THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 4
FINAL EXAMINATION – 2010/2011
INORGANIC CHEMISTRY CMU2122/CME4122 AND CHU2123/CHE4123

29th December 2010 (Wednesday) 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	$= 8.314$ 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 $[FeF(Cl)(en)(NH_3)_2]$ (**A**).
(ii) Determine the Effective Atomic Number of Fe in (**A**).
(Atomic number of Fe = 26) (15 marks)

(b) Draw the three **geometrical** isomers of $[Fe(acac)Cl_2(NH_3)_2]$.
(acac = acetylacetonate ion) (18 marks)

(c) Identify the **isomerism** shown by $[CrCl(NH_3)_5]SO_4$ (**B**) and $[Cr(SO_4)(NH_3)_5]Cl$ (**C**).
State a **chemical test** to distinguish (**B**) from (**C**). (09 marks)

(d) The substance $CoCl_3 \cdot 5NH_3$ has a molar conductivity of 250 m^{2}ohm^{-1}mol^{-1}.
Write the molecular formula of it? (08 marks)

(e) A part of the (4n+2) decay series is given below:

$$^{238}_{92}U \xrightarrow{-\alpha} X \xrightarrow{?} {}^{234}_{91}Pa \xrightarrow{-\beta} Y \xrightarrow{?} {}^{230}_{90}Th \longrightarrow \longrightarrow \longrightarrow {}^{?}_{82}Pb$$

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

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

(i) ${}^{14}_{7}N(n,\ ){}^{14}_{6}C$ (ii) $(n,p)\ {}^{33}_{15}P$ (iii) ${}^{59}_{27}Co\ (n,\ )\ {}^{56}_{25}Mn$ (15 marks)

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

(i) Positron emission by ${}^{15}_{8}O$

(ii) α decay by ${}^{235}_{92}U$

(iii) Electron capture by ${}^{82}_{38}Sr$

(iv) Boron-10 is used in control rods for nuclear reactors because it can absorb neutrons and emit α particles.

(20 marks)

(h) Explain the variation of atomic radii from Cerium (Ce) to lutetium (Lu). How does this affect the separation of pure metal ions from a mixture of lanthanides? (15 marks)

(i) The molar enthalpies, ΔH_f^0(298 K) for HF(g), HCl(g), HBr(g) and HI(g) are respectively -285, -92.4, -36.2 and +25.9 kJ mol^{-1}. How would you expect (i) thermal stabilities (ii) acid strengths to vary within the group? (10 marks)

(j) An active metal can be used to reduce NO_3^- to NH_3 in basic solution according to the equation given below.

$$NO_3^- + 4\,Zn + 7\,OH^- + 6\,H_2O \rightarrow 4\,Zn(OH)_4^{2-} + NH_3(g)$$

The ammonia produced can be neutralized by passing the gas into excess HCl(aq). The unreacted HCl can then be titrated with standard NaOH. This way a quantitative estimation of Nitrate is possible.

In such an analysis a 25.00 cm^3 sample of a solution containing nitrate ion was treated according above equation. The liberated ammonia was passed into 50.00 cm^3 0.150 M HCl. The excess HCl required 32.10 cm^3 of 0.100 M NaOH for its titration. What was the $[NO_3^-]$ in the original sample? (25 marks)

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

(i) Symmetry plane

(ii) Vertical plane

(12 marks)

(l) Consider a molecule with the molecular formula XY_3.

(i)Draw and briefly describe (in order to clearly define) a structure each (using standard notation used in drawing structural formulae) which has the following symmetry properties.

(α) A structure with a C_3 axis and no other axes of rotation.

(β) A structure with a C_3 axis and some other axes of rotation. (20 marks)

(ii) Locate all the symmetry planes in each of the two structures you have drawn in part (i) above. (18 marks)

2. (a) (i) Give the IUPAC name of $[Co_2(\mu\text{-}Cl)_2(CO)_4]$ (**D**).

(ii) (**D**) is a symmetrical molecule without a metal-metal bond. Draw the **molecular structure** of (**D**).

(iii) What is the coordination Number of each Co in (**D**). (25 marks)

(b) Draw the structures of the **four geometrical** isomers with the **square pyramidal** geometry for $[FeBr(I)(NH_3)_3]$. (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 $[Fe(CN)_6]^{3-}$?

CN^- is a strong field ligand. (Atomic number of Fe is 26).

(ii) Calculate the Crystal Field Stabilisation Energy (**CFSE**) in kJ mol^{-1} if $\Delta_t = 300$ kJ mol^{-1}.

(iii) Calculate the Total Stabilisation Energy (**TSE**) in kJ mol^{-1} if Pairing Energy = 120 kJ mol^{-1}.

(iv) Calculate the spin only magnetic moment (μ_s) of $[Fe(CN)_6]^{3-}$. (40 marks)

(d) The terdentate ligand, $H_2NCH_2CH_2NHCH_2CH_2NH_2$, (dien) reacts with $PtCl_2$ to give a **square planar** complex (**A**) with a molar conductivity of 100 $m^2ohm^{-1}mol^{-1}$. Draw the structure of (**A**). (15 marks)

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

Part A

(a) How would you prepare *trans*-$[PtCl_2(NH_3)(CO)]$ from $[PtCl_4]^{2-}$ if the *trans*-effect order is $CO > Cl^- > NH_3$. (20 marks)

(b) (i) State three assumptions made in Valence Bond Theory.

(ii) Using Valence Bond Theory, predict the hybridization of Fe in the **diamagnetic** complex ion $[Fe(CN)_6]^{4-}$ (atomic number of Fe = 26) (20 marks)

(c) The $\log K_1$, $\log K_2$, $\log K_3$ and $\log K_4$ values for the reaction between Ni^{2+} and ammonia are 2.8, 2.2, 1.7 and 1.2 (K = stepwise formation constant). Calculate the overall formation constant β_4 for the following reaction.

$$Ni^{2+} + 4NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$$ (10 marks)

Part B

(d) (i) State the Jahn Teller Theorem.

(ii) $[CuBr_2(NH_3)_4]$ shows a distorted octahedral geometry with two elongated Cu–Br bonds, predict the *d*-electron distribution in the e_g level. (15 marks)

(e) (i) What are the characteristics of an **oxidative addition** reaction? Give an example.

(ii).Predict the product(s) of the following reactions using the hint given in the brackets..

(α) $[PtCl_4]^{2-} + CH_2 = CH_2 \rightarrow ? + ?$ (substitution)

(β) $[Mn(CH_3)(CO)_5] + CO \rightarrow ?$ (insertion) (15 marks)

(f) $[Mn(H_2O)_6]^{2+}$ is off-white but $[V(H_2O)_6]^{2+}$ is purple. Explain. (10 marks)

Part C

(g). Explain the following:

(i) Hydrogen is considered as a "greener" fuel than petrol.

(ii) Old oil paintings which contain lead carbonate as a white pigment may be darkened on exposure to air polluted with hydrogen sulphide which could be restored by treatment with hydrogen peroxide. (20 marks)

(h) A "Breathalyzer test" is used by the police to identify the drunken drivers. It involves blowing of air from the lungs through acidified potassium dichromate (VI) crystals to detect the presence of methanol in the breath. State what is observed when a positive test results. Give relevant chemical equations. (10 marks)

(i) The standard electrode potentials of the reactions involved in the first stage of rusting of iron are

$$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s) \qquad E^0 = -0.44\ V$$

$$O_2(g) + 2\,H_2O(l) + 4e \rightleftharpoons 4\,OH^-(aq) \qquad E^0 = 0.40\ V$$

(α) Write an overall equation for the first stage in the rusting of iron.

(β) Is this process a spontaneous one? Explain.

(γ) Explain how magnesium metal attached to a sheet of iron prevents it from rusting. (20 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 in the following fission reaction:

$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{142}_{56}Ba + {}^{91}_{36}Kr + 3\,{}^{1}_{0}n$, given the masses (amu or u) of $^{235}_{92}U$, $^{142}_{56}Ba$ and $^{91}_{36}Kr$ as 235.0439, 141.9164 and 90.9234 respectively. (15 marks)

(b) Briefly explain the method of radiocarbon dating. Comment on its limitation(s). (20 marks)

(c) One method of dating rocks is based on their $^{87}Sr/^{87}Rb$ ratio. ^{87}Rb is a β emitter with a half- life of 5×10^{11} y. A certain rock is found to have an $^{87}Sr/^{87}Rb$ mass ratio of 0.004 : 1.00. What is the age of the rock? (15 marks)

Part B - for CMU2122 students only

(d) (i) Define the term 'half- life' of a radionuclide.

(ii) Express the activity of 1 mg of pure ^{239}Pu ($t_{1/2}$ = 24000 y) in Becquerel. (25 marks)

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

(i) $^{11}_{6}C$ (ii) $^{120}_{50}Sn$ (iv) $^{22}_{9}F$

If any of the above nuclides is radioactive, predict the type nuclear decay process. Write nuclear equations for such decay process. (25 marks)

Part C- for CHU2123 students only

(f) Calculate the binding energy per nucleon in MeV for the nucleus $^{40}_{18}Ar$ which has a mass of 39.9525 amu. (15 marks)

(g) Write applications of radioisotopes in industry. (20 marks)

(h) (i) Acetic acid is not an acid in H_2SO_4. Explain
(ii) What is meant by an "Amphoteric solvent". Give two examples. (15 marks)

5. (a) Iron has bcc structure at room temperature. At temperatures between 912 ^{0}C and 1334 ^{0}C, the crystal structure changes to fcc.
(i) Draw the bcc and fcc unit cells.
(ii)Express the change in density from bcc to fcc as a percentage of the original density. (30 marks)

(b) Potassium chloride has a structure similar to sodium chloride. Density of potassium chloride is 1.98×10^3 kg m^{-3}. If the molecular mass is given as 74.6×10^{-3} kg mol^{-1}, calculate the length of the unit cell of potassium chloride in pm. (20 marks)

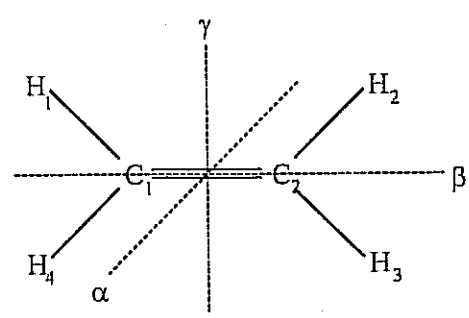
(c) (i) Show by means of sketches how Schotty defect in AgCl defers from a Frenkel defect.
(ii) The violet color of fluorite (CaF_2) is due to an imperfection in the crystal lattice. Describe the possible imperfection in the lattice. (30 marks)

(d) Potassium iodide has the same crystalline structure as NaCl, with d= 0.353 nm. A monochromatic X-ray beam shows a diffraction maximum when the angle is 7.60 ^{0}. Calculate the wavelength of X-rays (assume first order reflection). (20 marks)

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

Part A

(a) Three axes of rotation of an ethylene molecule, designated as α, β and γ, are shown in broken lines in the following diagram. β and γ are on the plane of the molecule and α is perpendicular to the plane of the molecule.



(i) State the order of each of the axes, α, β and γ.

(ii) Giving reasons identify the principal axis of an ethylene molecule.

(iii) Locate the inversion centre of the above molecule.

(iv) Draw the resultant configuration when an inversion operation is performed, on the configuration in the above diagram, about the centre of inversion of the molecule.

(v) By drawing the configuration of the molecule after each operation, show that an inversion symmetry operation of the molecule is equivalent to a single rotational symmetry operation about one of the above axes.

(vi) Show that an inversion symmetry operation of the molecule is equivalent to the composite operation of a rotational symmetry operation about one of the above axes and a rotational symmetry operation about another of the above axes. None of the above mentioned symmetry operations are the identity operation.

(50 marks)

Part B

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

(α) An improper rotation

(β) Improper rotational symmetry operation

(γ) Improper axis of rotation

(ii) (α) Draw a Newmann projection formula for the ethane molecule in its staggered configuration. Label the hydrogen nuclei as 1,2 3, ,6 as usual.

(β) State the location of the inversion centre of the molecule.

(γ) Using Newmann projection formula, draw the resultant configuration when an inversion operation is performed on the configuration you have drawn in part (α) above.

(δ) Using Newmann projection formulae show that the C-C bond axis of an ethane molecule in its staggered configuration is an improper axis of rotation of the molecule. Deduce its order.

(50 marks)

Part C

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

(10 marks)

(d) (i) Explain why disproportionation is a feature of the chemistry of many of the elements of the d-block but none of those in the s-block.

(ii) In the reaction,

$$IO_3^-(aq) + 5\,I^-(aq) + 6\,H^+(aq) \rightarrow 3\,I_2(s) + 3\,H_2O(l)$$

Iodine is simultaneously oxidized and reduced. Explain why it is not a disproportionation reaction.

(20 marks)

(e) Write the half ionic equations and the redox equation when an acidified solution of potassium dichromate(VI) is added to a solution of an iron(II) compound. A 0.204 g sample of steed was reacted with dilute sulphuric acid. The resultant solution required 27.4 cm^3 of 0.022 mol dm^{-3} potassium dichromate(VI) solution for complete reaction.
Calculate the percentage of ion in the sample.

(20 marks)
