

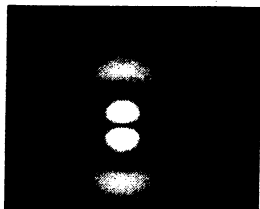
Answer all questions

## SECTION A

[1 X 15 = 15 marks]

Only one answer is correct

1. From the projection of the hydrogenic orbital shown below, guess the quantum numbers  $n$  and  $l$ .



- (a)  $n=3, l=1$   
(b)  $n=2, l=1$   
(c)  $n=3, l=2$   
(d)  $n=2, l=0$
2. For the four possible combinations of  $1s$  and  $2p$  orbitals that can lead to the formation of MO's, in which combination the overlap integral  $S$  will be zero.  
(a)  $1s + 1s$   
(b)  $2p_x + 2p_y$   
(c)  $2p_z + 2p_z$   
(d)  $1s + 2p_z$
3. Which of the following statement is correct about the physical nature of these main group compounds (ionic, molecular covalent or polymeric)  
(a)  $KH$ ,  $NaH$  and  $MgH_2$  are polymeric  
(b)  $Al_2O_3$ ,  $SiO_2$  and  $GeO_2$  are molecular covalent  
(c)  $AlF_3$ ,  $GaF_3$  and  $SnF_4$  are polymeric  
(d)  $Cl_2O$ ,  $ClO_2$  and  $XeO_3$  are ionic
4. Which of the following statements is INCORRECT?  
(a)  $BF_3$  is a gas, whereas the other Group 13 trifluorides are all high-melting solids.  
(b)  $BF_3$  and  $AlF_3$  both readily act as Lewis acids toward  $F^-$  ions to give  $[BF_4]^-$  and  $[AlF_4]^-$ ; however,  $TiF_3$  does not form an analogous adduct with  $F^-$ .  
(c)  $GaF$  and  $InF$  are known as unstable gaseous species but  $TiF$  is stable.  
(d)  $SiF_4$  is a high melting point solid, whereas  $AlF_3$  is a gas at room temperature.
5. Consider the following two reactions:  
(I)  $2M(s) + Cl_2(g) \longrightarrow 2 MCl(s)$   
(II)  $2M(s) + 2H_2O(l) \longrightarrow H_2(g) + 2M^+(aq) + 2OH^-(aq) + \text{energy}$   
where  $M$  is  $Li/Na/K$

Which of the following statements is correct?

- A) The expected trend in reducing ability for reaction (I) and (II) is  $K > Na > Li$   
B) The expected trend in reducing ability for reaction (I) and (II) is  $Li > Na > K$

- C) The expected trend in reducing ability for reaction (I) is  $\text{Li} > \text{Na} > \text{K}$  while that for reaction (II) is  $\text{K} > \text{Na} > \text{Li}$   
 D) The expected trend in reducing ability for reaction (II) is  $\text{Li} > \text{Na} > \text{K}$  while that for reaction (I) is  $\text{K} > \text{Na} > \text{Li}$

6. The relative M-Cl bond strengths of Group 14 halides will be:

- A)  $\text{Si-Cl} > \text{C-Cl} > \text{Ge-Cl} > \text{Sn-Cl}$   
 B)  $\text{C-Cl} > \text{Si-Cl} > \text{Ge-Cl} > \text{Sn-Cl}$   
 C)  $\text{C-Cl} < \text{Si-Cl} < \text{Ge-Cl} < \text{Sn-Cl}$   
 D)  $\text{Si-Cl} < \text{C-Cl} < \text{Ge-Cl} < \text{Sn-Cl}$

7. Which of the following compounds are unknown?

- A)  $\text{SbBr}_5$   
 B)  $\text{PBr}_5$   
 C)  $\text{BiBr}_5$   
 D)  $\text{NCl}_3$

8. Which of the following chlorine oxide is paramagnetic?

- A)  $\text{OCl}_2$   
 B)  $\text{ClOOC}$   
 C)  $\text{ClO}_2$   
 D)  $\text{Cl}_2\text{O}_7$

9. Arrange the following Lewis Bases according to their increasing base strength for the Lewis Acid  $\text{BBR}_3$ .

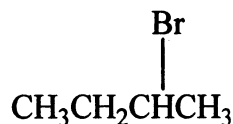
- A)  $\text{NH}_3 < \text{PH}_3 > \text{AsH}_3 >> \text{SbH}_3$   
 B)  $\text{NH}_3 << \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$   
 C)  $\text{NH}_3 < \text{PH}_3 > \text{AsH}_3 < \text{SbH}_3$   
 D)  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 >> \text{SbH}_3$

10. Which of the following statements is NOT correct in describing the properties of white phosphorous?

- A) It is a soft yellow waxy solid  
 B) Combines violently with all halogens  
 C) Ignites at a temperature above  $260^\circ\text{C}$   
 D) Structure consists of discrete  $\text{P}_4$  tetrahedra.

11. Which of the following reacts by the  $\text{E1}$  mechanism in ethanol most readily?

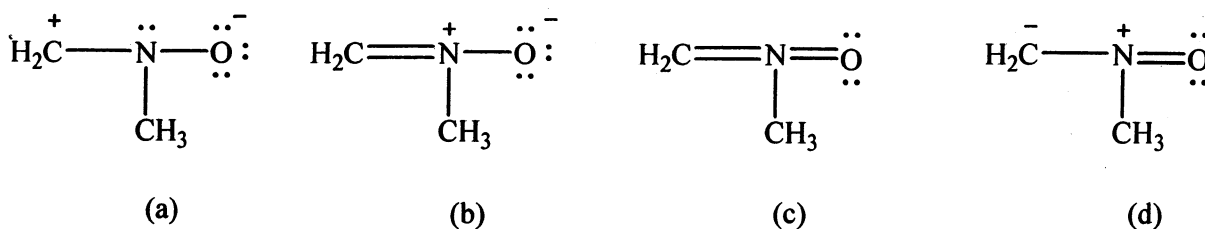
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  (b)  $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$  (c)  $(\text{CH}_3)_3\text{CBr}$  (d)



12. Which species contains a  $\text{sp}^3$ -hybridized atom?

- (a)  $\text{CH}_3^+$  (b)  $\text{H}_2\text{C}=\text{OH}^+$  (c)  $\text{H}_3\text{O}^+$  (d)  $\text{H}_2\text{C}=\text{NH}$

13. Among the following four structures, one is *not* a permissible resonance form. Identify the wrong structure.



14. Which of the following statements is false?

- (a) The  $\pi$  molecular orbitals of buta-1,3-diene are derived from 2p atomic orbitals of carbon atoms, and there are four of them.
- (b) The complete set of molecular orbitals obtained by combining atomic orbitals includes an increased number of nodes.
- (c) The HOMO of butadiene is higher in energy than ethylene.
- (d) The LUMO of butadiene is higher in energy than ethylene.

15. Which of the following statements is true?

- (a) In a  $\text{S}_{\text{N}}2$  reaction, the nucleophile attacks the  $\sigma^*$  orbital of an alkyl halide at  $90^\circ$  angle.
- (b) The favoured geometry for E2 elimination is syn/cis co-planar.
- (c) On the basis of MO interactions, a reaction is favoured if the orbital overlap as well as the energy gap between the HOMO and LUMO is large.
- (d) On the basis of MO interactions, a reaction is favoured if the orbital overlap is large but the energy gap between the HOMO and LUMO is small.

## SECTION B

[60 marks]

16. In a single graph with proper axes labels, draw the Radial Function and the Radial distribution function for 1s, 2s and 2p orbitals for a Hydrogen atom indicating nodes and relative position of the maxima. Quantitatively explain what happens in case of the other hydrogenic atoms such as  $\text{Li}^{2+}$ ?

[4 marks]

17. For the hypothetical molecule  $\text{PO}_2\text{F}$ , draw three alternative Lewis structures- one with two doubly-bonded oxygen atoms, one with only one doubly-bonded oxygen and one with only one single bonds to oxygen. For all three structures, determine the formal charges on the phosphorous and each of the oxygen atoms.

[4 marks]

18. Sulfanyl ( $\text{HS}^\bullet$ ), also known as the mercapto radical, is a simple radical molecule consisting of one hydrogen and one sulfur atom. The radical appears in metabolism in organisms as  $\text{H}_2\text{S}$  is detoxified. Sulfanyl is one of the top three sulfur containing gasses in gas giants such as Jupiter and is very likely to be found in brown dwarfs and cool stars. The orbital energies are as follows: H(1s) 13.6 eV; S (3s) 20.7 eV; S (3p) 11.7 eV.

- A) Complete the MO energy-level diagram for  $\text{HS}^\bullet$ . Place the correct number of electrons in the energy levels of  $\text{HS}^\bullet$ ?
- B) Draw pictures of the sigma bonding and antibonding molecular orbitals in  $\text{HS}^\bullet$ .
- C) Which of the two MO's has the greater hydrogen 1s character?
- D) Predict whether the bond order of  $\text{SH}^+$  is greater than, less than, or the same as that of  $\text{HS}^\bullet$ . Explain.

[8 marks]

19. Captain Kirk has set a trap for the Klingons, who are threatening an innocent planet. He has sent small groups of fighter rockets to sites that are invisible to Klingon radar and put a

*[Handwritten signatures]*

decoy in the open. He calls this the "fishhook" strategy. Mr. Spock has sent a coded message to the chemists on the Fighters to tell the ships what to do next. The outline of the message is:

\_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_  
 (1) (2)    (3)    (4)    (5)    (6),  
 \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_    \_\_\_\_ \_  
 (7)    (8) (9)    (10) (8) (8) (11)

Fill in the blanks of the message using the following clues:

- (1) Symbol of the halogen which is present in the growth-regulating hormone thyroxine.
- (2) Symbol of the halogen that is the only hydrogen halide, HX, which is a weak acid in aqueous solution.
- (3) Symbol of the element whose existence on the sun was known before its existence on earth was discovered
- (4) Symbol of the group 15 element whose salt was used as talc in the middle ages. When chloride ions are added to an aqueous solution of this metal ion, a white precipitate forms with formula  $\text{MOCl}$ . It is also widely used in stomach medicines.
- (5) Symbol of the Group 16 element that has the highest boiling and melting point among the chalcogens. Also forms acids with the composition  $\text{X}(\text{OH})_6$  where X is the group 16 element.
- (6) Symbol for the element that has a boiling point of  $445^\circ\text{C}$ . When heated to temperature above its boiling point and then poured into cold water, it becomes a flexible plastic that stretches considerably before it breaks.
- (7) Symbol for the element that exists as diatomic molecules, is not colorless, and was a major component of the chemical compounds that lead to the formation of the ozone hole.
- (8) Symbol of an element X whose potassium salt  $\text{KX}_2$  is used in space stations to remove  $\text{CO}_2$ .
- (9) Symbol for the element that seems to give some protection against cancer when a diet rich in this element is consumed. Its oxide is also an oxidizing agent that is widely used in organic transformations
- (10) Symbol of an element whose diatomic molecule under 3 million atm of pressure forms an opaque solid that conducts electricity like a metal. However, the diatomic molecule does not get atomized at this pressure. It is also a key component of fuel cells.
- (11) Symbol for the element which is critical to the functioning of ion channels

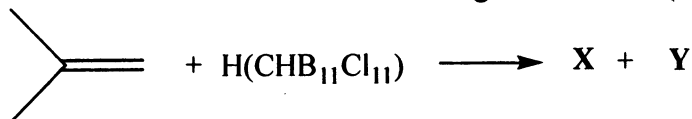
[11 marks]

20. Red phosphorous ( $\text{P}_4$ ) can be partially oxidized to  $\text{P}_4\text{O}_6$  and fully oxidized to  $\text{P}_4\text{O}_{10}$ . Draw the structure of  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ .

[4 marks]

21. Carborane superacid  $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$  are one million times stronger than sulphuric acid. What is the X and Y for the following reaction of  $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ ?

[3 marks]



22. The homonuclear single bond energies of group 14 and group 15 elements ( $\text{kJ mol}^{-1}$ ) are given below:

[6 marks]

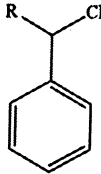
C-C (346)	N-N (167)
Si-Si (222)	P-P (201)

Ge-Ge (188)	As-As (196)
Sn-Sn (146)	Sb-Sb (121)

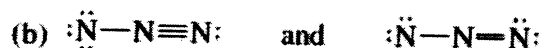
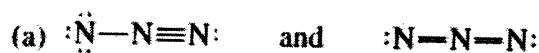
- (i) Explain why the bond energies in group 14 elements decrease as we go down a group?
- (ii) Why this trend is not followed in group 15 elements?

23. If NaCN reacts with butyl bromide and butyl iodide in the  $S_N2$  mode, which reaction would be faster? Explain with a comparative MO diagram. [3 marks]

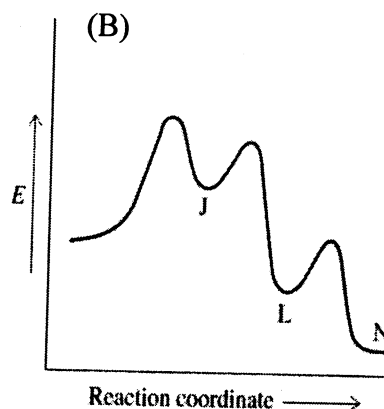
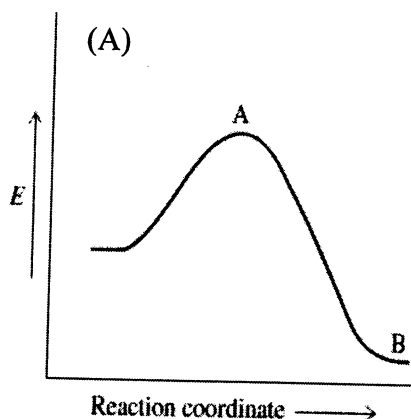
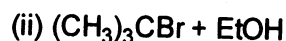
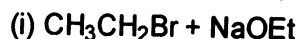
24. Explain the relative rates of the following compounds in the  $S_N1$  reaction. [3 marks]

	R	Relative rate
	CH <sub>3</sub>	540
	CH <sub>3</sub> CH <sub>2</sub>	125
	(CH <sub>3</sub> ) <sub>2</sub> CH	27
	(CH <sub>3</sub> ) <sub>3</sub> C	1

25. In each of the following pairs, determine whether the two represent resonance forms of a single species or depict different substances. Also indicate the formal charges on all the atoms in each structure. [4 marks]



26. Match each of the following transformations to the correct reaction profile shown here, and draw the structures present at all points on the energy curves marked by the capital letters (A, B, J, L and N). [4 marks]

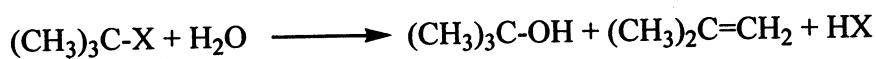


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27. Match column A (reactions) with the appropriate entries from column B and C (MOs involved in the reaction, geometry, mechanism, *etc*). [3 marks]

Column A	Column B	Column C
1. $\text{H}^- + \text{BH}_3$	(a) Elimination bimolecular	(a) LUMO: $\pi^*$ orbital
2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KOC}(\text{CH}_3)_3$	(b) Nucleophile approaches the electrophilic centre at $109^\circ$ angle	(b) Alkene
3. $\text{CH}_3\text{CH}_2\text{ONa} + \text{CH}_3\text{CHO}$	(c) HOMO: filled s orbital	(c) LUMO: Non-bonding p orbital

28. As a part of the Master's project, a student was given the task of investigating the hydrolysis of three t-butyl halides as shown in the table below. [4 marks]



Alkyl halide	Ratio Substitution:Elimination
1. $(\text{CH}_3)_3\text{CCl}$	95:5
2. $(\text{CH}_3)_3\text{CBr}$	95:5
3. $(\text{CH}_3)_3\text{CI}$	96:4

The following observations were noted by him.

(a) The ratio of the substitution and elimination products was practically same for all the three alkyl halides.

(b) One of alkyl halides reacted faster than the other two.

Do you think the observations (a) and (b) are correct? Explain your answer.

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