1. For the given reaction
A + B → Products
Following data were given

<table>
<thead>
<tr>
<th>Initial conc. (m/L)</th>
<th>Initial conc. (m/L)</th>
<th>Initial rate [mL⁻¹s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A]</td>
<td>[B]</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a) Write the rate equation.

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 \( 2 = [2]^y \)

\( x = 1 \)

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

\( 1 = [2]^y \)

\( y = 0 \)

b) Calculate the rate constant.

\[ \text{rate equation} = r = K[A]B^y \]
\[ 0.1 = K[0.2] \]
\[ K = 0.5 \text{ Sec}^{-1} \]

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 \( \Delta H \) & \( \Delta U \).

\[ \Delta H = 0, \quad \Delta q_p = \Delta U - W \]
\[ W = PdV \]
\[ = 100 \times 1 \text{ atm} \times 1 \text{ mL} \]
\[ = 10^{-2} \text{ KJ} = \Delta U \]

3. Draw the shape of XeF₄ and OSF₆ according to VSEPR theory. Show the lone pair of electrons on the central atom.

\[ \text{XeF}_4 \quad \text{and} \quad \text{OSF}_6 \]

\[ \text{sp}^3d^2 \quad \text{and} \quad \text{sp}^3d^2 \]

(sol)
4. The structure of D-Glucose is as follows

\[ \text{CHO} \]
\[ \begin{array}{c}
\text{HO} \\
\text{H} \\
\text{HO} \\
\text{H} \\
\text{H} \\
\text{OH} \\
\text{HO} \\
\end{array} \]

a) Draw the structure of L-Glucose.

b) Give the reaction of L-Glucose with Tollens reagent.

\[ \text{CHO} \]
\[ \begin{array}{c}
\text{HO} \\
\text{H} \\
\text{HO} \\
\text{H} \\
\text{H} \\
\text{OH} \\
\text{HO} \\
\end{array} \]

\[ (\text{L} \text{ glucose}) \]

\[ \text{NH}_2\text{Ag} \rightarrow \text{NH}_2\text{Ag} \]

\[ \text{HO} \\
\text{H} \\
\text{HO} \\
\text{H} \\
\text{H} \\
\text{OH} \\
\text{HO} \\
\]

\[ (\text{L} \text{ glucose}) \]

5. a) Draw Newmann’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) 
\[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array} \]

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

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

\[ \text{Cl}_2\text{O}_2, \text{BaO}, \text{SO}_3, \text{CO}_2, \text{B}_2\text{O}_3 \]

Sol. \[ \text{Cl}_2\text{O}_2 < \text{SO}_3 < \text{CO}_2 < \text{B}_2\text{O}_3 < \text{BaO} \]

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

Sol.
\[ 3\text{KF} + \text{AlF}_3 \rightarrow \text{K}_3\text{AlF}_6 \]
\[ \text{K}_3\text{AlF}_6 + 3\text{BF}_3 \rightarrow \text{AlF}_3 + 3\text{KBF}_4 \]

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 \( \frac{1}{\sqrt{3}} \) nm and the observed density is 20 Kg/m\(^3\). Find the

a) density in Kg/m\(^3\) and

b) type of defect
9. Which of the following is more acidic and why?

\[
\text{NH}_3^+ \quad \text{and} \quad \text{NH}_3^+ \\
\]

Sol. \( \text{NH}_3^+ \) 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 \( \text{Ag}^+ (\text{aq}) \), Explain.

Sol.

Aromatic Ion (highly stable)

\[
\begin{aligned}
\text{Br} &\quad \text{Br} \\
\end{aligned}
\]

Antiaromatic Ion (highly unstable)

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

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

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) \( 92 \times 234 \rightarrow 71 \times 60 \rightarrow Y \). Find out atomic number, mass number of Y and identify it.

Sol.

\( a) \quad \Psi_{2s}^2 = \) probability of finding electrons at any place

\[ \therefore \Psi^2 = 0 \text{ at node} \]
∴ $\Psi^2 = 0 = \frac{1}{4 \sqrt{2\pi}} \left( \frac{1}{a_0^3} \right) \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}$

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

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

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

c) Yes $\mu^2_{P,206}$

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$_2^-[\text{AsF}_6]$.

**Sol.**

O$_2$ = $\sigma^1s^2, \sigma^1s^2, \pi^2s^2, \pi^2s^2$; $\pi^2p^6, \pi^2p^6$

Bond order $= \frac{10 - 6}{2} = 2$

O$_2^-$ = $\sigma^1s^2, \sigma^1s^2, \pi^2s^2, \pi^2s^2, \sigma^2p^4, \pi^2p^6, \pi^2p^6$

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

O$_2^-$ = $\sigma^1s^2, \sigma^1s^2, \pi^2s^2, \pi^2s^2, \sigma^2p^4, \pi^2p^6, \pi^2p^6$

Bond order $= \frac{10 - 5}{2} = \frac{5}{2}$

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

13. a) In the following equilibrium

N$_2$O$_4$(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

$\Delta G^\circ_{\text{f}}(\text{N}_2\text{O}_4) = 100\text{KJ}$

$\Delta G^\circ_{\text{f}}(\text{NO}_2) = 50\text{KJ}$

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

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

$= 100 - 100$

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

$\Delta G = RT \ln Q$

$= 2.303 \times 0.082 \times 298 \times \log 9.9 = 56.0304 \text{ Lit atm.} = \text{Positive}$
ii) Therefore reaction will shift towards backward direction.

b) \[
\begin{align*}
\left( P + \frac{aP^2}{(PV)^2} \right) \left( PV - b \right) &= RT \\
\left( P + \frac{aP^2}{(PV)^2} \right) PV &= RT \\
\Rightarrow \left( P + \frac{aP^2}{(PV)^2} \right) (PV - b) &= P(PV)^2RT \\
\Rightarrow (PV)^3 &= (PV)^2 RT \\
\end{align*}
\]

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 \( \Delta T_b \) and \( K_b \) are given as:

i) In 100 g \( CH_3COCH_3 \), \( \Delta T_b = 0.17 \)
\[
K_b = \frac{1.7}{100} Kg \text{ Kelvin/mol}
\]

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

Find out the molecular weight of \( C_6H_5 COOH \) 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 \( \alpha << 1 \)

Sol. a) In first case

i) \( \Delta T_b = K_b \times m \)
\[
0.17 = 1.7 \times \frac{1.22}{100 \times 10^{-3}} \Rightarrow M = 122
\]

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 = \( \frac{0.1}{2} M \)

\( \therefore \) pH of salt of weak acid and strong base

\[
\text{pH} = \frac{pK_a + pK_w + \log_2}{2} = \frac{1}{2} \left[ 14 + 5.30 \times 10^{-6} + [-1.30] \right] \Rightarrow \text{pH} = 9.
\]

15. Convert \[
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2
\end{array}
\]
to \[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]
in not more than four steps. Also mention the temp and reaction condition.

Sol.

\[
\begin{align*}
\text{NO}_2 & \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{NO}_2 \\
& \xrightarrow{\text{NH}_4\text{HSO}_4} \text{NO}_2 \\
& \xrightarrow{\text{NaNO}_3/\text{HCl}} \text{NO}_2 \\
& \xrightarrow{\text{H}_2\text{O}} \text{NO}_2
\end{align*}
\]

16. Identify A to D.
17. A₁ & A₂ are two ores of metal M. A₁ on calcination gives black precipitate, CO₂ & water.

Calcination → Black solid + CO₂ + H₂O

Black solid + CO₂ + H₂O → I₂ + ppt

A₂ → Metal + gas

K₂C₅O₅ + H₂SO₄ → green colour

Sol. A₁ = Cu(OH)₂CuCO₃
A₂ = Cu₃S

Cu(OH)₂CuCO₃ → 2CuO + CO₂ + H₂O  (Calcination)
(Black Solid)

Cu(OH)₂CuCO₃ + 2KI → Cu₂I₂ + I₂ + 4KCl
2CuCl₂ + 4KI → Cu₂I₂ + I₂ + 4KCl
2Cu₂S + 3O₂ → 2Cu₂O + 2SO₂

A₂ → 2Cu₂O → 6Cu + SO₂

18. NiCl₂ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of

NiCl₂ + 2DMG → NiCl₂·2DMG

NH₄OH, giving a bright red colour.

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

Sol. Oxidation state of nickel is +2 and hybridization is dsp²

µₛ = √n(n + 2) B.M
n = 0
∴ µₛ = 0
19. Find the equilibrium constant for the reaction

\[
\text{Cu}^{2+} + \text{In}^{2+} \rightleftharpoons \text{Cu}^{+} + \text{In}^{3+}
\]

Given that

\[
E_{\text{Cu}^{2+}/\text{Cu}^{+}}^\circ = 0.15 \text{ V}
\]

\[
E_{\text{In}^{2+}/\text{In}^{+}}^\circ = -0.4 \text{ V}
\]

\[
E_{\text{In}^{3+}/\text{In}^{+}}^\circ = -0.42 \text{ V}
\]

**Sol.**

\[
\begin{align*}
\text{Cu}^{2+} + e^- & \rightarrow \text{Cu}^+ & \Delta G_1^0 &= -0.15 \text{ F} \\
\text{In}^{2+} + e^- & \rightarrow \text{In}^+ & \Delta G_2^0 &= +0.4 \text{ F} \\
\text{In}^+ & \rightarrow \text{In}^{3+} + 2 e^- & \Delta G_3^0 &= -0.84 \text{ F}
\end{align*}
\]

\[
- nF \cdot E_0^\circ = -0.59 \text{F}
\]

\[
-E_{\text{cell}}^\circ \cdot F = -0.59 \text{F}
\]

\[
E_{\text{cell}}^\circ = 0.59
\]

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

\[
0.59 = \frac{0.0591}{1} \cdot \log K_c
\]

\[
K_c = 10^{0.59}
\]

20. An organic compound ‘P’ having the molecular formula C₅H₁₀O treated with dil H₂SO₄ gives two compounds, Q & R both gives positive iodoform test. The reaction of C₅H₁₀O with dil H₂SO₄ gives reaction 10¹⁵ times faster then ethylene. Identify organic compound of Q & R. Give the reason for the extra stability of P.

**Sol.**

\[
\begin{align*}
\text{CH}_2 \, \text{O} & \rightarrow \text{CH}_3 \\
\text{CH}_3 & \rightarrow \text{CH}_3 \\
\text{C} & \rightarrow \text{CH}_3
\end{align*}
\]

P is stabilized by resonance

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**Note:** FITJEE solutions to IIT–JEE, 2004 Mains Papers created using memory retention of select FITJEE 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.