2018

CHEMISTRY

(Major)

Paper : 4.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following : 1×7=7

(a) Why is CO_2 a gas whereas SiO_2 is a polymeric singly bonded giant molecule?

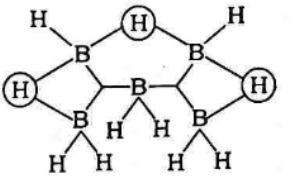
(b) Why is B—F bond distance in BF_3 shorter than expected theoretical value?

(c) Strong oxidizing agents like HNO_3 becomes non-oxidizing in liquid NH_3. Give reason.

(d) Arrange the perhalic acids in their increasing order of acid strength

$HClO_4$, $HBrO_4$, HIO_4

(e) Write the styx topology for B_5H_{11} :



(f) Write the structure of pyrosulphuric acid (oleum).

(g) Why are soft acids like Hg^{2+}, Pb^{2+} and Cd^{2+} toxic?

2. Answer the following : 2×4=8

(a) Silver perchlorate is significantly more soluble in benzene than in alkaline solvents. Explain.

(b) Second ionization energy of Mg is approximately twice its first ionization energy. Also, the second electron gain enthalpy of oxygen is positive. Why then Mg forms $Mg^{2+}O^{2-}$ rather than $Mg^{+}O^{-}$?

(c) Which member of the following pairs is stronger acid? Give reasons for your choice :

(i) $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$

(ii) H_2CrO_4 and $HMnO_4$

(d) From the Latimer diagram for plutonium, does Pu(IV) have a tendency to disproportionate into Pu(III) and Pu(V)?

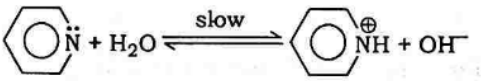
$$PuO_2^{2+} \xrightarrow{(1\cdot02)} PuO_2^{+} \xrightarrow{(1\cdot04)}$$

$$Pu^{4+} \xrightarrow{(1\cdot01)} Pu^{3+}$$

3. Answer the following (any *three*) : 5×3=15

(a) Define electronegativity of an element. How is it related to the state of hybridization of an element? Explain the following reactions : 1+1+3=5

$$CH_3\ddot{N}H_2 + H_2O \overset{\text{fast}}{\rightleftharpoons} CH_3\overset{\oplus}{N}H_3 + OH^-$$



$$CH_3{-}C{\equiv}\ddot{N} + H_2O \longrightarrow \text{No reaction}$$

(b) (i) Mention the advantages and disadvantages of using ammonia as non-aqueous solvent. 3

(ii) Disilylether is less basic than dimethylether. Explain. 2

(c) (i) Both hydrazine (N_2H_4) and dimethyl hydrazine $N_2H_2(CH_3)_2$ are used as rocket fuels. Given the following data, suggest which will be most efficient fuel : 3

Compounds	N_2H_4	$N_2H_2(CH_3)_2$	CO_2	H_2O
$\Delta_f H^\circ$ (kJ/mole)	+50·6	+42·6	–394	–242

(ii) Mention the structures of pent-oxides of phosphorus and nitrogen. 2

(d) What are cyanogens? Write one method of preparation of cyanogen. What significant results when stoichiometric mixture of O_2 and cyanogens burns? 2+1+2=5

(e) (i) Construct a Frost diagram from the Latimer diagram for Tl : 3

$$Tl^{3+} \xrightarrow{(1\cdot25)} Tl^{+} \xrightarrow{(-0\cdot34)} Tl$$

(ii) Use the Latimer diagram to calculate the value of E° for the couple $HClO/Cl^-$ in aqueous acidic solution for Cl_2 system : 2

$$HClO_2 \xrightarrow{(0\cdot68)} HClO \xrightarrow{(0\cdot42)} Cl_2 \xrightarrow{(1\cdot36)} Cl^{(-)}$$

4. Answer the following (any *three*) : 10×3=30

(a) *(i)* What do you mean by effective nuclear charge? Using Slater's rules, calculate the effective nuclear charge (Z^*) experienced by one of the 4*s* electrons of nickel (Ni). 2+3=5

(ii) PbO_2 is stronger oxidizing agent than SnO_2. Explain. 2

(iii) The first ionization enthalpy values of group 13 elements are given in the table :

Element	B	Al	Ga	In	Tl
IE (kJ/mole)	801	577	579	558	589

How would you explain this deviation from the general trend? 3

(b) *(i)* Give one method of preparation of diborane. Discuss the bonding and structure of diborane. What happens when diborane reacts with ammonia? 1+3+1=5

(ii) Use Wade's rule to classify the following into *closo-*, *nido-* and *arachno*-geometry : 5

B_8H_{14}, B_2H_6, $B_{12}H_{12}^{2-}$, $C_2B_{10}H_{12}$ and $C_2B_6H_8$

(c) (i) Discuss liquid HF as non-aqueous solvent in terms of acid-base reaction. 3

(ii) What do you mean by superacids? Explain with examples. 3

(iii) The reaction

$(CH_3)_3SiI + AgBr \rightarrow (CH_3)_3SiBr + AgI$

is irreversible. Explain. 2

(iv) Use Fajans' rules to explain the thermal stability of $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$. 2

(d) (i) What are *ortho*-hydrogen and *para*-hydrogen molecules? Discuss the effect of temperature on the relative properties of the two forms in ordinary hydrogen. Give one method of preparation of pure *para*-hydrogen molecule. 2+2+1=5

(ii) How many series of salts can be formed from orthophosphoric acid? Mention the salts with examples. 2

(iii) What are superoxides? Give one method of preparation of super-oxide. Discuss the uses of potassium superoxide. 3

(e) (i) Give one method of preparation of hydrazoic acid. How does it react with alkalies and active metals? Which alkali metal azide is used in the air balloon of a car for safety purpose?

1+2+2=5

(ii) What are metallic hydrides? Why are metallic hydrides known as potential hydrogen storage media? Which metal hydride is known as 'hydrogen sponge'? Name one metal hydride used in the construction of rechargeable batteries. 2+1+1+1=5

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