

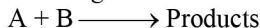
# Solutions to IITJEE-2004 Mains Paper

## Chemistry

Time: 2 hours

Note: Question number 1 to 10 carries 2 marks each and 11 to 20 carries 4 marks each.

1. For the given reaction



Following data were given

Initial conc. (m/L).	Initial conc. (m/L)	Initial rate $[\text{mL}^{-1}\text{s}^{-1}]$
[A]	[B]	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

- Write the rate equation.
- Calculate the rate constant.

Sol. a) Let the order w.r.t A & B are x any y respectively

$$r = K[A]^x [B]^y$$

$$0.05 = K[0.1]^x [0.1]^y$$

$$0.1 = K[0.2]^x [0.1]^y$$

$$\text{or } 2 = [2]^x$$

$$x = 1$$

$$0.05 = K[0.1]^x [0.1]^y$$

$$0.05 = K[0.1]^x [0.2]^y$$

$$1 = [2]^y$$

$$y = 0$$

b) rate equation =  $r = K[A] [B]^0$

$$0.1 = K[0.2]$$

$$K = 0.5 \text{ Sec}^{-1}$$

2. 100 ml of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 ml at this constant pressure. Find the  $\Delta H$  &  $\Delta U$ .

Sol.  $\Delta H = 0$ ,  $\Delta q_p = \Delta U - W$

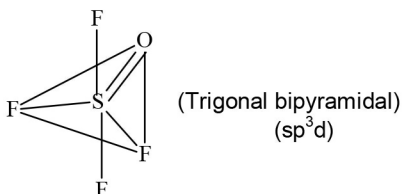
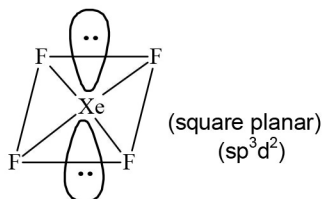
$$W = PdV$$

$$= 100 \times 1 \text{ atmmL}$$

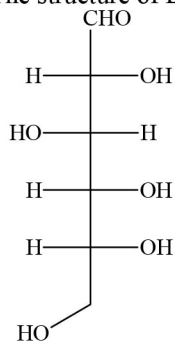
$$= 10^{-2} \text{ KJ} = \Delta U$$

3. Draw the shape of  $\text{XeF}_4$  and  $\text{OSF}_4$  according to VSEPR theory. Show the lone pair of electrons on the central atom

Sol.

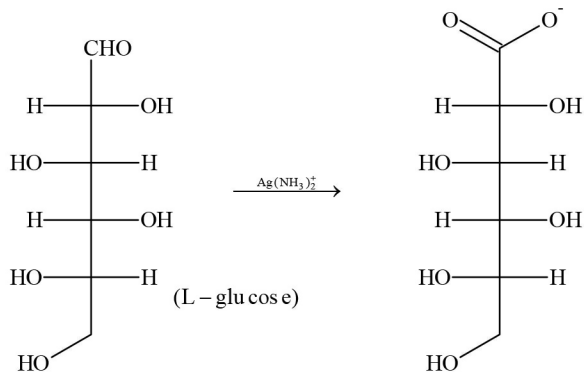


4. The structure of D-Glucose is as follows



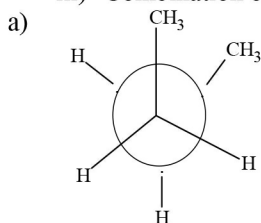
- a) Draw the structure of L – Glucose.  
b) Give the reaction of L – Glucose with Tollens reagent.

**Sol.**



5. a) Draw New mann's projection for the less stable staggered form of butane.  
b) Relatively less stability of the staggered form is due to  
i) Torsional strain.  
ii) Vander Waal's strain.  
iii) Combination of the above two.

**Sol.**



- b) Less stability is due to Vander Waal's strain

6. Arrange the following oxides in the increasing order of Bronsted basicity.



**Sol.**  $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{CO}_2 < \text{B}_2\text{O}_3 < \text{BaO}$

7.  $\text{AlF}_3$  is insoluble in anhydrous  $\text{HF}$  but when little  $\text{KF}$  is added to the compound it becomes soluble. On addition of  $\text{BF}_3$ ,  $\text{AlF}_3$  is precipitated. Write the balanced chemical equations.

**Sol.**  $3\text{KF} + \text{AlF}_3 \longrightarrow \text{K}_3\text{AlF}_6$   
 $\text{K}_3\text{AlF}_6 + 3\text{BF}_3 \longrightarrow \text{AlF}_3 + 3\text{KBF}_4$

8. The crystal AB (rock salt structure) has molecular weight  $6.023 y$  amu. where  $y$  is an arbitrary number in amu.. If the minimum distance between cation & anion is  $y^{1/3} \text{ nm}$  and the observed density is  $20 \text{ Kg/m}^3$ . Find the

- a) density in  $\text{Kg/m}^3$  and  
b) type of defect

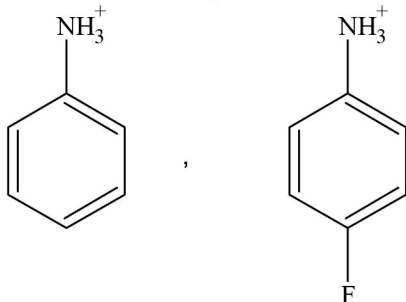
**Sol.** a) 
$$\text{Density} = \frac{4 \times 6.023 \times y}{6.023 \times 10^{23} \times 8 \times y \times 10^{-27}} \quad [\text{Since } a = 2y^{1/3}]$$

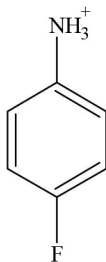
$$= 5 \times 10^3 \text{ g/m}^3$$

$$= 5 \text{ Kg/m}^3$$

b) Since the (density) calculated < density observed, it means the defect is metal excess defect.

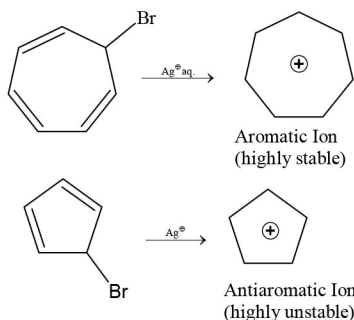
9. Which of the following is more acidic and why?



**Sol.**  is more acidic due to – inductive effect of fluorine

10. 7-bromo-1,3,5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1,3-cyclopentadiene doesn't ionise even in presence of  $\text{Ag}^+$  (aq), Explain.

**Sol.**



11. a) The schrodinger wave equation for hydrogen atoms is

$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/a_0}$$

Where  $a_0$  is Bohr's radius. Let the radial node in 2s be at  $r_0$ . Then find  $r$  in terms of  $a_0$ .

b) A base ball having mass 100 g moves with velocity 100 m/sec. Find out the value of wave length of base ball.

c)  ${}_{92}\text{X}^{234} \xrightarrow[-6\beta]{-7\alpha} \text{Y}$ . Find out atomic number, mass number of Y and identify it.

**Sol.** a)  $\Psi_{2s}^2$  = probability of finding electrons at any place  
 $\therefore \Psi^2 = 0$  at node

$$\therefore \Psi^2 = 0 = \frac{1}{4} \frac{1}{\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^3 \left( 2 - \frac{r}{a_0} \right)^2 \times e^{-r/a_0}$$

$$\left( 2 - \frac{r}{a_0} \right) = 0 \Rightarrow 2 = \frac{r}{a_0} \Rightarrow 2a_0 = r$$

$$\text{b) } \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{100 \times 10^{-3} \times 100}$$

$$\lambda = 6.626 \times 10^{-35} \text{ m} = 6.626 \times 10^{-25} \text{ \AA}$$

$$\text{c) } \text{Y is } {}_{84}\text{Po}^{206}$$

12. On the basis of ground state electronic configuration arrange the following molecules in increasing O-O bond length order.  
 $\text{KO}_2$ ,  $\text{O}_2$ ,  $\text{O}_2[\text{AsF}_6]$ .

**Sol.**  $\text{O}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{matrix} \right\}$

$$\text{bond order} = \frac{10-6}{2} = 2$$

$$\text{O}_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{matrix} \right\} \text{ in } [\text{KO}_2]$$

$$\text{bond order} = \frac{10-7}{2} = \frac{3}{2}$$

$$\text{O}_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{matrix} \right\}$$

$$\text{in } [\text{O}_2(\text{AsF}_6)]$$

$$\text{bond order} = \frac{10-5}{2} = \frac{5}{2}$$

$$\text{Bond length order is } \text{O}_2^+ < \text{O}_2 < \text{O}_2^-$$

13. a) In the following equilibrium  
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$   
 when 5 moles of each are taken, the temperature is kept at 298 K the total pressure was found to be 20 bar. Given that  
 $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 \text{ KJ}$   
 $\Delta G_f^\circ(\text{NO}_2) = 50 \text{ KJ}$   
 i) Find  $\Delta G$  of the reaction  
 ii) The direction of the reaction in which the equilibrium shifts  
 b) A graph is plotted for a real gas which follows Vander Waal's equation with  $PV_m$  taken on Y-axis & P on X-axis. Find the intercept of the line where  $V_m$  is molar volume

**Sol.** a) i)  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$\text{Reaction quotient} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{100}{10} = 10 \text{ atm}$$

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G_f^\circ(\text{NO}_2) - \Delta G_f^\circ(\text{N}_2\text{O}_4)$$

$$0 = 100 - 100$$

$$\Delta G = \Delta G^\circ + RT \ln K$$

$$\therefore \Delta G = RT \ln Q$$

$$= 2.303 \times 0.082 \times 298 \times \log 9.9 = 56.0304 \text{ Lit atm.} = \text{Positive}$$

ii) Therefore reaction will shift towards backward direction.

$$b) \therefore \left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

$$\left( P + \frac{aP^2}{(PV)^2} \right) \left( \frac{PV}{P} - b \right) = RT$$

$$[PV]^2 P + aP^2 [(PV) - b] = P(PV)^2 RT$$

$$\Rightarrow P[(PV)^2 + aP] (PV - bP) = P(PV)^2 RT$$

$$\text{Put } P = 0$$

$$\Rightarrow (PV)^3 = (PV)^2 RT$$

$$\text{Intercept} = RT$$

14. a) 1.22 g  $C_6H_5COOH$  is added into two solvent and data of  $\Delta T_b$  and  $K_b$  are given as:-

i) In 100 g  $CH_3COCH_3$   $\Delta T_b = 0.17$

$K_b = 1.7 \text{ Kg Kelvin/mol}$

ii) In 100 g benzene,  $\Delta T_b = 0.13$  and  $K_b = 2.6 \text{ Kg Kelvin/mol}$

Find out the molecular weight of  $C_6H_5COOH$  in both the cases and interpret the result.

b) 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given  $K_a(HA) = 5 \times 10^{-6}$  and  $\alpha \ll 1$

Sol. a) In first case

$$i) \Delta T_b = K_b \times m$$

$$0.17 = 1.7 \times \frac{1.22}{M \times 100 \times 10^{-3}} \Rightarrow M = 122$$

ii) In second case

$$\Delta T_b = K_b \times m$$

$$0.13 = 2.6 \times \frac{1.22}{M' \times 100 \times 10^{-3}}$$

$$M' = 244$$

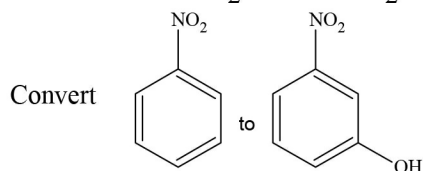
Benzoic acid dimerises in benzene

b) Since at end point molarity of salt =  $\frac{0.1}{2} \text{ M}$

$\therefore$  pH of salt of weak acid and strong base

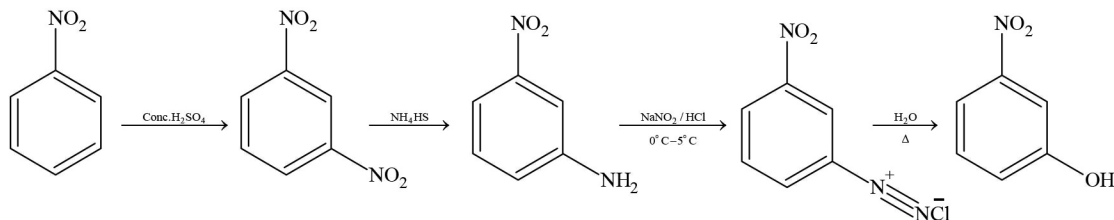
$$pH = \frac{(pK_w + pK_a + \log c)}{2} = \frac{1}{2} [14 + 5.3010 + [-1.3010]] \Rightarrow pH = 9.$$

15.

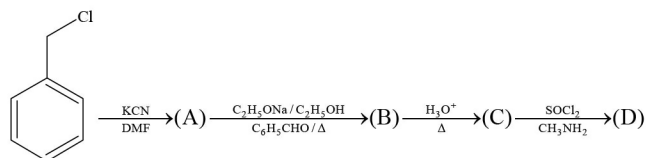


in not more than four steps. Also mention the temp and reaction condition.

Sol.

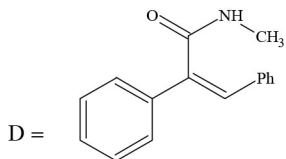
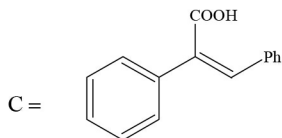
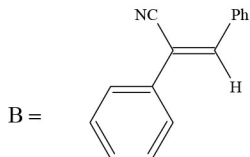
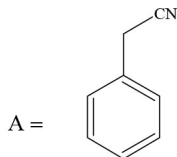


16.

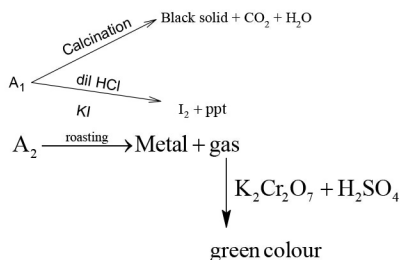


Identify A to D.

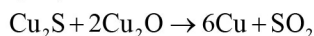
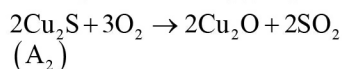
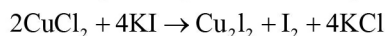
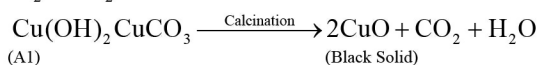
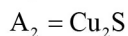
Sol.



17.  $A_1$  &  $A_2$  are two ores of metal M.  $A_1$  on calcination gives black precipitate,  $\text{CO}_2$  & water.



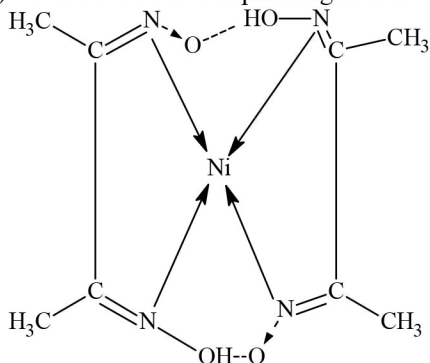
Sol.



18.  $\text{NiCl}_2$  in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of  $\text{NH}_4\text{OH}$ , giving a bright red colour.

- Draw its structure & show H-bonding
- Give oxidation state of Ni & its hybridisation.
- Predict whether it is paramagnetic or diamagnetic.

Sol.



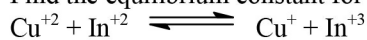
Oxidation state of nickel is +2 and hybridization is  $\text{dsp}^2$

$$\mu_s = \sqrt{n(n+2)} \text{ B.M}$$

$$n = 0$$

$$\therefore \mu_s = 0$$

19. Find the equilibrium constant for the reaction

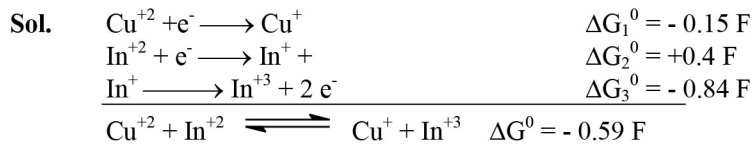


Given that

$$E^{\circ}_{\text{Cu}^{+2}/\text{Cu}^{+}} = 0.15\text{V}$$

$$E^{\circ}_{\text{In}^{+2}/\text{In}^{+}} = -0.4\text{V}$$

$$E^{\circ}_{\text{In}^{+3}/\text{In}^{+}} = -0.42\text{V}$$



$$-nFE^{\circ} = -0.59\text{F}$$

$$-E^{\circ}_{\text{cell}}\text{F} = -0.59\text{F}$$

$$E^{\circ}_{\text{Cell}} = 0.59$$

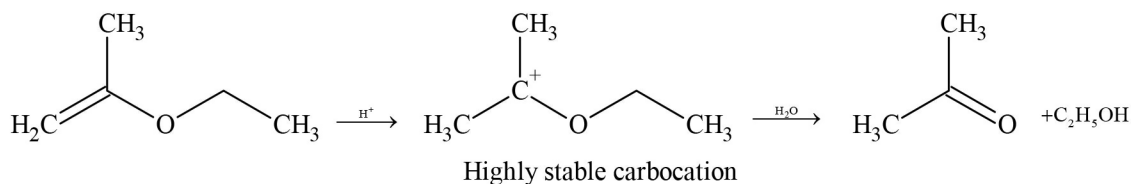
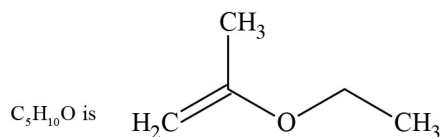
$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log K_c$$

$$0.59 = \frac{0.0591}{1} \log K_c$$

$$K_c = 10^{10}$$

20. An organic compound 'P' having the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  treated with dil  $\text{H}_2\text{SO}_4$  gives two compounds, Q & R both gives positive iodoform test. The reaction of  $\text{C}_5\text{H}_{10}\text{O}$  with dil  $\text{H}_2\text{SO}_4$  gives reaction  $10^{15}$  times faster than ethylene. Identify organic compound of Q & R. Give the reason for the extra stability of P.

**Sol.**



P is stabilized by resonance