Birla Institute of Technology and Science, Pilani (Rajasthan) First Semester 2023-24, 20th December, 2023 Comprehensive Examination (Open Book) Part -II CHEM F214; Inorganic Chemistry I

Q.1(a) Arrange the following compounds according to the increasing order of lattice energy and explain: CaO, LiCl, KBr, KCl. [1+3]

(b) pK_a of HI, HBr, HCl and HF are -10, -9, -7, 3 respectively. Provide the reason behind the trend observed for acidity. To differentiate the acids like HI, HBr, HCl, which solvent is better, H₂O or CH₃COOH and why? [2+2] (c) In which complex ion amongst $[Co(NH_3)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$, the ionic radius of Co³⁺ is higher? Justify your answer. [2]

(d) Write down the balanced reduction reaction of O_2 in aqueous acid. Calculate the emf for this reaction when $p_{O2} = 0.2$ bar and pH = 7 ($E^0 = 1.229$ V; 2.303RT/F = 0.0591V at 298 K) [1+3]

Q. 2 (a) R_2Sn exists in dimeric form in solid state. The bond order between Sn-Sn bond is 1.46. Comment on hybridization, hence on the structure of the compound with one-line justification. [1+1+1]

(b) Orthocarbonic acid, $C(OH)_4$ and orthonitric acid, $ON(OH)_3$ are unknown rather $O=C(OH)_2$ and $O_2N(OH)$ form, whereas orthosilicic acid Si(OH)₄ forms. Why does such difference exist? [3]

(c) The bond energies of BrF, BrF₃ and BrF₅ follow the order as BrF>BrF₃>BrF₅. Provide the justification. Why does not BrF₇ form whereas IF₇ is a stable compound? [2+2]

(d) (i) Stilbite is a natural zeolite of formula $Na_4Ca_8Al_{20}Si_{52}O_{144}.56H_2O$. Can it be converted to $Ca_{12}Al_{12}Si_{52}O_{144}.56H_2O$? Justify you answer. (ii) How can be any zeolite made more acidic in nature? [2+2]

Q. 3(**a**) From the perspective of structure and bonding, several polyhalides are analogous to $[py-I-Py]^+$ (py = pyridine). Name such two polyhalides and describe their bonding with a help of MO diagram (consider only the valence orbitals of interest) [1+3]

(b) Draw all of the structural isomers of P_4H_6 . Assume that inversion at phosphorous is slow and draw all possible stereoisomers. [4]

(c) Predict the products (A, B, C) of the following reactions.

 $[CH_3NH_3]Cl + BCl_3 \rightarrow A + B$

 $A + CH_3MgBr \rightarrow C$

[3]

(d) Find out the bond order of Mo-Mo bond in $Mo_2(MeCO_2)_4$ complex. In the σ bonding between two Mo atoms which orbitals are in use and why? [1+2]

Q.4(a) Compare the aromaticity of trimeric phosphazene, borazine with that of benzene and explain. Arrange them in the order of increasing aromaticity. In trimeric phosphazene, $P_3N_3Cl_6$, **justify** the orbitals utilized in π bonding (in-plane) from N and P atoms with mention of the orbital utilized. Amongst in-plane and perpendicular π bonding, which one do you think stabilize the molecule more? Explain [3+2+2] (b) Consider a $[B_{11}H_{14}]^-$ species. identify the number of framework electrons and B-H-B bonds. With the help of Wade's rule, find out the its structure. [1+1+2]

(c) Between infinite single chain of formula $[SiO_3]_n^{2n}$ and infinite double chain of formula $[Si_4O_{11}]_n^{6n}$ and a sheet or layer structure, $[Si_2O_5]_n^{2n}$ what is fundamental difference in terms of the number of shared oxygen atoms? [3]