

**IIT-JEE-Chemistry-1997****Time : Three Hours****Max. Marks : 100****Instructions:**

1. Answer all questions in the language of your choice as shown in your admit card.
2. The paper consists of eight printed pages 10 questions.
3. Answer to next question should start after drawing a separating horizontal line with a in the question paper.
4. All sub-questions of a question should be answered at one place in the same order as in the question paper.
5. There is no negative marking.
6. Use of all type of calculating devices, graph paper, trigonometric/statistical tables is prohibited.
7. Use of Lagarithmic Tables is permitted.

**Useful Data:**

Avogadro constant,	$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$
Faraday constant,	$F = 96500 \text{ C mol}^{-1}$
Gas constant,	$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$
	or
	$R = 0.082 \text{ dm}^{-3} \text{ atm K}^{-1} \text{ mol}^{-1}$
Relative atomic masses:	$H = 1.0; O = 16.0$
	$Cl = 35.5; Cr = 51.99; Ag = 107.8$
Atomic numbers	$Na = 11; Mg = 12$
	$V = 23; Cu = 29; Ag = 47$

1. There are fifteen sub-questions in this question. For answering each sub-question, four alternatives are given, and only one of them is correct. Indicate your answer for each sub-question by writing one of the letters A, B, C or D only in the answerbook.

(i) For a d-electron, the orbital angular momentum is :

- (A)  $\sqrt{6} (h/2\pi)$  (B)  $\sqrt{2} (h/2\pi)$   
(C)  $(h/2\pi)$  (D)  $2 (h/2\pi)$

(ii) The standard reduction potentials of  $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Cu}^{2+}|\text{Cu}^+$  are 0.337 V and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^+|\text{Cu}$  half cell is:

- (A) 0.184 V (B) 0.827 V  
(C) 0.521 V (D) 0.490 V

- (iii) The compressibility factor for an ideal gas is :  
(A) 1.5 (B) 1.0  
(C) 2.0 (D)  $\infty$
- (iv) Which contains both polar and non-polar bonds :  
(A)  $\text{NH}_4\text{Cl}$  (B)  $\text{HCN}$   
(C)  $\text{H}_2\text{O}_2$  (D)  $\text{CH}_4$
- (v) The critical temperature of water is higher than that of  $\text{O}_2$  because the  $\text{H}_2\text{O}$  molecule has :  
(A) fewer electrons than  $\text{O}_2$  (B) two covalent bonds  
(C) V-shape (D) dipole moment.
- (vi) Which one of the following species is not a pseudohalide:  
(A)  $\text{CNO}^-$  (B)  $\text{RCOO}^-$   
(C)  $\text{OCN}^-$  (D)  $\text{NNN}^-$
- (vii) Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is :  
(A)  $\text{CrO}_3$  (B)  $\text{Cr}_2\text{O}_3$   
(C)  $\text{Cr}$  (D)  $\text{CrO}(\text{O}_2)$ .
- (viii) Which one of the following compounds has  $\text{sp}^2$  - hybridization :  
(A)  $\text{CO}_2$  (B)  $\text{SO}_2$   
(C)  $\text{N}_2\text{O}$  (D)  $\text{CO}_2$
- (ix) The number of moles  $\text{KMnO}_4$  that will be needed to react with one mole of sulphite ion in acidic solution is :  
(A)  $2/5$  (B)  $3/5$   
(C)  $4/5$  (D) 1
- (x) Which of the following compounds is expected to be coloured :  
(A)  $\text{Ag}_2\text{SO}_4$  (B)  $\text{CuF}_2$   
(C)  $\text{MgF}_2$  (D)  $\text{CuCl}$
- (xi) How many optically active stereoisomers are possible for butane-2, 3-diol:  
(A) 1 (B) 2  
(C) 3 (D) 4
- (xii) When cyclohexane is poured on water, it floats, because :  
(A) cyclohexane is in 'boat' form  
(B) cyclohexane is in 'chair' form  
(C) cyclohexane is in 'crown' form  
(D) cyclohexane is less dense than water.

(xiii) Which of the following is an organometallic compound :

- (A) Lithium methoxide (B) Lithium acetate  
(C) Lithium dimethylamide (D) Methyl lithium.

(xiv) In the reaction p-chlorotoluene with  $\text{KNH}_2$  in liq.  $\text{NH}_3$ , the major product is :

- (A) o-toluidine (B) m-toluidine  
(C) p-toluidine (D) p-chloroaniline

(xv)  $(\text{CH}_3)_3\text{CMgCl}$  on reaction with  $\text{D}_2\text{O}$  produces:

- (A)  $(\text{CH}_3)_3\text{CD}$  (B)  $(\text{CH}_3)_3\text{OD}$   
(C)  $(\text{CD}_3)_3\text{CD}$  (D)  $(\text{CD}_3)_3\text{OD}$

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(C)  $(\text{CD}_3)_3\text{CD}$  (D)  $(\text{CD}_3)_3\text{OD}$

2. Fill in the blanks (write only your answers in the answer book sequentially) :

(a) In the Arrhenius equation,  $k = A \exp(-E/RT)$ , A may be termed as the rate constant at .....

(b) When  $\text{Fe}(s)$  is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .....

(c) A liquid which is permanently supercooled is frequently called a .....

(d) Enthalpy is an ..... property.

(e) In the reaction  $\text{I}^- + \text{I}_2 \rightarrow \text{I}_3^-$ , the Lewis acid is .....

(f) Silver jewellery items tarnish slowly in the air due to their reaction with .....

(g) Compounds that formally contain  $\text{Pb}^{4+}$  are easily reduced to  $\text{Pb}^{2+}$ . The stability of the lower oxidation state is due to .....

(h) Glycerine contains one ..... hydroxy group.

- (i) 1, 3-Butadiene with bromine in molar ratio generates predominantly .....  
(j) Vinyl chloride on reaction with dimethyl copper gives .....

3. (a) A sample of AgCl was treated with 5.00 mL of 1.5 M Na<sub>2</sub>CO<sub>3</sub> solution to give Ag<sub>2</sub>CO<sub>3</sub>. The remaining solution contained 0.0026 g of Cl<sup>-</sup> per litre. Calculate the solubility product of Ag Cl [K<sub>sp</sub> (Ag<sub>2</sub>CO<sub>3</sub>) = 8.2 × 10<sup>-12</sup>]

(b) The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log (k/s^{-1}) = 14.34 - (1.25 \times 10^4 K) / T$$

- (i) What is the energy of activation for this reaction ?  
(ii) At what temperature will its half-life period be 256 minutes?

4. (a) Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 35 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

Average bond energies : C—H, 415 kJ/mol

C—O, 356 kJ/mol

O—H, 463 kJ/mol

(b) To a 25 mL H<sub>2</sub>O<sub>2</sub> solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H<sub>2</sub>O<sub>2</sub> solution.

5. (a) Write balanced equations for the following :

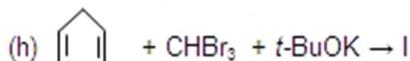
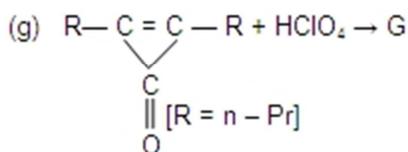
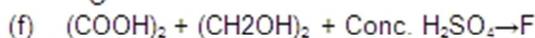
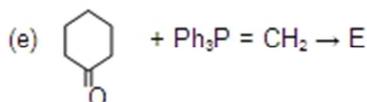
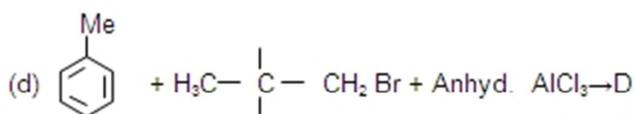
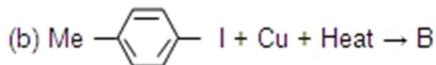
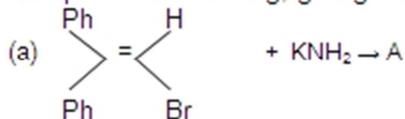
- (i) Phosphorus is treated with concentrated nitric acid.  
(ii) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.  
(iii) Manufacture of phosphoric acid from phosphorus.  
(iv) Reaction of aluminium with aqueous sodium hydroxide.  
(v) Reaction of zinc with dilute nitric acid.

(b) Write the formulae of the following complexes:

- (i) Pentamminechlorocobalt (III)  
(ii) Lithium tetrahydroaluminate (III).

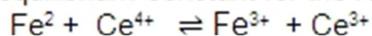
(c) Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide. Identify A, B, C and D.

6. Complete the following, giving the structures of the principal organic products :



7. (a) How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in + 1 oxidation state of period of 8.0 hours at a current of 8.6 Amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm<sup>3</sup>.

(b) Calculate the equilibrium constant for the reaction



(given  $E^{\ominus}_{\text{Ce}^{4+}|\text{Ce}^{3+}} = 1.44\text{V}$ ;  $E^{\ominus}_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.68\text{V}$ )

(c) Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm<sup>3</sup>?

(d) An acid type indicator,  $\text{HIn}$  differs in colour from its conjugate base ( $\text{In}^-$ ). The human eye is sensitive to colour differences only when the ratio  $[\text{In}^-] / [\text{HIn}]$  is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change

( $K_a = 1.0 \times 10^{-5}$ )?

8. (a) A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound.

(b) A soluble compound of poisonous element M, when heated with  $\text{Zn}/\text{H}_2\text{SO}_4$ , gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N.

(c) Between  $\text{Na}^+$  and  $\text{Ag}^+$ , which is a stronger Lewis acid and why?

(d) The crystalline salts of alkaline earth metals contain more water of crystallization than the corresponding alkali metal salts. Why?

(e) Anhydrous  $\text{AlCl}_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.

(Ionisation energy for  $\text{Al} = 5137 \text{ kJ mol}^{-1}$ ;  $\Delta H_{\text{hydration}}$  for  $\text{Al}^{3+} = 4665 \text{ kJ mole}^{-1}$ ;  $\Delta H_{\text{hydration}}$  for  $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$ )

9. (a) Acetophenone on reaction with hydroxylamine-hydrochloride produce two isomeric oximes. Write structures of the oximes.

(b) 2, 2-Dimethyloxirane can be cleaved by acid ( $\text{H}^+$ ). Write mechanism.

(c) Which of the following is the correct method for synthesizing methyl-t-butyl ether and why?

(i)  $(\text{CH}_3)_3\text{CBr} + \text{NaOMe} \rightarrow$

(ii)  $(\text{CH}_3)_3\text{COH} + \text{NaO}-t\text{-Bu} \rightarrow$

(d) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why?

(e) The hydrocarbon, A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with  $\text{KMnO}_4$ , a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain.

**10.** (a) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction.

(b) Arrange the following ions in order of their increasing radii:  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Al}^{3+}$

(c) Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability :  $\text{BeSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{SrSO}_4$

(d) Write a balanced equation for the reaction  $^{14}\text{N}$  with  $\alpha$ -particle.