Birla Institute of Technology and Science, Pilani (Rajasthan) First Semester 2022-23, December 21, 2022 Comprehensive Examination (Open Book) Part -II CHEM F214; Inorganic Chemistry I

Time: 2 hours 25 Mins Max. Marks: 56

Q.1(a) Δ = (actual bond energy) - (energy for 100% covalent bond). Find out the Pauling electronegativities of C and Cl where the Δ values of C-H and H-Cl are 24.3 and 102.3 kJ/mol respectively [consider $\chi_H = 0$]. If χ_H is shifted to 2, is there any advantage in the scale? [3] (b) Discuss the effect of aniline added to ammonia based on leveling effect. [2] (c) There exists a relationship between energy band gap and electronegativity of the elements present in a compound. What is the relation these hold? Can you provide some reasons for the existing relationship? [1+2] (d) Calculate the equilibrium constant for the disproportionation reaction: $2Cu^{+}$ (aq) \leftarrow $Cu(s) + Cu^{2+}$ (aq) at 298 K $[E^{0}(Cu^{+}/Cu) = 0.52 \text{ V} \text{ and } E^{0}(Cu^{2+}/Cu^{+}) = 0.15\text{V}; 2.303\text{RT/F} = 0.0591\text{V at } 298 \text{ K}].$ [4] (e) Account for the fact that CH₃CH₂O⁻ is much more basic than CH₃COO⁻. [2] Q. 2 (a) How would you synthesize P(SiMe₃)₃ from Phosphorus? Draw the structure of P(SiMe₃)₃. Write down the expected product of the reaction between CH₃COCl and P(SiMe₃)₃. (b) Account for the fact that in aqueous solution, lithium is as good a reducing agent as Cs despite of having higher ionization energy. (c) With the mention of the products obtained when CCl₄ and SiCl₄ individually reacting with H₂O, provide justification to support the observations for these two reactions. (d) What is the role of (n-Pr₄N)OH in the synthesis of ZSM-5? Which property of ZSM-5 will be tweaked by Si to Al ratio? If you want to introduce Fe²⁺ ions in ZSM-5, how would you proceed? Q. 3(a) To prepare I₃⁺, an oxidizing agent like bis(fluorosulpuryl)peroxide FSO₂OOSO₂F is used to react with I₂. Would you prefer H₂O₂ over FSO₂OOSO₂F for this reaction? Justify your answer. (b) Plenty of fluoride compounds of Xe are known. What could be the possible reason(s) for not having reports of formation of fluorides of Ne? If you imagine a Ne-fluoride compound, what would be the formula and what type of bonding is expected? (c) Find out the symmetry point group of boron-phosphorus analogue of borazine B₃P₃((Ph)₆ [Consider the -Ph group as an atom] and mention the symmetry elements present. Amongst B₃P₃((Ph)₆ and borazine, who is more prone to non-planar structure and why? [2+2](d) Comment on the aromaticity of S₄N₂ having a closed ring structure. [3] Q.4(a) Justify the participation of specific orbitals in π bonding from P and N atoms in trimeric phosphazene, P₃N₃Cl₆. With the typical sets of orbitals once chosen from P and N centers, discuss the 'island model' for the molecule P₃N₃Cl₆. (b) Draw the molecular orbitals of the 3c-2e bond considering a hypothetical model with the atoms as H-B-H in B₂H₆. Why is the 3c-2e bonds on B-H-B system justified over 3c-2e bond on H-B-H system? (c) Explain the bond order of Re-Re bond in [Re₂Cl₈]⁴. Justify the arrangement of chlorine atoms around each Re atom relatively and the geometry of each Re atom. [2+3]

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