00338

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 4
FINAL EXAMINATION – 2012/2013
INORGANIC CHEMISTRY CMU2122/CME4122 AND CHU2123/CHE4123

06th June 2013 (Thursday) 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 $[FeBr_2(CO)(NH_3)_3]$ (**A**).
(ii) Determine the Effective Atomic Number of Fe in (**A**).
(Atomic number of Fe = 26) (15 marks)

(b) **Draw** and **identify** the three **geometrical** isomers of $[FeBr_2(CO)(NH_3)_3]$ (**A**).
Does (**A**) show optical isomerism? (17 marks)

(c) Identify the isomerism shown by the substance with the composition $Fe{\cdot}SCN{\cdot}5NH_3$ (**B**). Draw the structures of the isomers.
Note: (**B**) has the octahedral geometry. (10 marks)

(d) The substance with the composition $FeCl_3{\cdot}5NH_3{\cdot}H_2O$ has a molar conductivity of 430 $m^2 ohm^{-1} mol^{-1}$ (*i.e.* 1:3 electrolyte). Write the molecular formula of it? (08 marks)

(e) A part of a decay series is given below:

$$^{235}_{92}U \xrightarrow{-\alpha} X \xrightarrow{-x} {}^{231}_{91}Pa \xrightarrow{-\alpha} Y \xrightarrow{-y} {}^{227}_{90}Th \longrightarrow \longrightarrow \longrightarrow {}^{207}_{82}Pb$$

Identify
(i) the type of decay series.
(ii) the atomic numbers and mass numbers of X and Y.
(iii) the unknown particles, x and y (25 marks)

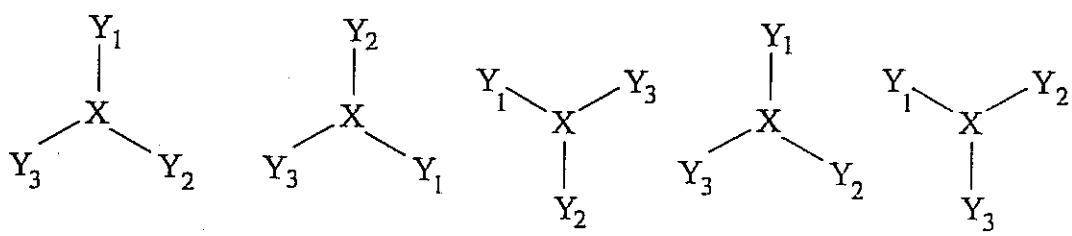
(f) Write complete nuclear equation for each of the following notations:
(i) ${}^{35}_{17}Cl(n,\ )^{35}_{16}S$ (ii) $(\alpha, p)^{26}_{12}Mg$ (10 marks)

(g) Write balanced equations for the nuclear reactions described below:
(i) α decay by ${}^{226}_{88}Ra$ (ii) β^- decay by ${}^{234}_{90}Th$
(iii) β^+ emission by ${}^{40}_{19}K$ (15 marks)

(h) In an experiment to determine the concentration of ethanol in an alcoholic beverage, 10.0 cm^3 of a sample of the beverage was diluted to 250.0 cm^3. 25.0 cm^3 portions of the diluted beverage were withdrawn. To each portion, 25.0 cm^3 of 0.156 M $K_2Cr_2O_7$(aq) and excess dilute H_2SO_4 were added. The mixtures obtained were allowed to stand at room temperature overnight. The excess $K_2Cr_2O_7$ in each mixture was then titrated against 0.118 M $(NH_4)_2Fe(SO_4)_2$(aq) with an appropriate indicator. The mean value was obtained as 12.20 cm^3.

(i) Write an equation for the reaction of ethanol with dichromate ions under acidic condition.
(ii) Calculate the concentration of ethanol, in mol dm^{-3}, in the alcoholic beverage. (50 marks)

(i) Five configurations, (a), (b), (c), (d) and (e), of a planar molecule, XY_3, are shown below.



(a) (b) (c) (d) (e)

The plane of the molecule coincides with the plane of the paper in the above diagrams. Three Y nuclei are labeled as 1, 2 and 3. All YXY bond anglers are equal to 120°.

(α) Giving reasons, identify the configurations which are
(i) identical to each other. (ii) equivalent to each other. (26 marks)

(β) Describe, fully, a single operation (in each case) that can bring about each of the following changes in configuration.
(i) (a) → (b) (ii) (a) → (e) (24 marks)

2 (a) (i) State the three assumptions made in Valence Bond Theory (VBT).
(ii) Using VBT, predict the hybridization of Fe in the **paramagnetic** complex ion $[Fe(H_2O)_6]^{2+}$ with $\mu_s = 4.9$ BM. (Group number of Fe = 8) (20 marks)

(b) Draw the structures of the **five geometrical** isomers with the **trigonal bipyramidal** geometry for $[FeBrCl_2(CO)_2]$. (20 marks)

(c)(i) According to **Crystal Field Theory** what is the d-electron configuration (number of t_{2g} and e_g electrons) of cobalt in $[Co(NH_3)_6]^{2+}$?
Consider NH_3 as a **strong** field ligand. (Group number of Co is 9).
(ii) Calculate the Crystal Field Stabilisation Energy (**CFSE**) in kJ mol^{-1} if $\Delta_o = 250$ 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 $[Co(NH_3)_6]^{2+}$. (40 marks)

(d) One mole of $PtCl_2$ reacts with **two** moles of $H_2NCH_2CH_2NH_2$ (en) to give a four coordinate platinum(II) complex (**C**). (**C**) gives **two** moles of AgCl (precipitate) with excess $AgNO_3$. Group number of Pt is 10.
(i) Write the molecular formula of (**C**).
(ii) Draw the structure of (**C**).
(iii) Comment on the geometry of (**C**). (20 marks)

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

Part A

(a) (i) Write the **chemical formula** of diamminedibromo(glycinato)chromium(III) (**D**). Glycinato = $H_2NCH_2COO^-$
(ii) If (**D**) is optically **inactive**, draw the two possible structures for (**D**). (20 marks)

(b) (i) Write the relationship between the overall formation constant β_4 and stepwise formation constants K_1, K_2, K_3 and K_4.
(ii) If the $\log K_1$, $\log K_2$, $\log K_3$ and $\log K_4$ values for the reaction between Co^{2+} and KCN are 6.0, 4.4, 3.9 and 2.4.
Calculate the overall formation constant β_4 for the following reaction.

$$Co^{2+} + 4\,KCN \rightleftharpoons K_2[Co(CN)_4] + 2\,K^+$$ (15 marks)

(c) In the presence of ammonia, $NiCl_2$ reacts with 2 equivalents of dimethylglyoxime (dmgH), MeC(=NOH)C(=NOH)Me, to give a red precipitate $[Ni(dmg)_2]$ (**E**). Draw the structure of (**E**).
Briefly, comment on geometrical/optical isomerism of (**E**). (15 marks)

Part B

(d) Ionic radius of $[V(H_2O)_6]^{2+}$ is less than $[Mn(H_2O)_6]^{2+}$, Explain.
Water is a weak field ligand. (Group Nos. of V & Mn are 5 & 7).
Hint: Think about t_{2g} and e_g values. (20 marks)

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

(ii) $[RhCl(PPh_3)_3]$ undergoes oxidative addition reaction with chlorine to give a Rh(III) complex (**P**). Write the molecular formula of (**P**).

(iii) $[Pt(NH_3)_4]^{2+}$ undergoes an **associative** substitution reaction with Cl^- to give an **intermediate** (**X**) which rapidly looses a ligand (**Y**) to form a square planar complex cation (**Z**). Identify (**X**), (**Y**) and (**Z**).
Note: clearly indicate the charge of (**X**), (**Y**) and (**Z**), if any. (30 marks)

Part C

(f) Explain why,
(i) $MgCO_3$ is more easily decomposed by heat than $BaCO_3$.
(ii) A "Barium meal" can be used in medical diagnosis.
(iii) Phosphorous and Arsenic can show a covalency of 5, but nitrogen cannot. (24 marks)

(g) Using your knowledge on oxidation states explain how you could classify the reaction $ClO^-(aq) \rightarrow Cl^- + ClO_3^-$ as a disproportionation reaction. (10 marks)

(h) Use VSEPR theory to predict the shapes of interhalogen compounds, IF_3 and BrF_5. (16 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 nuclear fusion:
$^3_1H + {}^2_1H \rightarrow {}^1_0n + {}^4_2He$ given the masses (amu or u) of ^3_1H, ^2_1H and ^4_2He as 3.0160492, 2.0141017 and 4.0026033 respectively. (15 marks)

(b) If we start with 1.000 g of strontium-90, 0.953 g will remain after 2 years. What is the half-life of strontium-90? (15 marks)

(c)(i) Briefly explain the principles behind the method of radiocarbon dating.
(ii) Carbon-14 is a β emitter with a half- life of 5730 years; each gram of carbon in living tissue has a constant β ray activity of 15.3 disintegration per minute (dpm). If a piece of charcoal from a prehistoric site is found to emit 1.53 β particles per minute per gram of carbon.
Calculate the age of the campsite. (20 marks)

Part B - for CMU2122 students only

(d) (i) Define the term 'radioactivity' of a nuclide.
(ii) Calculate the activity of 1 μg of pure carbon-14 in Becquerel (Bq).
Half- life of carbon-14 is 5730 years. (20 marks)

(e) Indicate, giving reasons, whether each of the following nuclides will be expected to be stable or not.
(i) ^4_2He (ii) $^{16}_8O$ (iii) $^{18}_9F$ (15 marks)

(f) Predict the mode of decay of the following radionuclides.
Write nuclear equations for such decay processes.
(i) ^8_5B (ii) $^{22}_9F$ (15 marks)

Part C- for CHU2123 students only

(g) Calculate the binding energy per nucleon in MeV for an α particle (^4_2He) which has a mass of 4.002603 amu. (20 marks)

(h) Using examples, write a brief description of applications of radioisotopes in medicine. (20 marks)

(i) Acetic acid is a strong acid in liquid ammonia. Explain. (10 marks)

5.(a). Potassium crystallizes in a body centred cubic lattice.
Molar mass of potassium = 39 g mol^{-1}.
(i) Draw the unit cell of a body centred cubic lattice.
(ii) Do all atoms indicated in your diagram belong to the unit cell? Give reasons for your answer.
(iii) Calculate the approximate number of unit cells in 4.0 g of potassium. (25 marks)

(b) Stainless steel contains selected transition metals added to iron (atomic radius = 125 pm) to improve its properties. The composition of stainless steel and the atomic radii of the elements are given in the table below.

Element	Atomic radius/pm	% by mass in stainless steel
Cr	128	15% - 20%
Mn	127	1% -5%
Ni	124	5% -10%
C	77	1%
P	106	0.05%
Si	111	1% - 3%

Considering composition of stainless steel and the table of atomic radii of elements given, predict (**with reasons**) which type of impurity is represented by each element that are present in at least 0.05 % by mass. (50 marks)

(c) Iron metal has a body-centered cubic (bcc) unit cell with an edge length of 286.65 pm. Molar mass of Fe = 55.8 g mol^{-1}. Use the given data to calculate the density of iron. (25 marks)

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

Part A

(a) Define the following as applied in studying symmetry in molecules.
(i) Symmetry plane (ii) Vertical symmetry plane
(iii) Improper axis of rotation (18 marks)

(b) Consider a methane molecule (CH_4).
(i) Describe the location of a C_2 axis in the molecule.
(ii) How many such C_2 axes are present in a CH_4 molecule?

(iii) Using standard notation, draw a Neumann projection formula of the molecule on the plane perpendicular to the C_2 axis you have described above and passing through the carbon nucleus.

(iv) Using appropriate Neumann projection formulae in representing the resultant configurations when symmetry operations are performed, show that the C_2 axis you have described above is a S_4 axis of the molecule.

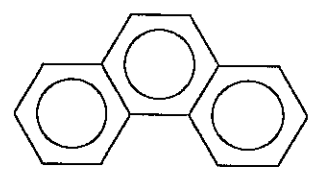
(32 marks)

Part B

(c) (i) Using appropriate diagrams, show that the dipole moment of a molecule with an axis of symmetry must lie along that axis.

(ii) Using symmetry arguments show that a methane molecule (CH_4) cannot have a dipole moment. (25 marks)

(d) Consider the following aromatic hydrocarbon molecule (phenanthrene).



Based on symmetry arguments (write down your arguments) deduce the number of different monochloro phenanthrenes. (16 marks)

(e) Indicate the molecule(s), which has a centre of symmetry out of the following. Indicate the location of the centre of symmetry in each molecule.

(a) C_6H_6 (b) *cis*-CHCl=CHCl (c) *trans*-CHCl=CHCl (d) SF_6 (09 marks)

Part C

(f) (i) Using appropriate calculations select the best source of Nitrogen out of sodium nitrate, ammonium nitrate and ammonium sulphate to be used as a fertilizer. (Relative atomic masses: Na = 23, N = 14, O = 16, H = 1, S = 32)

(ii) Mention one environmental problem which may be associated with large scale use of fertilizer. (20 marks)

(g) Predict the products of each of the following by writing a balanced chemical equation.

(i) $Cl_2(aq) + Br^-(aq) \rightarrow$ (ii) $Li(s) + N_2(g) \rightarrow$

(iii) $Fe_2O_3 + C \rightarrow$ (15 marks)

(h) How do the fullerenes differ from the other two allotropic forms of carbon? What specific structural features of graphite enables it to behave as

(i) an electrical conductor (ii) a lubricant (15marks)
