

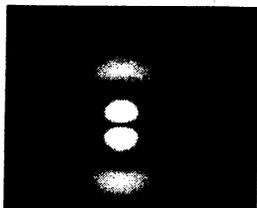
Answer all questions

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) SbBr_5
 B) PBr_5
 C) BiBr_5
 D) NCl_3

8. Which of the following chlorine oxide is paramagnetic?

- A) OCl_2
 B) ClOOCl
 C) ClO_2
 D) Cl_2O_7

9. Arrange the following Lewis Bases according to their increasing base strength for the Lewis Acid BBr_3 .

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

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°C
 D) Structure consists of discrete P_4 tetrahedra.

11. Which of the following reacts by the 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 sp^3 -hybridized atom?

- (a) CH_3^+ (b) $\text{H}_2\text{C}=\text{OH}^+$ (c) H_3O^+ (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.

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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)

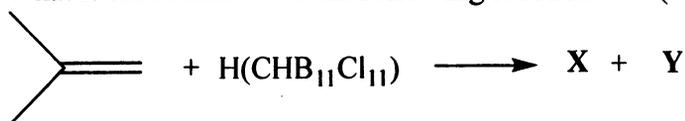
Fill in the blanks of the message using the following clues:

- (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 $MOCl$. 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 $X(OH)_6$ where X is the group 16 element.
- (6) Symbol for the element that has a boiling point of 445°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 KX_2 is used in space stations to remove 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 (P_4) can be partially oxidized to P_4O_6 and fully oxidized to P_4O_{10} . Draw the structure of P_4O_6 and P_4O_{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 (kJ mol^{-1}) are given below: [6 marks]

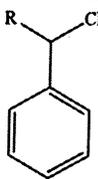
| | |
|-------------|-----------|
| C-C (346) | N-N (167) |
| Si-Si (222) | P-P (201) |

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

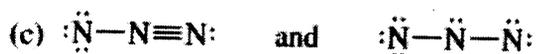
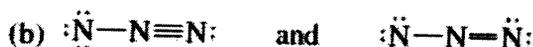
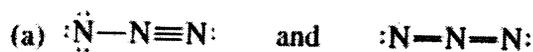
- (i) Explain why the bond energies in group 14 elements decrease as we go down a group?
- (ii) Why this trend is not followed in group 15 elements?

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]

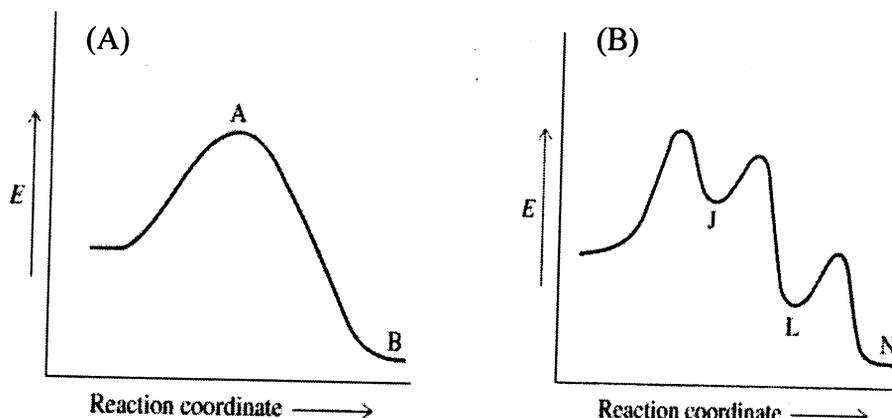
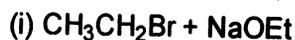
24. Explain the relative rates of the following compounds in the S_N1 reaction. [3 marks]

| | R | Relative rate |
|---|------------------------------------|---------------|
|  | CH ₃ | 540 |
| | CH ₃ CH ₂ | 125 |
| | (CH ₃) ₂ CH | 27 |
| | (CH ₃) ₃ 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. [3 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]

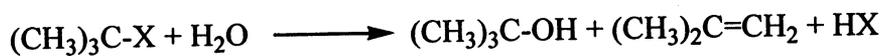


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27. Match column A (reactions) with the appropriate entries from column B and C (MOs involved in the reaction, geometry, mechanism, etc). [3 marks]

| Column A | Column B | Column C |
|-----------------------------------|--|---------------------------------|
| 1. $H^- + BH_3$ | (a) Elimination bimolecular | (a) LUMO: π^* orbital |
| 2. $CH_3CH_2CH_2Br + KOC(CH_3)_3$ | (b) Nucleophile approaches the electrophilic centre at 109° angle | (b) Alkene |
| 3. $CH_3CH_2ONa + CH_3CHO$ | (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. $(CH_3)_3CCl$ | 95:5 |
| 2. $(CH_3)_3CBr$ | 95:5 |
| 3. $(CH_3)_3CI$ | 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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