SET 1

Section A: 2.5 Marks

- 1. Pyrophosphoric acid $(H_4P_2O_7)$ and pyrophosphorous acid $(H_4P_2O_5)$ are oxyacids of phosphorous. The number of P–OH bonds present in pyrophosphoric acid and pyrophosphorous acid, respectively, are
 - A. 4, 3
 - B. 4, 4
 - C. 4, 2
 - D. 2,4
- 2. The pair of molecules having the same shape is
 - A. PF_5 and BrF_5
 - B. O₃ and I_3^-
 - C. BF₃ and ClF₃
 - D. XeO_3 and PF_3
- 3. Boron on reaction with fluorine forms \mathbf{P} , which on reaction with NaH at a high temperature produces \mathbf{Q} along with a sodium salt. \mathbf{P} on reaction with NH₃ in 1:1 ratio gives \mathbf{R} . \mathbf{Q} on reaction with NH₃ in 1:2 ratio at an elevated temperature gives \mathbf{S} . The correct statement is
 - A. B-N bond in **R** is covalent in nature.
 - B. All B–H bonds in **Q** are equivalent.
 - C. The shape of **S** is tetrahedral.
 - D. Compound \mathbf{Q} when dissolved in water gives an acid.

4. Among the following graphs, the one that represents the correct trend in the third ionization energy of lanthanum and the lanthanoids is



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- 5. The ground state electronic energy of He atom (E_{He}) can be expressed in terms of the ground state energy of the hydrogen atom (E_{H}) and the electron-electron interaction energy (E_{ee}) in the He atom. If E_{ee} is equal to x times the magnitude of E_{H} , then E_{He} is given by
 - A. $E_{\text{He}} = 4E_{\text{H}} + xE_{\text{H}}$
 - B. $E_{\text{He}} = 2(4E_{\text{H}} + xE_{\text{H}})$
 - C. $E_{\text{He}} = 8E_{\text{H}} xE_{\text{H}}$
 - D. $E_{\text{He}} = 8E_{\text{H}} + xE_{\text{H}}$
- 6. Consider a metal crystal with simple cubic, fcc, and bcc structures. Assume that the nearest neighbour atoms (spheres) touch each other in the unit cells. The correct statement is
 - A. The percentage of the void space in different crystal structures follow the order: fcc < bcc < simple cubic.
 - B. The number of atoms in the unit cell are 14, 9 and 8 for fcc, bcc and simple cubic structures, respectively.
 - C. The lowest percentage of the void space among the three crystal structures is approximately 48%.
 - D. The percentage of the void space in any of the above crystal structures will depend on the lattice parameter and hence cannot be predicted without the knowledge of the lattice parameter.

- 7. A certain amount (*n* moles) of a monoatomic ideal gas changes from an initial state X (P_1 , V_1 , T_1) to a final state Y (P_2 , V_2 , T_2). Let ΔU , ΔH , and ΔS represent the changes in internal energy, enthalpy, and entropy, respectively in this process. The correct expression is
 - A. $\Delta H = \Delta U + P_2(V_2 V_1).$
 - B. $\Delta H = \Delta U + P_2(V_2 V_1) + V_2(P_2 P_1)$
 - C. $\Delta S = C_v \ln(T_2/T_1) + nR \ln(V_2/V_1)$
 - D. $\Delta S = (3/2)(P_1V_1/T_1)\ln(T_2/T_1) + (P_2V_2/T_2)\ln(V_2/V_1)$
- 8. A mixture of 0.1 mol of a weak acid HX and 0.2 mol of another weak acid HY is dissolved in 1 kg of water. The degrees of ionization of the two acids HX and HY in the final solution are 0.1 and 0.2, respectively. Assuming Rault's law to be valid, the elevation of boiling point (ΔT_b) , in terms of the boiling point elevation constant (K_b), is given by
 - A. $\Delta T_b = 0.25 K_b$
 - B. $\Delta T_b = 0.35 K_b$
 - C. $\Delta T_b = 0.30 K_b$
 - D. $\Delta T_b = 0.32K_b$
- 9. When levorotatory 2-methylbutan-1-ol (**P**) is heated with concentrated HCl, dextrorotatory 1-chloro-2-methylbutane (**Q**) is formed. The correct statement is
 - A. **P** and **Q** have identical absolute configuration.
 - B. The reaction takes place at the asymmetric centre.
 - C. The reaction involves a carbocationic intermediate.
 - D. If the concentration of \mathbf{P} is doubled, keeping the concentration of HCl unchanged, the rate of the reaction does not change.

10. In the reaction shown below,



the major hydrocarbon product is



11. Among the following pairs,



the pairs that represent resonance structures are

- A. P, Q and R
- B. Q, R and S
- C. \mathbf{Q} and \mathbf{S}
- D. $\boldsymbol{R} \text{ and } \boldsymbol{S}$

12. In the reaction shown below,



Section B: 4 Marks

- 13. The reaction of the alkali metals with oxygen results in the formation of different alkali metal oxides, monoxides, peroxides and superoxides. These oxides have interesting chemical properties and applications. The ease of formation and stability of these oxides depend mainly on the charge and size of the alkali metals in relation to the size of the anions. In an application like in a space suit, a chemical may be used which gives oxygen and also absorbs carbon dioxide from exhalation. In this context, the correct statement(s) is(are):
 - A. The order of the stability of alkali metal monoxides is $Li_2O < Na_2O < K_2O$.
 - B. Superoxide formation decreases down the group.
 - C. Na_2O_2 on reaction with CO_2 gives Na_2CO_3 and itself gets oxidized to oxygen.
 - D. Potassium superoxide can be used in a space suit.
- 14. Negatively charged monodentate strong field ligand (X^-) and weak field ligand (Y^-) form complexes $[MnX_6]^{4-}$ and $[MnY_6]^{4-}$, respectively, under certain reaction conditions. Let the crystal field splitting energy for $[MnX_6]^{4-}$ and $[MnY_6]^{4-}$ be $(\Delta_0)_1$ and $(\Delta_0)_2$, respectively. The correct statement(s) is(are):
 - A. Electron pairing energy in $[MnX_6]^{4-}$ is smaller than $(\Delta_0)_1$.
 - B. $[MnY_6]^{4-}$ is more stabilized than $[MnX_6]^{4-}$.
 - C. The t_{2g} orbitals in $[MnX_6]^{4-}$ are stabilized by $2(\Delta_0)_1$ as compared to degenerate *d* orbitals.
 - D. $[MnY_6]^{4-}$ is intense in colour as compared to $[MnX_6]^{4-}$.
- 15. The bonding in the species HeH can be studied in a way similar to that of the H₂. The correct statement(s) is(are):
 - A. The dipole moment of HeH is larger than that of H_2^+ .
 - B. Among HeH, HeH^+ , and HeH^{2+} , the species that is most stable is HeH^{2+} .
 - C. Among HeH, HeH⁻, and HeH⁺, the system with the smallest bond length is HeH⁺.
 - D. HeH⁺ has symmetrical distribution of electrons about the bond axis.

- 16. The hydrolysis of sucrose in excess acid solution follows first-order kinetics and results in D-glucose and D-fructose. Since, sucrose, D-glucose, and D-fructose are optically active compounds, the progress of the reaction can be monitored by measuring the angle of rotation of the polarized light in a polarimeter at different times. In a certain experiment, 1 L of 0.1 M sucrose solution is hydrolyzed and the angle of rotation (R_t) is measured at different times (t). Let $R_0 = 25^\circ$, $R_\infty = -15^\circ$, and $R_{30} = 5^\circ$ be the angles of rotation at times $t = 0 \min$, $t = \infty$, and $t = 30 \min$ respectively. The concentration of sucrose at time t is proportional to the change in the angle of rotation ($R_t R_\infty$). Molecular mass of sucrose is 342.3 g/mol. The correct statement(s) is(are):
 - A. The half-life of the reaction is 15 min.
 - B. The rate constant (*k*) is $3.85 \times 10^{-4} \text{ s}^{-1}$.
 - C. The mass of sucrose hydrolysed in 60 min is 25.6 g.
 - D. The rate of the reaction at 30 min is $1.925 \times 10^{-5} \text{ Ms}^{-1}$.
- 17. Consider the following mechanism of a reaction.



The correct statement(s) is(are):

- A. The same mechanism will operate, if compound **P** does not have one of the methyl groups.
- B. The reaction involves both oxidation and reduction of **P**.
- C. The equilibrium is favoured towards products **T** and **W** because **T** and **W** are weaker conjugate base and acid as compared to **R** and **S** respectively.
- D. Hydride is a nucleophile in the reaction of \mathbf{Q} with \mathbf{P} .