

2014

CHEMISTRY

( Major )

Paper : 4.1

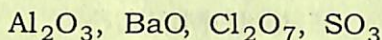
Full Marks : 60

Time : 2½ hours

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

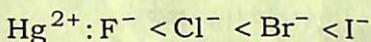
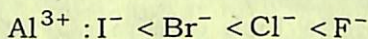
1. (a) Which of the following elements has the most negative electron gain enthalpy? 1
- (i)  $[\text{Ne}]3s^23p^3$
- (ii)  $[\text{Ne}]3s^23p^4$
- (iii)  $[\text{Ne}]3s^23p^5$
- (b) Write the styx number for the structure of diborane. 1
- (c) Why the heavier *p*-block elements of groups 13, 14 and 15 prefer to exist in an oxidation state two units lower than their maximum oxidation state? 1
- (d) Sketch the structure of hypophosphorous acid. Why is it monobasic? 1

- (e) Arrange the following according to increasing basic character : 1



- (f) What is the trend in the solubilities of the lithium halides (LiF, LiCl, LiBr, LiI) in water? 1

- (g) Why the complexing ability of the halide ions shows reverse trend with  $\text{Al}^{3+}$  and  $\text{Hg}^{2+}$ ? 1



2. (a) Will metallic tin reduce  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$ ? Explain. Given

$$E_{\text{Sn}^{4+}/\text{Sn}}^{\circ} = -0.13 \text{ V}$$

$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} = +0.15 \text{ V} \quad 2$$

- (b) The solubility of the sulphates of alkaline earth metals decreases on descending the group from Be to Ba while the solubility of fluorides of these metals increases on moving down the group. Explain giving appropriate reasons. 2





- (ii) Give one preparation of hydroxylamine and describe two of its major uses. 2
- (c) (i) The electronegativity of an atom depends on its orbital involved and for the hybrid orbitals, it follows the sequence  $sp > sp^2 > sp^3$ . Justify the statement with suitable example. 1+2=3
- (ii) Explain the preparation and structure of an oxygen fluoride. 2
- (d) (i) What are Fajan's rules? Describe the factors favouring the formation of covalent bond in reference to Fajan's rule. 4
- (ii) Give one clinical use of  $N_2O$ . 1
- (e) (i) Give reasons for the following : 1+1=2  
 $AgI_2^-$  is stable but  $AgF_2^-$  is not;  $CsF$  reacts with  $LiI$  even though both are ionic.
- (ii) What do you understand by *ortho*- and *para*-hydrogen? How and why does the ratio of *ortho*- to *para*-hydrogen vary with temperature? 1+2=3



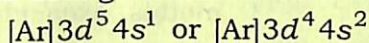
4. Answer any *three* of the following :  $10 \times 3 = 30$

- (a) (i) Select the better choice in each of the following and explain your selection briefly :  $1+1+1=3$

Higher ionization energy : Mg or Ca

Higher electron affinity : Si or P

Electronic configuration of Cr :

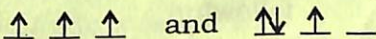


- (ii) Single and multiple bonds of nitrogen and carbon are characterized by the following energy and length :

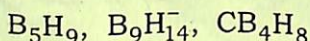
	$\text{--}\ddot{\text{N}}=\ddot{\text{N}}\text{--}$	$\text{--}\ddot{\text{N}}\text{--}\ddot{\text{N}}\text{--}$	$\text{--}\text{C}=\text{C}\text{--}$	$\text{--}\text{C}\text{--}\text{C}\text{--}$
$E, \text{ kJ mol}^{-1}$ :	418	155	606	334
$d, \text{ nm}$ :	0.125	0.146	0.135	0.155

Explain the great differences in stability of homochains of nitrogen and carbon. 4

- (iii) Determine the Coulombic and exchange energies for the following configurations and determine which configuration is favoured : 3



- (b) (i) Discuss liquid  $\text{SO}_2$  as a solvent in terms of precipitation reaction, acid-base reaction and complex formation reaction. 3
- (ii) What are intercalation compounds? Describe in detail, the intercalation compounds of graphite with alkali metals, oxoacids, metal halides and halogens. 1+4=5
- (iii) Explain the term symbiosis with suitable example. 2
- (c) (i) Write about the preparation and use of superoxides. Show the differences in bonding in peroxide and superoxide ions on the basis of molecular orbital treatment. 2+2=4
- (ii) Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why? 3
- (iii) Use Wade's rule to classify the following : 3





- (d) (i) Some physical properties of the group 14 elements are given below :

M	Melting Point of M (°C)	Melting Point of MO <sub>2</sub> (°C)
C	>4000	-57 (pressure)
Si	1410	1730
Ge	960	1120
Sn	232	1130
Pb	327	290

Comment on the following observations :

4

- (1) The sharp drop in melting point from elemental carbon to silicon
- (2) The fairly regular decrease in melting point from Si to Pb
- (3) The anomalous melting point of CO<sub>2</sub>
- (4) The markedly low thermal stability of PbO<sub>2</sub>

- (ii) "Compared to Me<sub>3</sub>N, (SiH<sub>3</sub>)<sub>3</sub>N has got almost no basicity." Explain giving appropriate reason.

2

- (iii) Discuss the mechanism of formation and depletion of ozone layer in the stratosphere.

4

- (e) (i) Write about the structures of oxoacids of sulphur. 4
- (ii) Using Slater's rules, calculate  $Z^*$  for the valence electron in Zn. 2
- (iii) Sketch the structures of  $P_4O_6$  and  $P_4O_{10}$ . The oxides of nitrogen are monomeric (e.g.,  $N_2O_3$ ,  $N_2O_5$ ) while those of phosphorus are dimeric containing  $P_4$  unit (e.g.,  $P_4O_6$ ,  $P_4O_{10}$ ). Explain giving appropriate reason.  $2+2=4$

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