

Time: 2 Hours

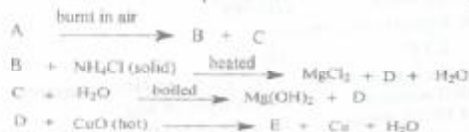
Full Marks: 100

Answer all questions

1. Choose A, B, C or D as the correct answer (no explanation needed): 1x10
- The maximum number of 3d electrons having spin quantum number  $s = +\frac{1}{2}$  is  
(A) 10 (B) 5 (C) 2 (D) 1
  - The solubility of  $As_2S_5$  is  $x$  moles/litre. Its solubility product is  
(A)  $6x^2$  (B)  $64x^4$  (C)  $108x^5$  (D)  $36x^5$
  - Which of the following ions has the highest ionic radius?  
(A)  $Na^+$  (B)  $O^{2-}$  (C)  $F^-$  (D)  $N^{3-}$
  - Which of the following would decrease the pH of 25 cm<sup>3</sup> of a 0.01 M HCl solution?  
(A) addition of 25 cm<sup>3</sup> of a 0.2 M HCl solution (B) addition of Mg  
(C) addition of 25 cm<sup>3</sup> of a 0.005 M HCl solution (D) none of these
  - At NTP 1.0 mole of  $H_2$  and 1.0 mole of He gas have  
(A) equal molecular speed (B) equal kinetic energy  
(C) different volume (D) equal diffusion rate
  - In hydrogen atom the angular momentum of the electron will increase with the increase of  
(A) velocity (B) kinetic energy (C) radius of the orbit (D) none of these
  - Concentrated nitric acid can be stored in a container made up of  
(A) Cu (B) Ag (C) Mg (D) Al
  - Both polar and nonpolar bonds are present in  
(A)  $H_2O_2$  (B)  $NH_3$  (C)  $NH_2OH$  (D)  $PCl_3$
  - The standard reduction potentials for monovalent cations of P, Q, R and S are +0.5, -2.5, -1.5 and -1.0 volts, respectively. Which has the highest reducing power?  
(A) P (B) Q (C) R (D) S
  - $K_{sp}$  for AgCl in water at 25°C is  $1.8 \times 10^{-10}$ . If  $10^{-5}$  mole of  $Ag^+$  is added to the solution,  $K_{sp}$  will be  
(A)  $1.8 \times 10^{-10}$  (B)  $1.8 \times 10^{-5}$  (C)  $1.8 \times 10^{-10}$  (D) none of these
2. Identify the species having the highest and the lowest values of the indicated properties mentioned in the parentheses (write highest first): 2x5
- $HO^-$ ,  $H_2O$ ,  $H^+$ ,  $H_3O^+$  (basicity)      ii)  $CO_3^{2-}$ ,  $CH_3COO^-$ ,  $CO$ ,  $CO_2$  (C-O bond length)
  - B, C, N, O (first ionization energy)      iv) HCl,  $NH_4Cl$ , NaCl, NaCN (pH of the aqueous solution)
  - $Zn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  (number of unpaired electrons)
3. a) Write the c.g.s. unit of
- $n^3h^2/4\pi^2me^2$  ( $n$  is an integer,  $h$  is Planck's constant,  $m$  is the mass of the electron and  $e$  is the electronic charge) 2+2
  - $\sqrt{3P/d}$  ( $P$  is the pressure and  $d$  is the density of a gas) 2
- b) Complete the following: 2
- $${}_{15}^{30}P \longrightarrow ? + {}_{+1}^0e \quad ; \quad {}_{51}^{129}ICl_4^- \longrightarrow {}_{54}^{129}XeCl_4^+ ?$$
- c) Identify the species having the highest and the lowest electronegativity from the following: 2
- $Li^+$ ,  $Mg^{2+}$ ,  $F$ ,  $F^-$
- d) Draw only the plot of PV vs P at constant temperature for one mole of 2
- ideal gas and
  - van der Waals gas
4. a) Calculate  $\Delta G^\circ$  of the following cell reaction at 25°C: 3
- $$Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2 \quad (\text{Given, at } 25^\circ C, E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ Volt})$$
- b) At 25°C a first order reaction is 20% complete in 20 minutes. Calculate the half-life of the reaction at 25°C. 3
- c) What will be the effect on the equilibrium constant for the reaction (no explanation needed) 3
- $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad ; \quad \Delta H^\circ = -22.4 \text{ kcal}$$
- when i) pressure is increased at constant temperature ii) concentration of  $N_2$  is increased at constant temperature iii) temperature is raised at equilibrium?
- Calculate the standard enthalpy of formation of  $NH_3$  gas. 4

5. a) A certain ion  $A^{n+}$  is oxidized successively to  $AO_2^{2+}$  and  $AO_4^-$  by a powerful oxidizing agent. If the number of moles of the oxidizing agent required in two successive steps of oxidation for equimolar quantities of the reductants are in the ratio 4:1, find the value of  $n$ . 3
- b) If  $r_n$  be the radius of the  $n^{\text{th}}$  orbit of a hydrogen-like system of atomic number  $z$  and if  $a_0$  be the first Bohr radius of hydrogen atom, then show that  $r_n = n^2 a_0/z$ . 3
- c) A, B, C and D are the four elements in the same period in the periodic table having the following characteristics: i) A has the highest second ionization energy and D has the highest electronegativity in the period ii) B is diamagnetic and contains  $s$  electrons only iii) C is a paramagnetic electronegative element which contains same number of  $s$  and  $p$  electrons. Identify A, B, C and D. 4

6. a) Write the formulae of the compounds A to E in the following transformations: 5



- b) The density of a definite amount of neon enclosed in a container at 1 atm and  $27^\circ\text{C}$  is  $1.0 \times 10^{-2}$  g/mL. Calculate its density at 2 atm and  $327^\circ\text{C}$  (assume ideal behaviour). 3
- c) In the compound  $\text{CrO}_5$ , Cr is present in  $+6$  oxidation state. In acid medium the compound decomposes as  $4\text{CrO}_5 + 12\text{H}^+ \rightleftharpoons 4\text{Cr}^{3+} + 6\text{H}_2\text{O} + 7\text{O}_2$ . What is the value of  $n$ ? 2

7. a) An aqueous solution of urea has a boiling point  $100.18^\circ\text{C}$ . Calculate the freezing point of the above solution. Given,  $K_f = 1.86$ ,  $K_b = 0.52$  for water in the same unit. 3
- b) Indicate the change (increase/decrease) of entropy in the following cases: i) melting of a solid ii) expansion of a gas at constant temperature iii) polymerization (*no explanation needed*). 3
- c) In which of the following cases, a reaction is possible at any temperature? Give reason. 2
- i)  $\Delta H < 0$ ,  $\Delta S > 0$  ii)  $\Delta H > 0$ ,  $\Delta S < 0$
- d) The concentrations of A, B and C in the reaction below are 0.03, 0.01 and 0.008 mole/litre respectively at equilibrium. Calculate the initial concentrations of A and B. 2



8. a) Give the molecular formula of an unsaturated carboxylic ester containing  $n$  carbons and one carbon-carbon double bond. 2
- b) Write the structure of the simplest saturated  $3^\circ$  aliphatic amine having three kinds of nonequivalent hydrogens. 2
- c) Give the structure of bromoacetyl bromide. 2
- d) In propene molecule, what is the maximum number of atoms that can be coplanar? 2
- e) Which of the following would give a new white solid (acidic in nature) on reaction with benzamide? 2
- $\text{P}_2\text{O}_5$ ,  $\text{HNO}_2$ ,  $\text{I}_2$ ,  $\text{SO}_2\text{Cl}_2$

9. a) Hydrocarbon A ( $\text{C}_8\text{H}_8$ ) on ozonolysis furnishes two aldehydes B and C, each of which undergoes Cannizzaro reaction. Give the structures of A, B and C. 4
- b) Convert showing intermediate structures: 3x2
- i)  $\text{CH}_3\text{CH}=\text{CHBr} \longrightarrow \text{CH}_3\text{CH}=\text{CHD}$  (in two steps)
- ii) Benzene  $\longrightarrow$  Phenylacetylene (using the reagents:  $\text{NaNH}_2$ , anhyd.  $\text{AlCl}_3$ ,  $\text{PCl}_5$ ,  $\text{CH}_3\text{COCl}$ )
10. a) Compound X ( $\text{C}_2\text{H}_4\text{O}$ ) on treatment with dil.  $\text{NaOH}$  produces Y. Both X and Y give iodoform test. Y on heating with alkali affords Z which gives positive Tollens' test but does not respond to iodoform test. Write the structures of X, Y and Z. Give the equation for the iodoform reaction of Y showing the structures of the products. 5

- b) Give the structures of P, Q, R, S and T in the following reactions: 5

