of a radionuclide.
(ii) Express the activity of 1 mg of pure ^{14}C in Becquerel. $t_{1/2} = 5730\,yr$ (25 marks)

(d) Each of the following nuclei is radioactive. Predict the type nuclear decay process for each nucleus.

(i) ^8_5B (ii) $^{20}_9F$ (iv) $^{226}_{88}Ra$

Write nuclear equations for such decay process. (25 marks)

Part C - for CHU2123 students only

(e) Calculate the binding energy per nucleon for the nucleus $^{58}_{28}Ni$ which has a mass of 57.9199 a.m.u. (20 marks)

(f) Identifying the radioisotopes, write a short account of their applications in medicine. (15 marks)

(g) Briefly discuss the properties of liquid ammonia (15 marks)

5. (a) The Atomic packing factor (APF) is defined as the fraction of solid sphere volume in a unit cell.

In a face centred cubic unit cell (FCC), the cell edge length and the radius of an atom is given as "a" and "R" respectively. Considering the fact that the atoms in a face centred cubic unit cell touch one another across a face diagonal length, show that FCC is an efficient way of packing with interstitial space of only 26%.

(Hint: If the atomic radius is R, the volume for a sphere is given by where $\frac{4}{3}\pi R^3$).

(40 marks)

(b) Niobium (Nb) has an atomic radius of 0.1430 nm and a density of 8.57 g cm^{-3}. Determine whether it has an FCC or BCC crystal structure. (30 marks)

(c) If cupric oxide (CuO) is exposed to reducing atmospheres at elevated temperatures some of the Cu^{2+} ions will become Cu^{+}.

(i) Under these conditions, name one crystalline defect that you would expect to form in order to maintain charge neutrality.

(ii) How many Cu^{+} ions are required for the creation of each defect? (30 marks)

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

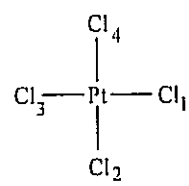
Part A

(a) Define the following as applied in studying symmetry of molecules.

(i) Principal axis of rotation.

(ii) Dihedral plane (20 Marks)

(b) Consider the following configuration of the planer ion, $PtCl_4^{2-}$, assumed to be on the plane of this paper.



(i) Locate all the axes of symmetry of $PtCl_4^{2-}$. Indicate their orders.

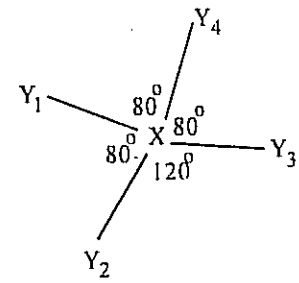
(ii) Giving reasons, state the order, n, of the principal axis of $PtCl_4^{2-}$?

(iii) Copy the configuration of $PtCl_4^{2-}$ shown above on to your answer script. Now draw the resulting configuration when a C_n^5 rotational operation about the principal axis is performed on the configuration you have drawn.

(30 marks)

Part B

(c) A student synthesized an exotic planar molecule with molecular formula XY_4. All four X–Y bond lengths are the same. However the bond angles are different as indicated. in a configuration of XY_4 in the following figure: three of the YXY bonds angles are equal to 80^o and the remaining YXY bond angle is 120^o.



(i) (α) Describe the location/s of all the rotational axis/axes of symmetry of the molecule.

(β) What is/are their order/s?

(γ) Copy the above configuration on your answer script and then draw the resultant configurations when the rotational symmetry operation with smallest angle about each of the above mentioned rotational axes is performed on this configuration.

(ii) Describe the location/s of all the symmetry plane/s of the molecule. Classify it/them as vertical plane or not.

(iii) For each symmetry plane of XY_4, indicate the number of distinct reflection symmetry operations that can be performed about it. (50 marks)

Part C

(d) NH_3OH^+ can act as an oxidizing agent in acidic solutions.

(i) Write a half equation to show the reduction of NH_3OH^+ to NH_4^+. Give the change in oxidation state of nitrogen.

(ii) If the E^0 value for the above reaction is found to be 1.35 V, state whether the oxidation of Fe^{2+} to Fe^{3+} occur in acidic solution with NH_3OH^+ as the oxidizing agent? Show all calculations.

$Fe^{3+} + e \rightarrow Fe^{2+}$ $E^0 = 0.77$ V; (30 marks)

(e) Use the information in the table to explain how the intermolecular forces vary from CO_2 to CS_2 to CSe_2.

Compound	State	Boiling point	Melting point
CSe_2	liquid	125 ^{0}C	- 45.5 ^{0}C
CS_2	liquid	46.5 ^{0}C	-111.6 ^{0}C

(20 marks)
