

**BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI
(RAJASTHAN)**

COMPREHENSIVE EXAMINATION, SEMESTER I (2016-17)

CHEM F214: Inorganic Chemistry 1 Close Book (Part A)

Marks: 30

Time: Max. 1h 30min

Date: 5th Dec., 2016

Instructions:

- I. All the questions are objective types
- II. Answer all the questions at the main answer sheet which should be marked as Part A
- III. Answer must be limited within 2-3 sentences only
- IV. After submission of Part-A answerscript, Part-B question paper should be taken
- V. The answer of Part-B question should be written in a separate answersheet which should be marked as Part B
- VI. Hand writing must be legible otherwise marks can be deducted

I. Answer all the questions within 2-3 sentences:

15 x 1 = 15M

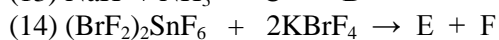
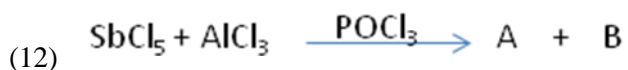
- (1) Draw the chemical structure of polythiazyl [(SN)_x].
- (2) How many nodal plane/s is/are present at the phosphazene ring based on Dewar model and show it/them.
- (3) How many different molecular orbitals are formed via 'linear combination of atomic orbitals (LCAO)' in case of BHB bonding? What are those?
- (4) In reaction with diborane, Me₃N results homolytic cleavage whereas NH₃ undergoes heterolytic cleavage reaction. What are the products formed in each case (only chemical structures are required).
- (5) There have been two theoretical arguments made against the participation of d-orbitals in non metals. Write down those arguments?
- (6) In PbMo₆S₈, Mo₆S₈ cube is rotated with respect to Pb lattice. How does such rotation arise?
- (7) Draw the molecular orbital (MO) diagram of the following molecule, Re₂Cl₄(PMe₂Ph)₄ including filling up of electrons in the resulting MOs (energy scale of the orbitals should be taken arbitrarily).
- (8) Write down the Born Lande equation of lattice energy.
- (9) What is thermochemical radii?
- (10) The boiling points of LiCl and LiI are observed to 845 and 449°C, respectively. Explain it.
- (11) Which are called F centre? Give example of it.
- (12) Et₃N and Me₃CN were treated with water separately. What products were expected? Explain it.
- (13) Write down the half-cell reaction along with the Nernst equation where water acting as an oxidizing agent.
- (14) Show the autoionization equilibrium present of POCl₃ involving its characteristic cations and anions.
- (15) Define donor number of aprotic solvent. Which solvent is expected to have higher donor number - toluene or acetone?

II. Fill in the blanks (Q.No.1-10) and write down the structure of A to H (Q.No. 11-15) (only write the appropriate answer on the answersheet)

15 x (0.5 x2) = 15M

- (1) The increasing effective nuclear charge on the central atom as a result of _____ would result _____ of the d orbitals.
- (2) The metal Bi often found to stable at _____ oxidation state which is because of _____.
- (3) In strongly heating of LiOH results _____ and _____, whereas mild heating of Li₂CO₃ produces ____ and _____.
- (4) In Re₃Cl₉, the number of Re-Re bonds and the terminal Re-Cl bonds remain _____ and _____, respectively.
- (5) _____ closest packed system has XYZ stacking pattern whereas _____ closest packed system has YX stacking pattern.

- (6) In CsCl structure the coordination number of chloride is _____ whereas in ZnS (wurtzite) structure, the coordination number of S is _____.
- (7) In defect where the missing ion has been dislocated to a nearby _____ position is called the _____ defect.
- (8) The charge coefficient measures the rate of change of _____ with charge and the second derivative of _____ with respect to charge.
- (9) Mulliken-Jaffe definition of electronegativity for various hybridizations involves the computation of _____ and _____ by adjusting for the promotion energy from the ground state.
- (10) An Ellingham diagram summarizes the _____ dependence of the standard Gibbs energies of formation of metal oxides and is used to identify the _____ at which reduction by carbon or carbon monoxide becomes spontaneous.
- (11) In Frost diagram, the reducing agent of the couple with the _____ positive slope is liable to undergo _____.



END

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COMPREHENSIVE EXAMINATION, SEMESTER I (2016-17)

CHEM F214: Inorganic Chemistry I

Open Book (Part B)

Marks: 50

Time: 1h 30min

Date: 5th Dec., 2016

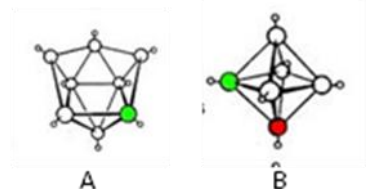
Instructions:

- I. Answer all the questions
- II. Answer all the parts of a particular question together
- III. Any inorganic chemistry book is allowed, but no solution manual
- IV. Hand writing must be legible otherwise marks can be deducted

Q1(a) Classify the following molecules as nido /closo /or arachno boranes with proper justification:

(i) $C_3B_5H_7$; (ii) $B_{10}H_{14}^{2-}$ (ii) $NCB_{10}H_{11}$

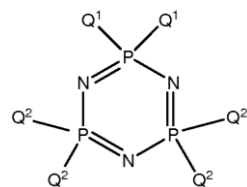
(b) Determine the total number of electrons and the number of framework electrons present in each of the above species. (c) How many vertices are present in each of the cases? (d) The structural framework of two borane clusters is given below. What type of boranes are these?



(e) Discuss the stability of cyclic $(PNBr_2)_3$ vs cyclic $(PNBr_2)_4$ in the light of Craig and Paddock model.

$$3 + 3 + 1.5 + 2 + 3.5 = 13M$$

Q2(a) In the following structure of phosphazene, in case 1: $Q1 = Q2 = F$ and case 2: $Q1 = \text{ethyl}$ and $Q2 = F$. In these two cases, what structural differences would be observed, and why such differences are observed.



(b) In the following two compounds, Cl_2FPO and $MeEt_2PO$, in which case the P-O IR stretching frequency is expected to be more and why? (c) In the following compounds, Ph_3NO and Ph_3PO which is expected to be more basic and why? (d) Out of the following species, $Me_3N^+CH_2^-$ and $Me_3P^+CH_2^-$ which one is expected to be more stable and why? (e) CCl_4 is stable whereas $PbCl_4$ is a powerful oxidizing agent. Why? (f) The S-S distance in S_2 , the major component of S vapor above $\sim 72^\circ C$, is 189 pm, significantly shorter than the S-S distance of 206 pm in S_8 . Suggest an explanation for the shorter distance in S_2 .

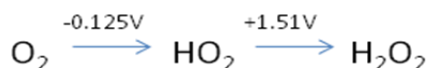
$$2 + 2 + 2 + 2 + 1 + 2 = 11M$$

Q3. (a) For the case of $Na_2Tc_2Cl_8$ molecule, Tc-Tc bond length was found to be exceptionally shorter. Why the bond length of Tc-Tc is found to be so short? Describe the detail bonding of the molecule. (b) Which are called naked clusters and why? Give examples and draw the structure of it. (c) Use Born Haber cycle to calculate the enthalpy of formation of MgO , which is assumed to crystallizes in NaCl structure (Bond

energy of $O_2 = 247 \text{ kJmol}^{-1}$; ΔH (sublimation, Mg) = 37 kJmol^{-1} ; Internuclear distance of MgO (r) = 212 pm)

4 + 3 + 6 = 13M

Q4. (a) Bartlett's original reaction of xenon with PtF_6 apparently yielded products other than the expected $Xe^+PtF_6^-$. However, when xenon and PtF_6 are reacted in the presence of a large excess of SF_6 , $Xe^+PtF_6^-$ is apparently formed. Suggest the function of SF_6 in this reaction. (b) On the basis of VSEPR, predict the structure with drawing the appropriate geometry: (i) $XeOF_2$; (ii) PCl_3Br_2 ; (iii) TeF_4^{2-} ; (c) From the following Latimer diagram, calculate the value of E° for the reaction $2HO_2(aq) \rightarrow O_2(g) + H_2O(aq)$. Comment on the thermodynamic tendency of HO_2 to undergo disproportionation.



(d) Arrange the following compounds in decreasing order of acidity with explanation: BF_3 , BCl_3 and BBr_3 .
(e) Calculate the enthalpy of adduct formation predicted by Drago's E, C equation for the reactions of I_2 with each of diethyl ether and dimethyl sulfide.

2 + 3 + 4 + 2 + 2 = 13M

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