CH-105 Inorganic Chemistry

Roll No.:	Division:	batch:
Name:	Signature:	

Saturday, Sept. 09, 2017   **Duration: 2hrs**   **Marks: 25**   **Weightage: 50%**

Instructions

1. **NO** mobile phones, calculator or any electronic gadgets are allowed during the exam.
2. Use **PEN** even for drawing structures and plots. Please do not use pencil.
3. Please write your answers **in the space provided** below each question.

Please do not write anything in the boxes below

1	2	4	4	5	6	7	8	9	10

11	12	13	14	15	16	17	18	19	TOTAL

Q01. Calculate the effective nuclear charge (Z_{eff}) for (i) 3p electron of Aluminum; (ii) 3d electron of Molybdenum. *(1 Mark)*

Ans:

$Z_{eff} = Z - \sigma$

For Al E.C: $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$;   For Mo = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^5\,5s^1$

$Z_{eff}\,(Al) = 13 - (2 \times 0.35 + 8 \times 0.85 + 2 \times 1.0)$ $= 13 - 9.5$ $= 3.5$	Electrons in any group higher in this sequence than the electron under consideration contribute nothing to σ ; ,hence $Z_{eff}\,(Mo) = 42 - (17 \times 0.35 + 10 \times 1.0)$ $= 42 - 15.95$ $= 26.05$

Q02. Identify the period 2 element using the following ionization energy data: $IE_1 = 801$; $IE_2 = 2426$; $IE_3 = 3660$ and $IE_4 = 25018$kJ/mol. Write its electronic configuration and also explain why $IE_4 >>> IE_3$. *(1 Mark)*

Ans:

There are three ionization potential which are smaller than the fourth one suggests that there are three electrons (which can be easily removed) in the valence cell. Three valence electron containing group 2 element is boron and its electronic configuration is

B: $1s^2\,2s^2\,2p^1$ (0.5 Mark)

IE_4 is exceptionally high value because we are trying to remove an electron from an inert gas configuration (He: $1S^2$). Because of this the $IE_4 >>> IE_3$. ((0.5 Mark))

Q03. Place atoms Na, K, Mg, Ca and Alin the increasing order of their size:*(1 Mark)*

Ans: Al   < Mg < Na < Ca < K(for correct order 1 Mark)

(If first and last element order is correct offer 0.5 Mark)

Q04. (i) Which of the element (or elements) exist as diatomic gas at room temperature and pressure: neon, lithium, oxygen, bromine, carbon. *(0.5 Mark)*

Ans: O_2(0.5 Mark); If Br_2 included in the list still award mark

(**Note:** If only Br_2 given no marks awarded)

(ii) Which one of the following elements is most likely (highly preferred) to form a -2 ion: Ca, Fe, C, S & Br. *(0.5 Mark)*

Ans: Sulfur   (0.5 Mark)

Q05.   Write the expected product(s) (use HSAB), in the following reactions.*(1 Mark)*

(i) BaI_2 +2NaF →No reaction   (0.5 Mark)

(ii) $[Cr(CO)_3(NH_3)_3]$ + 3 PH_3→$[Cr(CO)_3(PH_3)_3]$ + $3NH_3$ (0.5 Mark)

Q06.   To a solution containing amixture of Co^{3+} and Pb^{2+} salts, sodium thiocyanate (NaSCN) solution is added. Identify the stable (predominant) product(s) that would form in the reaction mixture and show the mode of ligation (the binding mode) in each case. *(1 Mark)*

Ans:
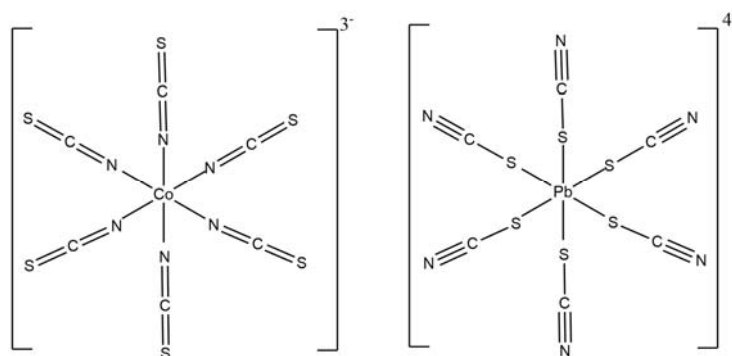
If structure is wrong, but connectivity is correct still marks are given.

Q07.   Pure titanium can be made from TiI_4 but not from TiF_4. Explain why?*(1 Mark)*

Ans:

 Titanium is hard acid and iodine is soft base. (0.5 Mark)

Hence the stability of TiI_4 is lower than TiF_4. (0.5 Mark)

Q08. Among CuO and Ag_2O, which one can be decomposed at lower temperature and why? *(1 Mark)*

Ans: Ag_2O (0.5 Mark)

Ag^+ is softer than Cu^{2+} and O^{2-} is hard base hence Ag_2O can be decomposed at lower temperature. (0.5 Mark).

Or alternate answer based on Ellingham diagram can also be accepted.

Q09. For the given transformations, (i) C → CO, (ii) C → CO_2 & (iii) CO → CO_2, draw schematic Ellingham diagram (all in one plot) and comment on the signs of the slopes and on the point of intersection of the corresponding curves. *(2.5 Marks)*

Ans:
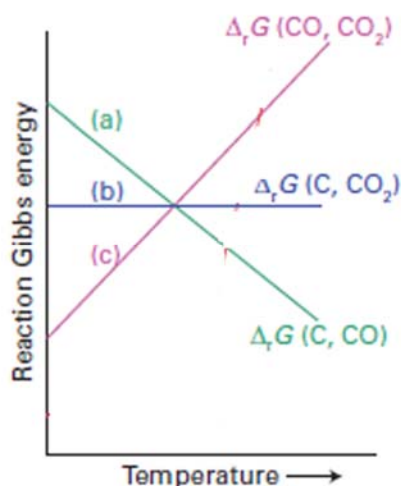
At 720°C all the curve will intersect. Below 720° C, CO_2 formation will be favourable and above 720°C, carbon monooxide formation is favourable.

(For each correct curve 0.5 Mark, labelling axes 0.5 Mark and rationale for intersection 0.5 Mark)

If the point of intersection is not common for all the three curves, 0.5 marks been reduced.

Q10. Reaction of Cr^{3+} and Mo^{3+} with cyanide yielded complexes containing six and seven ligands, respectively. (a) Explain why the coordination number is six in case of Cr^{3+} and seven in case of Mo^{3+}. (b) Draw all the possible geometries for both complexes.

(2 Mark)

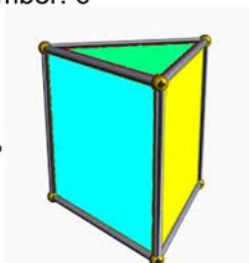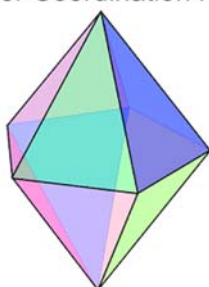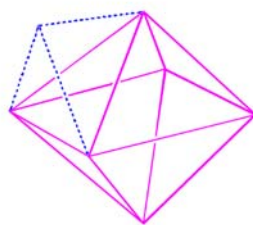For Coordination number: 6

Ans:
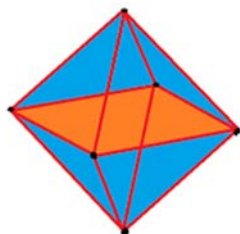
Octahedral   Trigonal prism

For Coordination number: 7

Pentagonal   Capped octahedron
bipyramidal

Since the size of Molybdenum ion is larger than Chromium ion, it can accommodate more ligand ie larger coordination number or an equivalent argument on the basis of possible hybridizations. (0.5 Marks)

For four correct isomers 1.5 marks awarded; For wrong structure/isomer proportionately marks have been reduced.

Q11. In a divalent octahedral complex (X), each H_2O contributes 2000 cm^{-1} to the Δ_o and each cyanide ligand contributes 5,500 cm^{-1} to Δ_o. The pairing energy for this ion is 18000 cm^{-1}. Identify the octahedral complex (X) with lowest number of cyanide ligands to be incorporated so that the resultant complex is low spin. Work out the formula and draw the possible structure(s) for X. *(2.5 Marks)*

Ans:

Pairing energy for this complex given 18000 cm^{-1}. Hence in order to get a low spin complex, Δ_0 must be larger than the pairing energy.
Its also given the low spin octahedral complex should have lowest number of –CN ligand.
Considering this fact, a combination of one cyanide and 5 water molecule will contribute only (5500+10000 = 15500 cm^{-1}) a high spin complex.
At the same time, 2 cyanide and 4 water molecule case, the resultant Δ_0 will be (11000+8000) 19000 cm^{-1}. Since the Δ_0 for this combination is greater than the pairing energy this will form low spin with the lowest number of cyanide. So the formula will be $[M^{II}(CN)_2(H_2O)_4]$. The cyanide will neutralize the two positive charge on the metal as well.

For working out the composition (1 Mark); Writing correct structure of the formula (1 Mark); For correct isomers (0.5 Mark)

Q12. 'Y' is a complex of nickel possessing water and ammonia as ligands, but not inequal in number. Complex 'Y' upon treatment with $AgNO_3$ gives two equivalents of AgCl; it gives a measured magnetic moment of 2.9 BM. Give the formula of the complex and draw its both theisomeric structures. *(2 Marks)*

Ans:

i) Its given that the complex Y gives two equ. Of AgCl upon reaction with AgNO3. Hence this suggest that there are two chloride ligand is outside the coordination sphere.

ii) Since the water and ammonia ligands are neutral and two halides outside the coordination sphere implies that the metal oxidation state should be +2.

iii) Complex Y shows mag. Moment value of 2.9 BM corresponds to an octahedral (spin only value) complex.

iv) AS it is stated, water and NH3 should not be equal in number, the only combination which will give octahedral complex, at the same time which will have two isomer formation for the proposed formula.

$[Ni(H_2O)_4(NH_3)_2]Cl_2$ or $[Ni(H_2O)_2(NH_3)_4]Cl_2$ (1.0 Mark)

Cis-isomer   trans-isomer
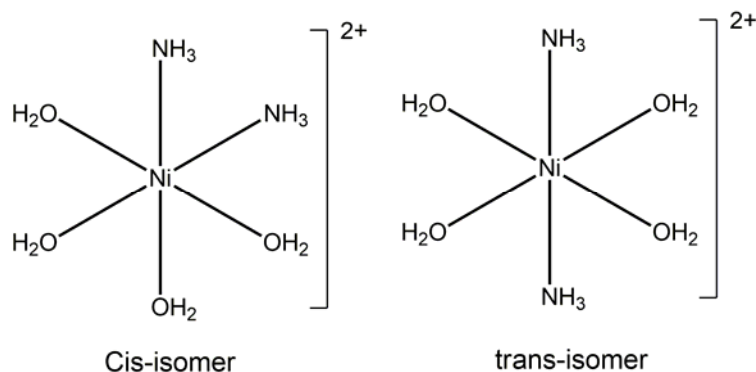
Isomers (1.0 Mark)

Incorrect charges on coordination sphere/ for not showing adequeate number of isomers attract penalty of 0.5 mark, each.

Q13. Four metal carbonyls are given: $[Fe(CO)_5]$, $[Mn(CO)_5]^-$, $[Co(CO)_5]^+$, $[Cr(CO)_5]^{2-}$. Arrange these complexes in the order of increasing strength of M-C bond. *(1 Mark)*

Ans: $[Co(CO)_5]^+$ < $[Fe(CO)_5]$ < $[Mn(CO)_5]^-$ < $[Cr(CO)_5]^{2-}$

(Either 1 or 0 Mark)

Q14. Work out and show whether $CuFe_2O_4$ is spinel or inverse spinel? *(1 Mark)*

Ans:

Cu^{2+} in Oh: $t_{2g}^6 e_g^3 = -0.6\ (\Delta_0)$

Fe^{3+} in Oh: $t_{2g}^3 e_g^2 = 0$

Since the CFSE gain in inverse spinel is more than the spinel structure, $CuFe_2O_4$ will prefer inverse spinel structure.

(Writing only inverse spinel (0.5 Mark)).

Q15. In the structures, **A** = $[Zn(H_2O)_6]^{2+}$ &**B** = $[Cu(H_2O)_6]^{2+}$, the Zn-O = 2.1 Å (all six bonds); and Cu-O = 2.3 Å (two bonds) & Cu-O = 1.98 Å (four bonds). Explain why?

What happens when large pressure is applied along the z-direction in both cases, explain your answer withsuitable orbital splitting diagram? *(2 Marks)*

Ans: Due to d^{10} configuration of Zn^{2+}, there is no distortion while in case of B, due to electronically degenerate level results in Jahn-Teller elongation hence, two bonds are longer than other four bonds. (1.0 Mark)
Application of Pressure leads to compression of orbital (0.5 Mark)
For A, applying pressure will have no influence on the orbital splitting. While applying pressure along Z-axis in B, leads to Jahn-Teller compression geometry.
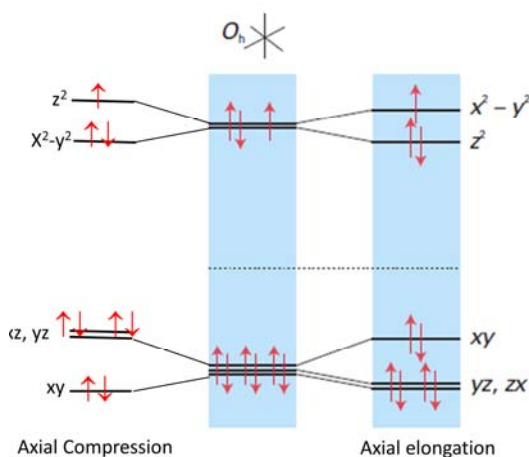
For orbital splitting diagram (0.5 Mark)

Q16. For the following octahedral iron complex the effective magnetic moment (magnetic susceptibility) changes at 300 K (A, μ_{eff} = 6.18 BM, $\chi_M T$ = 4.8 cm^3 K mol^{-1}), 240 K (B, μ_{eff}= 3.45 BM, $\chi_M T$ = 1.5 cm^3 K mol^{-1}) and 150 K (C, μ_{eff}= 0 BM,$\chi_M T$ = 0 cm^3 K mol^{-1}). Write the electronic configuration of the iron ion in the complex at step A and step C?*(1 Mark)*
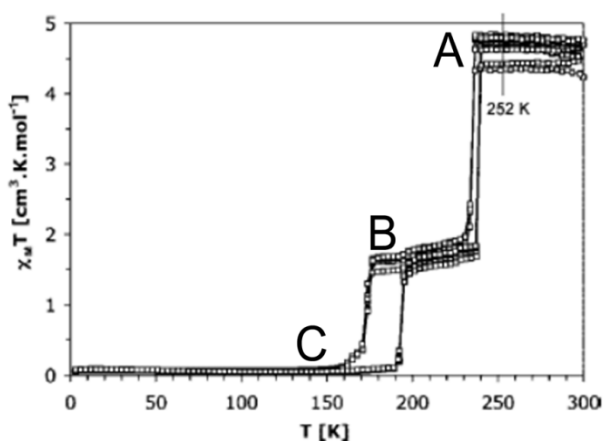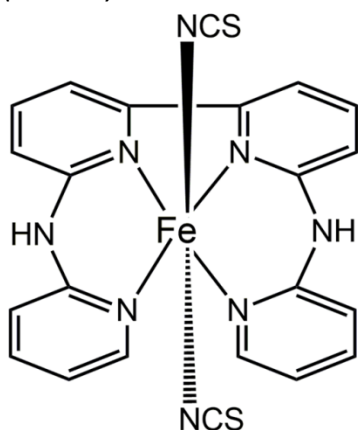
Ans: Based on the structure, it is understood that iron in +2 oxidation state. At, Aμ_{eff} = 6.18 BM for 4 unpaired electron suggests that Fe2+ in high spin state ($t_{2g}^{4}e_{g}^{2}$) ((0.5 Mark)).

At C, due to spin crossover from high spin to low spin the magnetic moment becomes zero. Hence the configuration is ($t_{2g}^{6}e_{g}^{0}$) (0.5 Mark)

Q17. Can the synthetic complex [Fe(porphyrinato)(pyridine)] exhibit reversible oxygen binding? Defend your answer by providing an explanation. *(1 Mark)*

Ans:

No (0.5 Mark),

Due to irreversible oxidation of Fe^{2+} to Fe^{3+}. The Fe^{3+} complex is a dimer called Hematin (Fe^{3+}-O-Fe^{3+}) or equivalent answer (0.5 Mark).
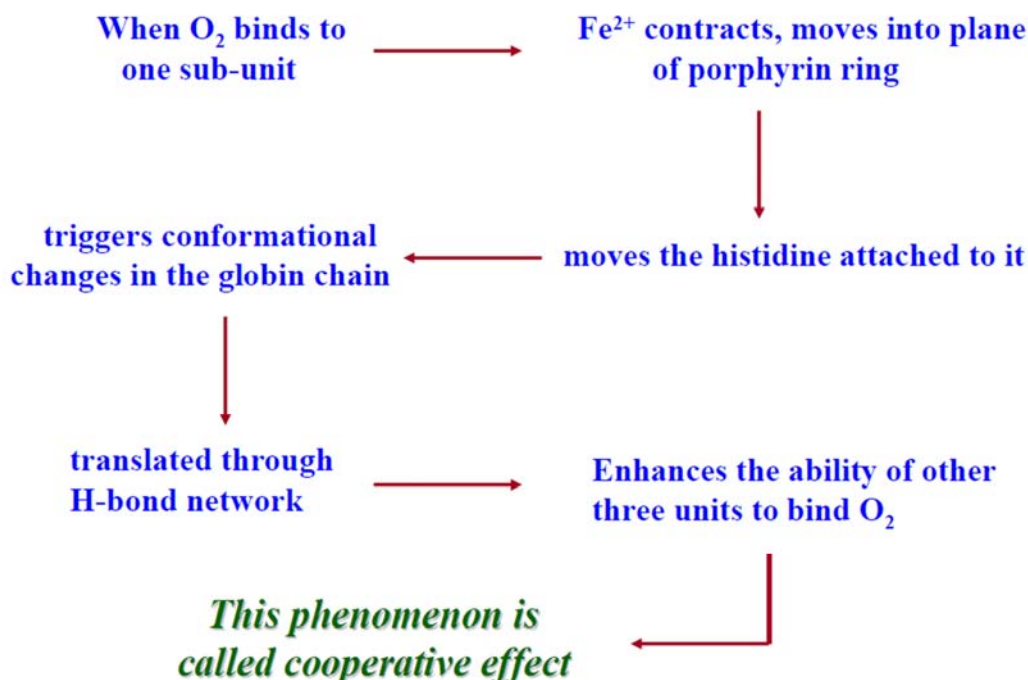
Q18. While cis-platin is an anti-cancer agent, its trans-isomer is not. Why? *(1 Mark)*

Ans:

Anticancer activity of the Cis-Platin is based on its effective cross-linking/chelation with DNA and inhibiting to copy the DNA by enzymes and thereby prevents the cell division

Q19. Write four important events that take place when O_2 is bound and released cooperatively to haemoglobin. *(1 Mark)*

Ans:

When O₂ binds to one sub-unit → Fe²⁺ contracts, moves into plane of porphyrin ring

↓

triggers conformational changes in the globin chain ← moves the histidine attached to it

↓

translated through H-bond network → Enhances the ability of other three units to bind O₂

This phenomenon is called cooperative effect

Rough Work

Rough Work

Rough Work

Rough Work