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
   \[ A + B \rightarrow \text{Products} \]
   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] 0.1</td>
<td>[B] 0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>[A] 0.2</td>
<td>[B] 0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>[A] 0.1</td>
<td>[B] 0.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

   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 \( 2 = [2]^y \)
   \[ x = 1 \]
   \[ 0.05 = K[0.1]^x[0.1]^y \]
   \[ 0.05 = K[0.1]^1[0.2]^y \]
   \[ 1 = [2]^y \]
   \[ y = 0 \]

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

3. Draw the shape of XeF₄ and OSF₄ according to VSEPR theory. Show the lone pair of electrons on the central atom

   Sol.
   [Diagram showing XeF₄ as square planar (sp³d²) and OSF₄ as trigonal bipyramidal (sp³d)]
4. The structure of D-Glucose is as follows

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

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

Sol.

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

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

\[
3\text{Ag} \left( \text{NH}_3 \right)^+ \rightarrow \text{O} \quad \text{O}^- \\
\]

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

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.

\[
\text{CH}_3 \\
\text{HH} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\]

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, 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 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
Sol. a) Density = \[ \frac{4 \times 6.023 \times y}{6.023 \times 10^{23} \times 8 \times y \times 10^{-37}} \] [Since \( a = 2y^{1/3} \)]

= \( 5 \times 10^4 \) g / m\(^3\)

= 5 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?

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

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.

\[ \text{Aromatic Ion (highly stable)} \]

\[ \text{Antiaromatic Ion (highly unstable)} \]

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

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

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) \( _{92}^{234} \text{X} \rightarrow _{67}^{234} \text{Y} \). Find out atomic number, mass number of \( Y \) and identify it.

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

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

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

b) \[ \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{100 \times 10^{-3} \times 100} \]
\[ \lambda = 6.626 \times 10^{-35} \text{ m} = 6.626 \times 10^{-25} \text{ A}^0 \]

c) \[ Y = \text{let} \text{Po}_{206} \]

12. On the basis of ground state electronic configuration arrange the following molecules in increasing O-O bond length order.

KO\textsubscript{2}, O\textsubscript{2}, O\textsubscript{2}[AsF\textsubscript{6}].

\[ \text{Sol.} \]

\[ \text{O}_2 = \sigma_1s^2, \sigma^*_1s^2, \sigma_2s^2, \sigma^*_2s^2, \sigma_2p^2, \sigma^*_2p^2 [\pi_2p^2, \pi^*_2p^2] \]

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

\[ \text{O}_2^+ = \sigma_1s^2, \sigma^*_1s^2, \sigma_2s^2, \sigma^*_2s^2, \sigma_2p^2, \sigma^*_2p^2 [\pi_2p^2, \pi^*_2p^2, \pi^*_1s^2] \]

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

\[ \text{O}_2^- = \sigma_1s^2, \sigma^*_1s^2, \sigma_2s^2, \sigma^*_2s^2, \sigma_2p^2, \sigma^*_2p^2 [\pi_2p^2, \pi^*_1s^2] \]

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

Bond length order is \( O_2^+ < O_2^- < O_2 \)

13. a) In the following equilibrium

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

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

\[ \Delta G^0_\text{f}(\text{N}_2\text{O}_4) = 100\text{KJ} \]

\[ \Delta G^0_\text{f}(\text{NO}_2) = 50\text{KJ} \]

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

\[ \text{Sol.} \]

a) i) \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

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

\[ \Delta G^0 \text{ reaction} = 2\Delta G^0_f(\text{NO}_2) - \Delta G^0_f(\text{N}_2\text{O}_4) \]

\[ 0 = 100 - 100 \]

\[ \Delta G = \Delta G^0 + RT \ln Q \]

\[ \therefore \Delta G = RT \ln Q = 2.303 \times 0.082 \times 298 \times \log 9.9 = 56.0304 \text{ Lit atm. = Positive} \]
ii) Therefore reaction will shift towards backward direction.

b) \[
\left( P + \frac{a}{P} \right) (\nu - b) = RT
\]

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

\[\begin{align*}
(PV)^2 & + aP^3(\nu - b)] = P(PV)^2RT \\
\Rightarrow (P)^2 & + aP(\nu - b) = P(PV)^2RT \\
\text{Put } P &= 0 \\
\Rightarrow (P)^2 & = (PV)^2RT
\end{align*}\]

Intercept = RT

14. a) 1.22 g C₆H₅ COOH is added into two solvent and data of ΔTₜ and Kₜ are given as:

i) In 100 g CH₃COCH₃, ΔTₜ = 0.17
   Kₜ = 1.7 Kg Kelvin/mol

ii) In 100 g benzene, ΔTₜ = 0.13 and Kₜ = 2.6 Kg Kelvin/mol

Find out the molecular weight of C₆H₅COOH 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 α << 1

Sol. a) In first case

i) ΔTₜ = Kₜ × m

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

ii) In second case

ΔTₜ = Kₜ × m

\[0.13 = 2.6 \times \frac{1.22}{M' \times 100 \times 10^{-3}} \Rightarrow M' = 244\]

Benzoic acid dimerises in benzene

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

:: pH of salt of weak acid and strong base

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

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

Sol.

[Diagram not provided]

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

\[ \text{Calcination} \]
\[ \text{A}_1 \xrightarrow{\text{Calcination}} \text{Black solid + CO}_2 + \text{H}_2\text{O} \]

\[ \text{Roasting} \]
\[ \text{A}_2 \xrightarrow{\text{Roasting}} \text{Metal + gas} \]

\[ \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \]

green colour

Sol.
\[ \text{A}_1 = \text{Cu(OH)}_2\text{CuCO}_3 \]
\[ \text{A}_2 = \text{Cu}_2\text{S} \]
\[ \text{Cu(OH)}_2\text{CuCO}_3 \xrightarrow{\text{Calcination}} 2\text{CuO + CO}_2 + \text{H}_2\text{O} \] (Black Solid)

\[ \text{Cu(OH)}_2\text{CuCO}_3 \xrightarrow{\text{dil HCl}} \text{CuCl}_2 + \text{CO}_2 + 3\text{H}_2\text{O} \]

\[ 2\text{CuCl}_2 + 4\text{KI} \rightarrow \text{Cu}_4\text{I}_2 + \text{I}_2 + 4\text{KCl} \]

\[ 2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2 \] (A₂)

\[ \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2 \]

18. NiCl₂ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH₄OH, giving a bright red colour.

a) Draw its structure & show H-bonding

b) Give oxidation state of Ni & its hybridisation.

c) Predict whether it is paramagnetic or diamagnetic.

Sol.
\[ \text{Oxidation state of nickel is } +2 \text{ and hybridization is } \text{dsp}^2 \]

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

\[ n = 0 \]

\[ \therefore \mu_s = 0 \]
19. Find the equilibrium constant for the reaction

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

Given that

\[ E^{\circ}_{\text{Cu}^{2+} / \text{Cu}^+} = 0.15 \text{V} \]
\[ E^{\circ}_{\text{In}^{2+} / \text{In}^+} = -0.4 \text{V} \]
\[ E^{\circ}_{\text{In}^+ / \text{In}^{3+}} = -0.42 \text{V} \]

**Sol.**

\[ \text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+ \quad \Delta G^0_1 = -0.15 \text{F} \]
\[ \text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+ \quad \Delta G^0_2 = +0.4 \text{F} \]
\[ \text{In}^+ \rightarrow \text{In}^{3+} + 2 \text{e}^- \quad \Delta G^0_3 = -0.84 \text{F} \]

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

\[ -nF \varepsilon^0 = -0.59 \text{F} \]
\[ -E^0_{\text{cell}} F = -0.59 \text{F} \]
\[ E^0_{\text{cell}} = 0.59 \]
\[ E_{\text{cell}} = E^0 - \frac{0.0591}{n} \log K_c \]
\[ 0.59 = \frac{0.0591}{1} \log K_c \]
\[ K_c = 10^{10} \]

20. An organic compound ‘P’ having the molecular formula \( \text{C}_5\text{H}_{10}\text{O} \) treated with dil H\(_2\)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 H\(_2\)SO\(_4\) gives reaction 10\(^{15}\) times faster then ethylene. Identify organic compound of Q & R. Give the reason for the extra stability of P.

**Sol.**

\[ \text{CH}_2 \text{O} \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]

\[ \text{P} \text{is stabilized by resonance} \]