THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 4
FINAL EXAMINATION – 2014/2015
INORGANIC CHEMISTRY CMU2122/CME4122

11th May 2015 (Monday) 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

$$\ln x = 2.303 \log_{10} x$$

Answer the COMPULSORY Question 1 (200 marks) and THREE other Questions (100 marks each)

1. (a) Give the IUPAC name of $[FeBrCN(en)(NH_3)_2]$(**A**). (08 marks)
   (en = $H_2NCH_2CH_2NH_2$)

   (b) Consider the complex $[CrCl_2(en)_2]Cl$ (**B**).
   (Atomic number of Cr is 24)
   (i) What is the oxidation number of Cr in (**B**)?
   (ii) Determine the Effective Atomic Number (EAN) of Cr in (**B**).
   (iii) Does it obey the EAN rule?
   (iv) Draw the **structures** of the two **optical** isomers of (**B**). (27 marks)

   (c) (i) Write the relationship between stepwise formation constants (K_i) and overall formation constant β_6 for the reaction given below.
   (ii) The **logK_6** value for this reaction between Co^{2+} and ammine is **-0.6**. Calculate the overall formation constant β_6 if β_5 is $\mathbf{10^{5.9}}$.

   $$Co^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$$ (15 marks)

   (d) Write complete nuclear equations for the reactions described below:
   (i) Deuterium ($^{2}_{1}H$) and tritium ($^{3}_{1}H$) undergo fusion to give α particle.

(ii) The nuclide, $^{40}_{19}K$ undergoes radioactive decay in three ways: electron capture (98.2%), β^- emission (1.35%) and β^+ emission (0.49%). (20 marks)

(e) Write complete nuclear equation for each of the following notations:
(i) $^{6}_{3}Li\,(n,?)^{4}_{2}He$ (ii) $^{10}_{5}B(n,\alpha)?$ (iii) $^{96}_{42}Mo\ (?,\ n)^{97}_{43}Tc$ (15 marks)

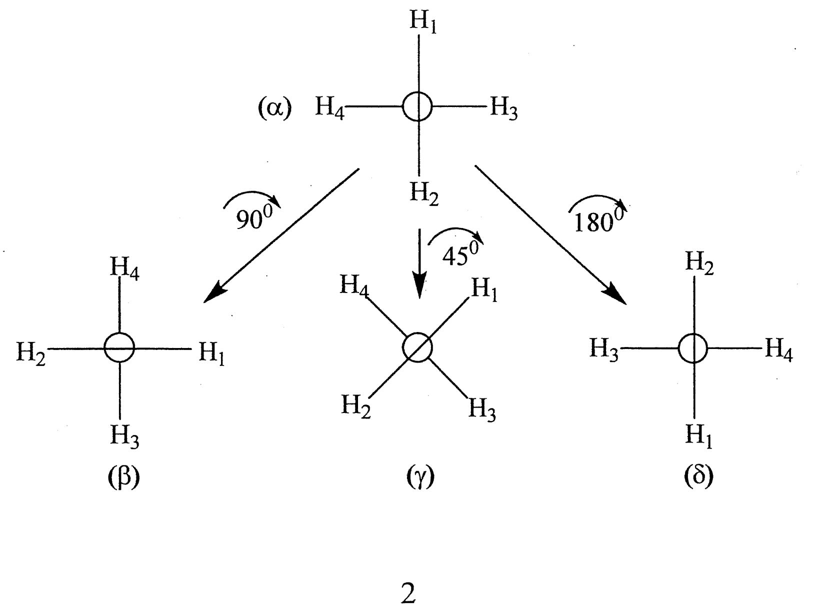
(f) At 12.00 noon, in a nuclear pharmacy, the activity of the radioactive indium-111 (^{111}In) was found to be 10 mCi. Calculate the activity of indium-111 in mCi at 1.30 p.m. the same day. The half life ($t_{1/2}$) of indium-111 is 2.83 days. (15 marks)

(g) The density of caesium is 1.87 g cm^{-3}.
(i) How many atoms of caesium are in 1.00 cm^3 of caesium?
(ii) If caesium atoms pack in BCC cells how many unit cells does 1.00 cm^3 of caesium contain? (molar mass of caesium = 132.9 g mol^{-1} (16 marks)

(h) State the species occupying the lattice points of the following crystalline substances. What type of bonding exists in each?
(i) Solid KF (ii) Solid CO_2
Will solid KF conduct electricity? Explain. (12 marks)

(i) Write down the Bragg equation and identify all terms in it.
X-rays from a molybdenum X-ray tube (λ = 71.0 pm) were diffracted at an angle of 7.23 degrees by a crystal of germanium. If the diffraction is of first-order. What is the interplanar spacing in germanium? (22 marks)

(j) Configuration (α) of a CH_4 (methane) molecule is shown in the Newman projection formula in the following diagram. Configurations (β), (γ) and (δ) are obtained by rotating (clockwise) the molecule in configuration (α) by 90^0, 45^0 and 180^0, respectively, about the axis in the plane of H_1CH_2 and passing through the carbon atom bisecting the H_1CH_2 angle.



(α) Giving reasons identify configuration/s, out of (β), (γ) and (δ), which is/are equivalent to the configuration (α). (12 marks)

(β) Explain why the axis mentioned above is a symmetry axis (of rotation) of CH_4. (10 marks)

(γ) Determine the order of the above mentioned axis of rotation. (06 marks)

(δ) Explain why the axis mentioned above is an improper axis of rotation of CH_4. (14 marks)

(ε) Determine the order of the improper axis mentioned above. (08 marks)

2. (a) Draw all **geometrical** isomers of $[Fe(CO)_2(en)(NH_3)]$ with the **square pyramidal** geometry. (en = $H_2NCH_2CH_2NH_2$) (20 marks)

(b) (i) Write the **molecular formula** of the complex Pentaaqua(thiocyanato)iron(II) chloride (**C**).
(ii) What are the **types of isomerism** shown by (**C**).
(iii) Draw the **structures** of all the isomers of (**C**). (25 marks)

(c) (i) List **three** factors which influence the crystal field splitting strength.
(ii) According to CFT what is the *d*-electron configuration (number of t_{2g} and e_g electrons) of Fe in $[FeBr_4]^{2-}$? (Assume bromide as a **weak field** ligand, Group number of Fe is 8).
(iii) Calculate the Crystal Field Stabilization Energy (**CFSE**) in kJ mol^{-1} if Δ_t = 180 kJ mol^{-1}.
(iv) Calculate the Total Stabilisation Energy (**TSE**) in kJ mol^{-1} if Pairing Energy = 200 kJ mol^{-1}.
(v) Calculate the **spin only magnetic moment** (μ_s) of $[FeBr_4]^{2-}$. (35 marks)

(d) The **octahedral** complex (**D**) with the empirical formula $CrBr_3 \cdot 3NH_3 \cdot 3H_2O$ **does not** conduct electricity.
(i) What is the molecular formula of (**D**)?
(ii) **Draw** and **identify** the **structures** of the two isomers of (**D**). (20 marks)

3. (a) A **neutral mononuclear** 16e-complex (**X**), contains a cobalt(I) centre which is coordinated **only** to chloride and carbon monoxide (CO) ligands. The Group number of cobalt is 9.
(i) What is the **molecular formula** of (**X**)?
(ii) Comment on the **geometry** of (**X**) and draw the **structure** of (**X**).
(iii) (**X**) is a diamagnetic compound. Using Valence Bond Theory, determine the hybridization of cobalt in (**X**). (25 marks)

(b) Identify **(K)**, **(L)**, **(M)** and **(N)**, if the *trans*-effect order is $Cl^- > NH_3$.

(i) Substitution of one chloride ligand of $[PtCl_4]^{2-}$ with NH_3 gives **(K)**, which reacts with another molecule of NH_3 to give **(L)**.

(ii) Substitution of one NH_3 ligand of $[Pt(NH_3)_4]^{2+}$ with a chloride gives **(M)**, which reacts with another molecule of chloride to give **(N)**.

Note: Indicate *cis-trans* isomerism and the charge of **(K)**, **(L)**, **(M)** and **(N)**, if any.

(20 marks)

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

$[MeRh(CO)_3]$ undergoes an **oxidative addition** reaction with Me–I to give a **neutral, octahedral** Rh(III) complex **(P)**. **(P)** undergoes a **reductive elimination** reaction to give an **alkane** **(Q)** and a **square planar** Rh(I) complex **(R)**. (15 marks)

(d) Deprotonation of glycine results in the formation of monoanionic bidentate ligand, $H_2NCH_2COO^- = gly^-$. Two equivalents of this anion react with one equivalent of $PtCl_2$ to give a **four-coordinate** Pt(II) complex **(Y)**.

(i) Write the **balanced equation** for the above reaction.

(ii) **Draw** and **identify** the **structures** of the two isomers of of **(Y)**. (20 marks)

(e) The neutral ligand (L) forms the **octahedral** complex ion $[CrL_6]^{2+}$. Using magnetic measurements how would you determine whether L is a strong field ligand or a weak field ligand? (Group number of Cr is 6). (20 marks)

4. (a) (i) Define term, 'binding energy' of a nuclide.

(ii) Calculate the average binding energy (in MeV) of beryllium-7, given the masses of the hydrogen atom and beryllium atom as 1.007825 a.m.u. and 7.016929 a.m.u. respectively.

(20 marks)

(b) (i) What do you mean by 'nuclear fusion'?

(ii) Calculate the energy released in MeV per fusion in the nuclear process:

$^{2}_{1}H + ^{3}_{2}He \rightarrow ^{4}_{2}He + ^{1}_{1}H$, given the masses (amu or u) of $^{2}_{1}H$, $^{3}_{2}He$ and $^{4}_{2}He$ as 2.014102, 3.016029 and 4.002602, respectively. (20 marks)

(c) (i) Define the terms 'half-life' and 'activity' of a radionuclide.

(ii) Carbon-11 is a positron emitter with a half life of 20.3 minutes; it is used in positron emission tomography (PET).

(α) Calculate the activity of 1 mg of pure carbon-11 in Becquerel (Bq).

(β) What percentage of initial number of carbon-11 atoms in a sample will remain after 81.2 minutes?

(30 marks)

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

(i) $^{8}_{5}B$ (ii) $^{16}_{8}O$ (iii) $^{22}_{9}F$

If the nuclide is not stable, predict its mode of decay. Write nuclear equation(s) for such decay process(es). (30 marks)

5. (a) A compound made up of elements 'A' and 'B' crystallizes in a cubic close packed structure. 'A' atoms are present in the corners as well as on the centre of faces whereas 'B' atoms are present on the centres of edges as well as body centre. What is the formula of the compound? (10 marks)

(b) Suppose we introduce the following point defect into the crystal. State what other changes in each structure might be necessary to maintain a charge balance?

(i) Fe^{2+} ions replace sodium ions in NaCl

(ii) Li^{+} ions substitute for Magnesium ions in MgO (20 marks)

(c) Draw 2-D sketches to show (i) Schottky defect (ii) Frenkel defect of a crystal AB. In each case state the effect of the defect that will have on the density of the crystal ? (20 marks)

(d) Atomic radii of Cu and Sn are 145 pm and 144 pm respectively. An alloy of Cu-Sn is formed by introducing tin atoms into a FCC copper crystal. The length of the unit cell of such an alloy was found to be 3.75×10^{-8} cm and the density as 8.772 g cm^{-3}.

(i) Draw a unit cell of FCC copper crystal.

(ii) Calculate the number of atoms belonging to a unit cell of FCC?

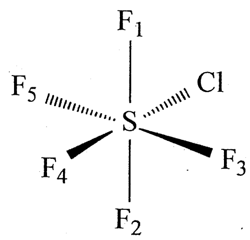
(iii) Justify the statement that "Sn is a substitutional impurity".

(iv) If the number of Sn atoms in the unit cell is X write an expression for the mass of Sn atoms present in the unit cell in terms of X.

(v) Write an expression for mass of Cu atoms present in the unit cell.

(vi) Calculate the average number of Sn atoms substituted in to the unit cell. (molar mass of Sn = 118.69 g mol^{-1}) (50 marks)

6. (a) Consider the molecule obtained by replacing one fluorine atom in a sulphur hexafluoride (SF_6) by a chlorine atom; see the figure. Assume that the bond angles and bond lengths in $SClF_5$ remain the same as in the original molecule, SF_6.



(i) Locate all the axis of rotation of $SClF_5$.

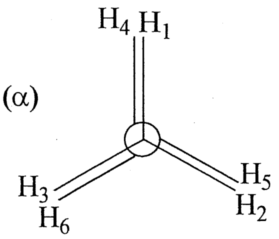
(ii) Deduce the order of each axis of rotation you have indicated in part (i) above.

(iii) Locate all the planes of symmetry of $SClF_5$.

(iv) Giving reasons, identify the classification of the planes you have indicated in part (iii) above as σ_v, σ_d or σ_h. (34 marks)

(b) Consider an ethane molecule in a staggered configuration, (α), which is shown in the Newman projection formula in the figure. Carbon-carbon bond axis is a C_3 axis of rotation of this molecule. It is also a S_3 axis as well. In standard notation the symmetry operation C_3^n indicates the performance of a C_3 operation n-times, one after the other, about a C_3 axis of rotation.

(α)



(i) By drawing appropriate Newman projection formulae, in representing the results of the performance of each C_3 operation (one at a time) on (α) about the carbon-carbon bond axis, show that $C_3^3 = E$, $C_3^4 = C_3$ and $C_3^6 = E$.

(ii) By drawing appropriate Newman projection formulae, in representing the results of the performance of each S_3 operation (one at a time) on (α) about the carbon-carbon bond axis, show that $S_3^3 \neq E$, $S_3^4 \neq S_3$ and $S_3^6 = E$. (34 marks)

(c) (i) Briefly explain why a molecule having more than one rotation axes of symmetry <u>cannot</u> have a dipole moment.

(ii) Briefly explain why the aromatic molecule shown below can have <u>only</u> two monochloro substituted products even though it has nine replaceable hydrogen atoms at positions 2, 3, 4, 6, 7, 8, 10, 11 and 12. (32 marks)