FIITJEE *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

$A + B \longrightarrow$ Products

Following data were given

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

a) Write the rate equation.
b) Calculate the rate constant.

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

$r = K[A]^x [B]^y$
$0.05 = K[0.1]^x [0.1]^y$
$0.1 = K[0.2]^x [0.1]^y$
or $2 = [2]^x$
$x = 1$
$0.05 = K[0.1]^x [0.1]^y$
$0.05 = K[0.1]^x [0.2]^y$
$1 = [2]^y$
$y = 0$

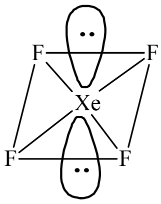
b) rate equation $= r = K[A] [B]^0$
$0.1 = K[0.2]$
$K = 0.5\ Sec^{-1}$

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 ΔH & ΔU.

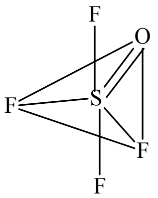
Sol. $\Delta H = 0,\ \Delta q_p = \Delta U - W$
$W = PdV$
$= 100\times 1$ atmmL
$= 10^{-2}$ KJ $= \Delta U$

3. Draw the shape of XeF_4 and OSF_4according to VSEPR theory. Show the lone pair of electrons on the central atom

Sol.

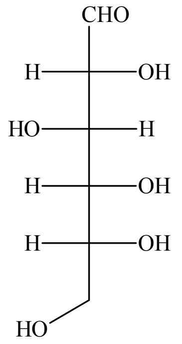


(square planar)
(sp^3d^2)



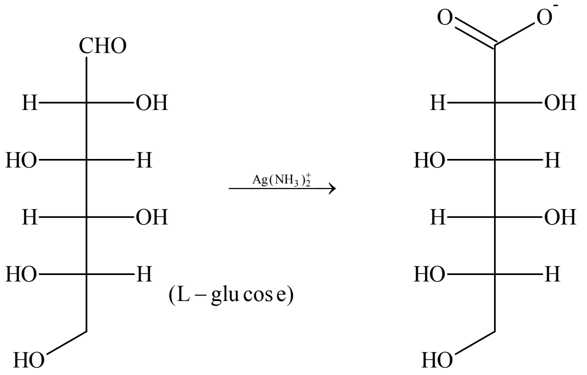
(Trigonal bipyramidal)
(sp^3d)

4. The structure of D-Glucose is as follows



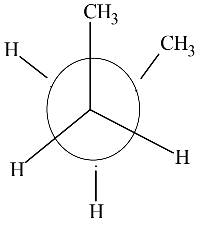
a) Draw the structure of L – Glucose.
b) Give the reaction of L – Glucose with Tollens reagent.

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. a)



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

6. Arrange the following oxides in the increasing order of Bronsted basicity.
Cl_2O_7, BaO, SO_3, CO_2, B_2O_3

Sol. $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$

7. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3 ,AlF_3 is precipitated. Write the balanced chemical equations.

Sol. $3KF + AlF_3 \longrightarrow K_3AlF_6$
$K_3AlF_6 + 3BF_3 \longrightarrow AlF_3 + 3KBF_4$

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 $y^{1/3}$nm and the observed density is $20\,Kg/m^3$. Find the
a) density in Kg/m^3 and
b) type of defect

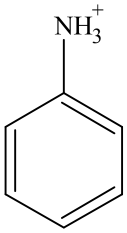
Sol. a) $\text{Density} = \dfrac{4 \times 6.023 \times y}{6.023 \times 10^{23} \times 8 \times y \times 10^{-27}}$ [Since $a = 2y^{1/3}$]

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

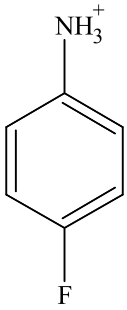
$= 5 \text{Kg/m}^3$

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

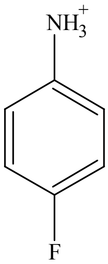
9. Which of the following is more acidic and why?



,



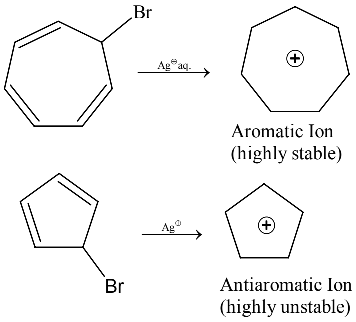
Sol.



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 Ag^+(aq), Explain.

Sol.



Aromatic Ion
(highly stable)

Antiaromatic Ion
(highly unstable)

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

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

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

Sol. a) ψ_{2s}^2 = probability of finding electrons at any place

$\therefore \Psi^2 = 0$ at node

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

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

b) $\lambda = \dfrac{h}{mv} = \dfrac{6.626\times10^{-34}}{100\times10^{-3}\times100}$

$\lambda = 6.626\times10^{-35}$ m $= 6.626\times10^{-25}$ A°

c) Yis ${}_{84}Po^{206}$

12. On the basis of ground state electronic configuration arrange the following molecules in increasing O-O bond length order.
KO_2, O_2, $O_2[AsF_6]$.

Sol. $O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{Bmatrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{Bmatrix}\begin{Bmatrix}\pi^* 2p_y^1 \\ \pi^* 2p_z^1\end{Bmatrix}$

bond order $= \dfrac{10-6}{2} = 2$

$O_2^- \; = \sigma_{1s^2}, \sigma^*{}_{1s^2}, \sigma_{2s^2}, \sigma^*{}_{2s^2}, \sigma_{2P_x^2} \begin{Bmatrix}\pi 2P_y{}^2 \\ \pi 2Pz^2\end{Bmatrix}\begin{Bmatrix}\pi^* 2P_y{}^2 \\ \pi^* 2P_z{}^1\end{Bmatrix}$ in $[KO_2]$

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

$O_2^+ \; = \sigma_{1s^2}, \sigma^*{}_{1s^2}, \sigma_{2s^2}, \sigma^*{}_{2s^2}, \sigma_{2P_x^2} \begin{Bmatrix}\pi 2P_y{}^2 \\ \pi 2Pz^2\end{Bmatrix}\{\pi^* 2p_y{}^1\}$

in $[O_2(AsF_6)]$

bond order $\dfrac{10-5}{2} = \dfrac{5}{2}$

Bond length order is $O_2^+ < O_2 < O_2^-$

13. a) In the following equilibrium
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
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
$\Delta G_f^0(N_2O_4) = 100KJ$
$\Delta G_f^0(NO_2) = 50KJ$
i) Find ΔG 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) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Reaction quotient $= \dfrac{P_{NO_2}^2}{P_{N_2O_4}} = \dfrac{100}{10} = 10$ atm

$\Delta G°$ reaction $= 2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4)$

$0 = 100 - 100$

$\Delta G = \Delta G° + RT\ln k$

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

$= 2.303\times.082\times298\times\log 9.9 = 56.0304$ Lit atm. = Positive

ii) Therefore reaction will shift towards backward direction.

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

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

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

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

Put $P = 0$

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

Intercept = RT

14. a) 1.22 g C_6H_5 COOH is added into two solvent and data of ΔT_b and K_b are given as:-

i) In 100 g CH_3COCH_3 $\Delta T_b = 0.17$
$K_b = 1.7$ Kg Kelvin /mol

ii) In 100 g benzene, $\Delta T_b = 0.13$ and $K_b = 2.6$ 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 Ka(HA)=5×10^{-6} and $\alpha << 1$

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

$\Delta T_b = K_b \times m$

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

$M' = 244$

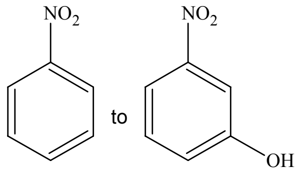
Benzoic acid dimerises in benzene

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

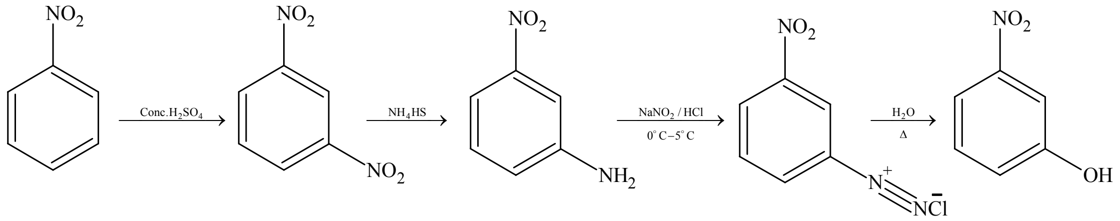
$\because$ pH of salt of weak acid and strong base

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

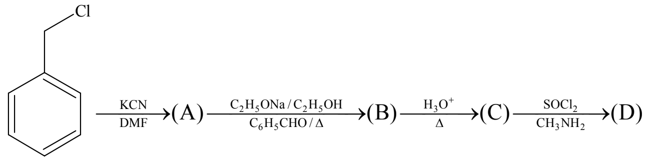
15.

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

Sol.



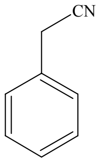
16.



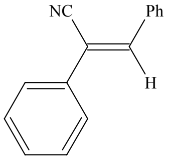
Identify A to D.

Sol.

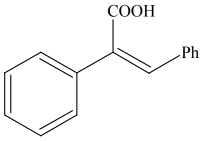
A =



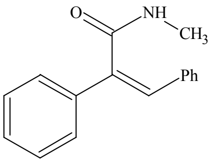
B =



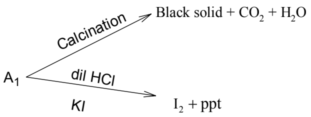
C =



D =



17. A_1 & A_2 are two ores of metal M. A_1 on calcination gives black precipitate, CO_2 & water.



$$A_2 \xrightarrow{\text{roasting}} \text{Metal} + \text{gas} \xrightarrow[]{K_2Cr_2O_7 + H_2SO_4} \text{green colour}$$

Sol. $A_1 = Cu(OH)_2CuCO_3$

$A_2 = Cu_2S$

$$\underset{(A1)}{Cu(OH)_2CuCO_3} \xrightarrow{\text{Calcination}} \underset{\text{(Black Solid)}}{2CuO} + CO_2 + H_2O$$

$$Cu(OH)_2CuCO_3 \xrightarrow{\text{dilHCl}} CuCl_2 + CO_2 + 3H_2O$$

$$2CuCl_2 + 4KI \rightarrow Cu_2I_2 + I_2 + 4KCl$$

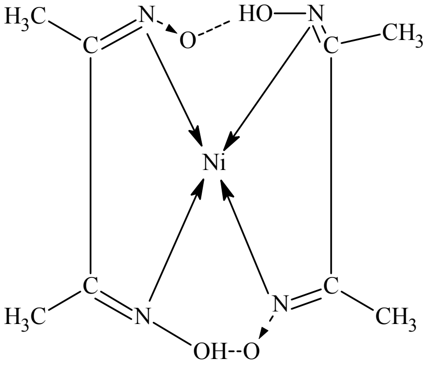
$$\underset{(A_2)}{2Cu_2S} + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

18. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red colour.

a) Draw its structure & show H-bonding
b) Give oxidation state of Ni & its hybridisation.
c) Predict wether it is paramagnetic or diamagnetic.

Sol.



Oxidation state of nickel is +2 and hybridization is dsp^2

$\mu s = \sqrt{n(n+2)}$ B.M

$n = 0$

$\therefore \mu s = 0$

19. Find the equilibrium constant for the reaction
$Cu^{+2} + In^{+2} \rightleftharpoons Cu^{+} + In^{+3}$
Given that

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

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

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

Sol.
$Cu^{+2} + e^{-} \longrightarrow Cu^{+}$ $\quad \Delta G_1^0 = -\ 0.15\ F$
$In^{+2} + e^{-} \longrightarrow In^{+} +$ $\quad \Delta G_2^0 = +0.4\ F$
$In^{+} \longrightarrow In^{+3} + 2\ e^{-}$ $\quad \Delta G_3^0 = -\ 0.84\ F$

$Cu^{+2} + In^{+2} \rightleftharpoons Cu^{+} + In^{+3}$ $\quad \Delta G^0 = -\ 0.59\ F$

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

$$-E^0_{cell}F = -0.59F$$

$$E^0_{Cell} = 0.59$$

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

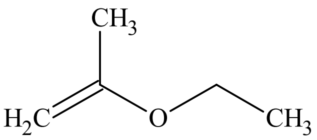
$$0.59 = \frac{0.0591}{1}\log Kc$$

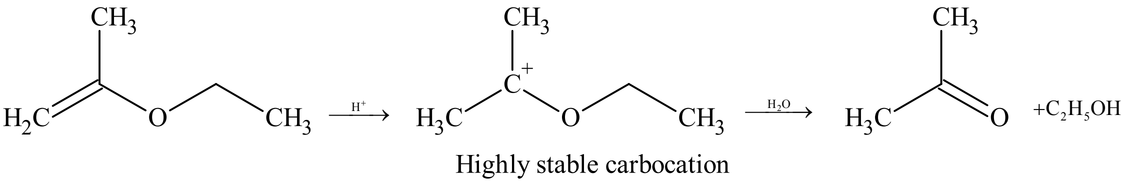
$K_c = 10^{10}$

20. An organic compound ‘P’ having the molecular formula $C_5H_{10}O$ treated with dil H_2SO_4 gives two compounds, Q & R both gives positive iodoform test. The reaction of $C_5H_{10}O$ with dil H_2SO_4 gives reaction 10^{15} times faster then ethylene. Identify organic compound of Q & R. Give the reason for the extra stability of P.

Sol.

$C_5H_{10}O$ is





P is stabilized by resonance

Note: ***FIITJEE solutions to IIT–JEE, 2004 Mains Papers created using memory retention of select FIITJEE students appeared in this test and hence may not exactly be the same as the original paper. However, every effort has been made to reproduce the original paper in the interest of the aspiring students.***