

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

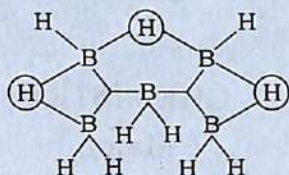
- (a) Why is  $\text{CO}_2$  a gas whereas  $\text{SiO}_2$  is a polymeric singly bonded giant molecule?
- (b) Why is B—F bond distance in  $\text{BF}_3$  shorter than expected theoretical value?
- (c) Strong oxidizing agents like  $\text{HNO}_3$  becomes non-oxidizing in liquid  $\text{NH}_3$ . Give reason.
- (d) Arrange the perhalic acids in their increasing order of acid strength





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(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 :  $2 \times 4 = 8$

(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  $Mg^+O^-$ ?

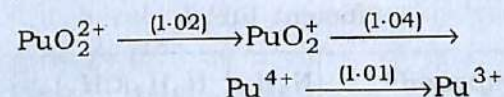
(c) Which member of the following pairs is stronger acid? Give reasons for your choice :

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

(ii)  $H_2CrO_4$  and  $HMnO_4$

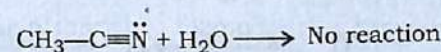
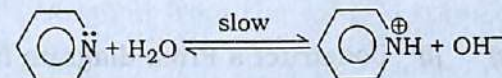
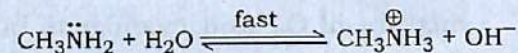
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(d) From the Latimer diagram for plutonium, does Pu(IV) have a tendency to disproportionate into Pu(III) and Pu(V)?



3. Answer the following (any three) :  $5 \times 3 = 15$

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



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

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

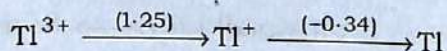


- (c) (i) Both hydrazine ( $\text{N}_2\text{H}_4$ ) and dimethyl hydrazine  $\text{N}_2\text{H}_2(\text{CH}_3)_2$  are used as rocket fuels. Given the following data, suggest which will be most efficient fuel : 3

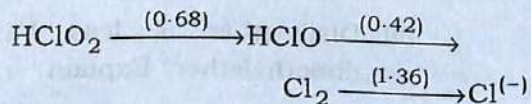
Compounds	$\text{N}_2\text{H}_4$	$\text{N}_2\text{H}_2(\text{CH}_3)_2$	$\text{CO}_2$	$\text{H}_2\text{O}$
$\Delta_f H^\circ$ (kJ/mole)	+50.6	+42.6	-394	-242

- (ii) Mention the structures of pentoxides of phosphorus and nitrogen. 2
- (d) What are cyanogens? Write one method of preparation of cyanogen. What significant results when stoichiometric mixture of  $\text{O}_2$  and cyanogens burns? 2+1+2=5

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



- (ii) Use the Latimer diagram to calculate the value of  $E^\circ$  for the couple  $\text{HClO}/\text{Cl}^-$  in aqueous acidic solution for  $\text{Cl}_2$  system : 2



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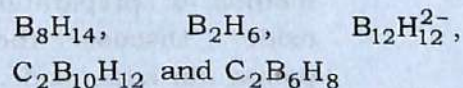
4. Answer the following (any three) : 10×3=30

- (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 4s electrons of nickel (Ni). 2+3=5
- (ii)  $\text{PbO}_2$  is stronger oxidizing agent than  $\text{SnO}_2$ . 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



( Turn Over )



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- (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  
 $(\text{CH}_3)_3\text{SiI} + \text{AgBr} \rightarrow (\text{CH}_3)_3\text{SiBr} + \text{AgI}$   
is irreversible. Explain. 2
- (iv) Use Fajans' rules to explain the thermal stability of  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$ . 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 superoxide. Discuss the uses of potassium superoxide. 3

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- (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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( Major )

Paper : 4.2

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks  
for the questions*

1. Select the correct answer/Answer the following questions : 1×7=7
- (a) Which one of the following is pseudo-halide?
- (i)  $\text{ICl}$
  - (ii)  $\text{IF}_5$
  - (iii)  $\text{CN}^-$
  - (iv)  $\text{I}_3^-$
- (b)  $\text{XeO}_3$  is prepared by the
- (i) direct combination of Xe and  $\text{O}_2$
  - (ii) hydrolysis of  $\text{XeF}_4$
  - (iii) oxidation of  $\text{XeO}_2$
  - (iv) hydrolysis of  $\text{XeF}_6$



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(c) Which of the following compounds has a cage structure?

(i) Borazine

(ii)  $B_2H_6$

(iii)  $P_4O_{10}$

(iv) Phosphazene

(d) Among the metals Mn, Fe, Co and Ni, the ones those would react in their native forms directly with CO giving metal carbonyl compounds are

(i) Co and Mn

(ii) Mn and Fe

(iii) Fe and Ni

(iv) Ni and Co

(e) In which one of the following is a metal-metal bond present?

(i) Cupric chloride

(ii) Mercurous chloride

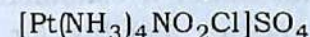
(iii) Stannous chloride

(iv) Mercuric chloride

(f) Write the possible geometrical isomers for octahedral  $[Co(OX)(PMe_3)_2NH_3Cl]$ .

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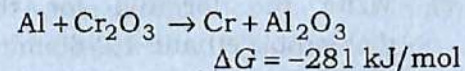
(g) Give the IUPAC name of the following compound :



2. Answer the following questions : 2×4=8

(a) Why transition metal exhibits highest oxidation state in oxides and fluorides?

(b) The reaction



is thermodynamically feasible but it does not take place at room temperature. Why?

(c) Write the reaction for preparation of  $1,7-B_{10}H_{10}C_2RR'$ .

(d) Which is more stable—chloric acid or perchloric acid? Justify.

3. Answer any *three* from the following questions : 5×3=15

(a) Discuss the nature of bonding in borazine. Justify why borazine does not show true aromatic character. 3+2=5

(b) Which special properties of Au make it so important in human civilization? How does gold occur in nature and how is it commercially extracted? 2+3=5



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- (c) Discuss the oxidation states of the elements of the first transition series. Indicate common oxidation states and their relative stability for the metals Cr—Cu. 5
- (d) Briefly describe the preparation, structure and properties of xenon fluorides. 5
- (e) Write the formula for the complex dichlorobis(ethane-1,2-diamine)cobalt(III) ion. Draw its geometrical and optical isomers. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands with the central metal ion?

1+2+2=5

4. Answer any three from the following questions : 10×3=30

- (a) Explain the different types of isomerism exhibited by coordination compounds in square planar, tetrahedral and octahedral geometry. 10
- (b) (i) Transition metals show variable oxidation states. Give examples of two different oxidation states shown by Mn in its compounds. In each case, give the oxidation state,

8A/1005

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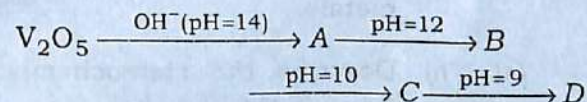
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and an example of a compound containing Mn in that oxidation state. 3

- (ii) Transition metals and their compounds are frequently used as catalysts. Name the catalysts employed in the following processes : 3

Haber process for the manufacture of ammonia, hydrogenation of carbon-carbon double bonds and contact process for the manufacture of sulphuric acid.

- (iii) Identify A, B, C and D in the following reactions : 4



- (c) (i) Compare the magnetic behaviour of the oxides and mixed oxides of iron with those of Ruthenium and Osmium. 5

- (ii) Give the method of preparation, properties and structure of  $\text{S}_4\text{N}_4$ .

2+1+2=5

8A/1005

( Turn Over )



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(d) Explain the following :  $2 \times 5 = 10$

(i) Chromium is a typical metal while mercury is a liquid metal.

(ii) Zn readily liberates  $H_2$  from cold dil.  $H_2SO_4$  but not from cold conc.  $H_2SO_4$ .

(iii) Transition elements and *d*-block elements.

(iv)  $Cu^+$  ion has  $3d^{10}4s^0$  configuration and colourless but  $Cu_2O$  is red and  $Cu_2S$  is black.

(v) Enthalpies of atomization of transition elements are higher than those of alkali and alkaline earth metals.

(e) (i) Describe the stereochemistries of Zn and Cd compounds. 5

(ii) Will  $Hg_2^{2+}$  ion disproportionate in aqueous solution into  $Hg^{2+}$  and  $Hg^0$ ? Given that

$$E^\circ_{Hg_2^{2+}/Hg^0}, E^\circ = 0.7960 \text{ V}$$

$$E^\circ_{Hg^{2+}/Hg_2^{2+}}, E^\circ = 0.9110 \text{ V}$$

$$E^\circ_{Hg^{2+}/Hg^0}, E^\circ = 0.8535 \text{ V} \quad 5$$

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(f) (i) What are silicates? Draw the structure of four different types of silicates and give the name and formula of each type. 6

(ii) Draw and describe the structure of the compound formed by  $CH_3COO^-$  with chromium. 4

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