G.C.E. (A/L) Examination - 2021 (2022)

02 - Chemistry

Distribution of Marks

Paper I   :   1 X 50   =   50

Paper II   :

    Part A   :   100 X 4   =   400

    Part B   :   150 X 2   =   300

    Part C   :   150 X 2   =   300

    Total   =   1000

    Paper II - Final Marks   =   100

Common Techniques of Marking Answer Scripts.

It is compulsory to adhere to the following standard method in marking answer scripts and entering marks into the mark sheets.

1. Use a red color ball point pen for marking. (Only Chief/Additional Chief Examiner may use a mauve color pen.)

2. Note down Examiner's Code Number and initials on the front page of each answer script.

3. Write off any numerals written wrong with a clear single line and authenticate the alterations with Examiner's initials.

4. Write down marks of each subsection in a $\triangle$ and write the final marks of each question as a rational number in a $\square$ with the question number. Use the column assigned for Examiners to write down marks.

Example: **Question No. 03**

   (i) .... $\sqrt{}$ $\dfrac{4}{5}$

   (ii) .... $\sqrt{}$ $\dfrac{3}{5}$

   (iii) .... $\sqrt{}$ $\dfrac{3}{5}$

03 (i) $\dfrac{4}{5}$ + (ii) $\dfrac{3}{5}$ + (iii) $\dfrac{3}{5}$ = $\dfrac{10}{15}$

MCQ answer scripts: (Template)

1. Marking templets for G.C.E.(A/L) and GIT examination will be provided by the Department of Examinations itself. Marking examiners bear the responsibility of using correctly prepared and certified templates.

2. Then, check the answer scripts carefully. If there are more than one or no answers Marked to a certain question write off the options with a line. Sometimes candidates may have erased an option marked previously and selected another option. In such occasions, if the erasure is not clear write off those options too.

3. Place the template on the answer script correctly. Mark the right answers with a 'v' and the wrong answers with a 'X' against the options column. Write down the number of correct answers inside the cage given under each column. Then, add those numbers and write the number of correct answers in the relevant cage.

structured essay type and assay type answer scripts:

1. Cross off any pages left blank by candidates. Underline wrong or unsuitable answers. Show areas where marks can be offered with check marks.

2. Use the right margin of the overland paper to write down the marks.

3. Write down the marks given for each question against the question number in the relevant cage on the front page in two digits. Selection of questions should be in accordance with the instructions given in the question paper. Mark all answers and transfer the marks to the front page, and write off answers with lower marks if extra questions have been answered against instructions.

4. Add the total carefully and write in the relevant cage on the front page. Turn pages of answer script and add all the marks given for all answers again. Check whether that total tallies with the total marks written on the front page.

Preparation of Mark Sheets.

Except for the subjects with a single question paper, final marks of two papers will not be calculated within the evaluation board this time. Therefore, add separate mark sheets for each of the question paper. Write paper 01 marks in the paper 01 column of the mark sheet and write them in words too. Write paper II Marks in the paper II Column and wright the relevant details.

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இலங்கை பரீட்சைத் திணைக்களம்
Department of Examinations, Sri Lanka

අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2021(2022)
கல்விப் பொதுத் தராதரப் பத்திர (உயர் தர)ப் பரீட்சை, 2021(2022)
General Certificate of Education (Adv. Level) Examination, 2021(2022)

රසායන විද්‍යාව	I
இரசாயனவியல்	I
Chemistry	**I**

02 E I

පැය දෙකයි
இரண்டு மணித்தியாலம்
*Two hours*

Instructions:

※ *Periodic Table is provided.*
※ *This paper consists of* **09** *pages.*
※ *Answer* **all** *the questions.*
※ ***Use of calculators is not allowed.***
※ *Write your* **Index Number** *in the space provided in the answer sheet.*
※ *Follow the instructions given on the back of the answer sheet carefully.*
※ *In each of the questions* **1** *to* **50**, *pick one of the alternatives from* (1), (2), (3), (4), (5) *which is* **correct** *or* **most appropriate** *and* **mark your response on the answer sheet with a cross** (×) *in accordance with the instructions given on the back of the answer sheet.*

Universal gas constant $R = 8.314$ J K^{-1} mol^{-1} Planck's constant $h = 6.626 \times 10^{-34}$ J s
Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1} Velocity of light $c = 3 \times 10^8$ m s^{-1}

1. Select the correct statement with regard to particles associated with cathode rays observed in a cathode ray tube.
   (1) The particles are uncharged.
   (2) They travel from anode to cathode along straight lines.
   (3) Their charge to mass ratio $\frac{e}{m}$ depends on the nature of gas and pressure inside the cathode ray tube.
   (4) Their direction of travel is affected by magnetic and electric fields.
   (5) They are not capable of ionizing the gas inside the cathode ray tube.

2. Which of the following statements is **incorrect** with regard to an energy level of an atom with principal quantum number (n), n = 3?
   (1) There are 3 sub shells associated with it.
   (2) There are 9 orbitals.
   (3) There can be a maximum of 18 electrons.
   (4) There can be a maximum of 10 electrons with angular momentum (azimuthal) quantum number (l), $l = 2$.
   (5) There can be a maximum of 8 electrons with magnetic quantum number (m_l), $m_l = 0$.

3. The **decreasing** order of the first ionization energy of the atoms H, He, Li, Be, B and Na is,
   (1) He > H > B > Be > Li > Na
   (2) He > H > Be > B > Li > Na
   (3) He > Be > H > Li > B > Na
   (4) H > He > B > Be > Li > Na
   (5) H > He > Be > B > Na > Li

4. The shapes of IF_4^+, IF_4^- and IF_5 are respectively,
   (1) see-saw, square planar and square pyramidal.
   (2) square planar, see-saw and square pyramidal.
   (3) tetrahedral, see-saw and trigonal bipyramidal.
   (4) see-saw, tetrahedral and square pyramidal.
   (5) tetrahedral, square planar and trigonal bipyramidal.

5. What is the IUPAC name of the following compound?

$$H_2N-CH_2-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2-CH_3$$
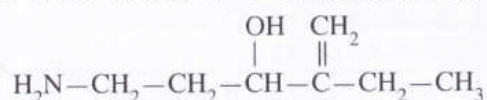
   (1) 1-amino-4-ethylpent-4-en-3-ol

   (2) 5-amino-2-ethylpent-1-en-3-ol

   (3) 2-ethyl-3-hydroxypent-1-en-5-amine

   (4) 4-ethyl-3-hydroxypent-4-en-1-amine

   (5) 5-amino-2-ethyl-3-hydroxypent-1-ene

6. Which of the following statements is correct with regard to boiling points?

   (1) N_2 has a higher boiling point than NO.

   (2) PH_3 has a higher boiling point than NH_3.

   (3) Xe has a higher boiling point than Kr.

   (4) CH_3CH_2OH has a higher boiling point than $CH_3CH_2CH_2OH$.

   (5) CH_3CHCH_3 has a higher boiling point than $CH_3CH_2CH_2CH_3$.
           $|$
          CH_3

7. $M(OH)_2$ is a sparingly water soluble solid. The concentration of M^{2+}(aq) in a saturated aqueous solution of $M(OH)_2$ at pH = 8.0 and at a given temperature is 1.0×10^{-6} mol dm^{-3}. The pH of a saturated aqueous solution of $M(OH)_2$ having M^{2+}(aq) concentration of 1.0×10^{-4} mol dm^{-3} at this temperature is,

   (1) 4.0   (2) 5.0   (3) 6.0   (4) 7.0   (5) 8.0

8. Select the correct statement.
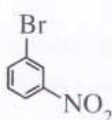
   (1) The electron pair geometry and shape of SF_5^+ are different from each other.

   (2) The increasing order of radii of atoms/ions F^-, Mg^{2+}, Al, Cl^- and K is $F^- < Mg^{2+} < Cl^- < Al < K$.

   (3) The number of resonance structures that can be drawn for nitric acid (HNO_3) is four.

   (4) CO_3^{2-} has the longest C−O bond among the molecules/ions CO, CO_2, CO_3^{2-} and CH_3OH.

   (5) Among the molecules CH_4, $COCl_2$ and HCN, the electronegativity of the carbon atom increases in the order $CH_4 < COCl_2 < HCN$.
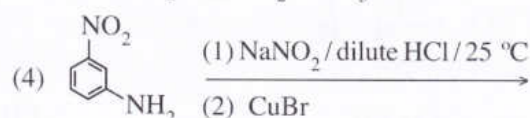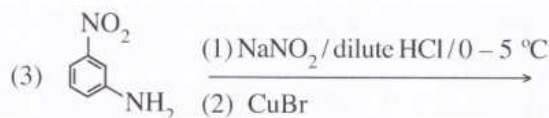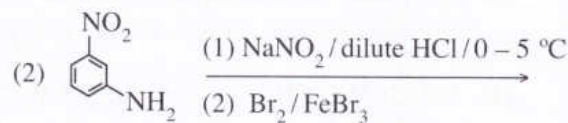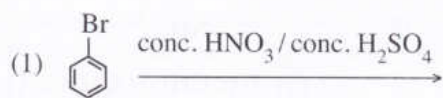
9. A and B are two organic compounds containing C, H and O. When A and B were separately treated with Br_2/H_2O, only A gave a white precipitate. The product formed when B was heated with concentrated H_2SO_4 decolourised Br_2/H_2O. The organic compounds A and B are respectively,

   (1) C_6H_5OH, CH_3OH

   (2) $C_6H_5CH_2OH$, CH_3CH_2OH

   (3) C_6H_5OH, CH_3CHCH_2OH
                                        $|$
                                      CH_3

   (4) C_6H_5CHO, C_6H_5OH

   (5) CH_3CHO, CH_3CHCH_2OH
                                        $|$
                                      CH_3

10. The elementary reaction $A(g) \rightarrow B(g) + C(g)$ occurs in a closed rigid container at constant temperature. The initial pressure of the container when only A(g) is present was measured to be $2P_0$. The pressure of the container after two half lives of A(g) would be,

   (1) $\dfrac{P_0}{2}$ (2) $\dfrac{P_0}{4}$ (3) $\dfrac{3P_0}{4}$ (4) $\dfrac{3P_0}{2}$ (5) $\dfrac{7P_0}{2}$

11. A suitable method to prepare (a benzene ring with Br and NO$_2$ in meta positions) is,

(1) (benzene with Br) $\xrightarrow{\text{conc. HNO}_3/\text{conc. H}_2\text{SO}_4}$

(2) (benzene with NO$_2$ and NH$_2$) $\xrightarrow{\begin{array}{l}(1)\ \text{NaNO}_2/\text{dilute HCl}/0-5\ ^\circ\text{C}\\(2)\ \text{Br}_2/\text{FeBr}_3\end{array}}$

(3) (benzene with NO$_2$ and NH$_2$) $\xrightarrow{\begin{array}{l}(1)\ \text{NaNO}_2/\text{dilute HCl}/0-5\ ^\circ\text{C}\\(2)\ \text{CuBr}\end{array}}$

(4) (benzene with NO$_2$ and NH$_2$) $\xrightarrow{\begin{array}{l}(1)\ \text{NaNO}_2/\text{dilute HCl}/25\ ^\circ\text{C}\\(2)\ \text{CuBr}\end{array}}$

(5) (benzene with NO$_2$) $\xrightarrow{\text{Br}_2}$
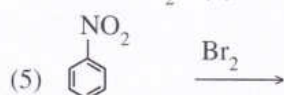
12. Which expression gives the correct volume (cm^3) of 70.0% $\left(\frac{w}{w}\%\right)$ concentrated HNO$_3$ acid with density 1.42 g cm^{-3} required to prepare 300 cm^3 of a 0.150 mol dm^{-3} solution of HNO$_3$? (Relative atomic mass: H = 1, N = 14, O = 16)

(1) $\dfrac{100}{1.42}\times\dfrac{70.0}{63}\times\dfrac{0.150}{1000}\times 300$

(2) $\dfrac{100}{1.42}\times\dfrac{63}{70.0}\times\dfrac{0.150}{1000}\times 300$

(3) $\dfrac{1.42}{100}\times\dfrac{63}{70.0}\times\dfrac{1000}{0.150}\times 300$

(4) $\dfrac{100}{1.42}\times\dfrac{63}{70.0}\times\dfrac{1000}{0.150}\times\dfrac{1}{300}$

(5) $\dfrac{1.42}{100}\times\dfrac{70.0}{63}\times\dfrac{0.150}{1000}\times 300$

13. The elementary reaction, $A(aq) + H_3O^+(aq) \rightarrow B^+(aq)$ occurs in an aqueous solution at constant temperature. Which of the following graphs correctly represents the relationship between Log(Initial rate) vs pH at a constant concentration of A(aq)?

Log(Initial rate)   Log(Initial rate)   Log(Initial rate)   Log(Initial rate)   Log(Initial rate)

 (1)   (2)   (3)   (4)   (5)

(pH axis for each)
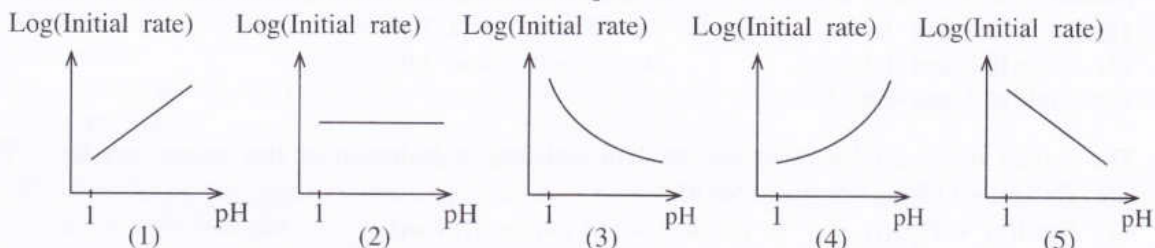
14. An excess amount of A(g) and a small amount of B(g) are introduced into an evacuated rigid container. Then, the following elementary reactions take place at a constant temperature.

$$A(g) + B(g) \rightarrow C(g) \qquad \text{fast}$$
$$A(g) + C(g) \rightarrow 3D(g) \qquad \text{slow}$$

Which of the following statements is correct regarding the variation of pressure of the system with time?

(1) Pressure remains unchanged.
(2) Pressure increases and then becomes constant.
(3) Pressure decreases and then becomes constant.
(4) Pressure decreases and returns to the initial value again.
(5) Pressure increases initially, then decreases and returns to the initial value again.

15. The solute **A** present in volume V of an aqueous solution is extracted twice using 2V volume portions of a water immiscible organic solvent. The partition coefficient of **A** between the organic solvent and water, $\dfrac{[\textbf{A}]_{(org)}}{[\textbf{A}]_{(aq)}} = 4.0$. The initial amount of **A** in the aqueous phase is a (mol). The amount (mol) of **A** remaining in the aqueous phase after the second extraction is,

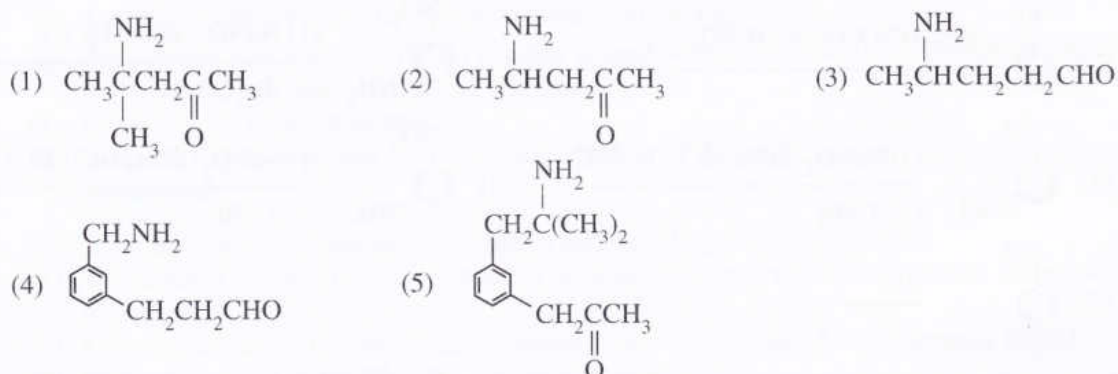(1) $\dfrac{a}{2}$ (2) $\dfrac{a}{9}$ (3) $\dfrac{a}{18}$ (4) $\dfrac{a}{25}$ (5) $\dfrac{a}{81}$

16. Compound **A** reacts with $NaNO_2$/dilute HCl to give **B**. When **B** is treated with acidified aqueous $K_2Cr_2O_7$, the solution turns green. When treated with Fehling's reagent **A** did not give a brick red precipitate. Compound **A** could be,

(1) $CH_3\overset{\overset{\displaystyle NH_2}{|}}{C}CH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_3$ with CH_3 below

(2) $CH_3\overset{\overset{\displaystyle NH_2}{|}}{C}HCH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_3$

(3) $CH_3\overset{\overset{\displaystyle NH_2}{|}}{C}HCH_2CH_2CHO$

(4) benzene ring with CH_2NH_2 and CH_2CH_2CHO

(5) benzene ring with $CH_2\overset{\overset{\displaystyle NH_2}{|}}{C}(CH_3)_2$ and $CH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_3$

17. MCl_2 is a solid which is sparingly soluble in water $(K_{sp} = 1.0 \times 10^{-8}\ mol^3\ dm^{-9})$. Which of the following is correct regarding a saturated aqueous solution of MCl_2?
    (1) Evaporation of water from the solution increases M^{2+} and chloride ion concentrations of the solution.
    (2) Chloride ion concentration of the solution can be increased by adding NaCl(s).
    (3) The solution cannot be acidified by adding HCl.
    (4) Chloride ion concentration of the solution cannot be increased above $1.0 \times 10^{-4}\ mol\ dm^{-3}$.
    (5) Chloride ion concentration of the solution can be lowered by adding distilled water and maintaining the saturated condition.

18. When a mass of 0.0119 g of KBr is dissolved in 500.0 cm^3 of distilled water, the K^+ composition of the solution in $mol\ dm^{-3}$ and ppm $(mg\ kg^{-1})$ are respectively,
    (Relative atomic mass: K = 39, Br = 80; density of solution = 1.00 $kg\ dm^{-3}$)
    (1) 1.0×10^{-4} and 3.9   (2) 1.0×10^{-4} and 7.8
    (3) 2.0×10^{-4} and 1.3   (4) 2.0×10^{-4} and 3.9
    (5) 2.0×10^{-4} and 7.8

19. The correct reaction relevant to the standard enthalpy of hydration of the sodium ion is,
    (1) $Na^+(g) + OH^-(aq) \longrightarrow NaOH(s)$
    (2) $NaCl(g) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + HCl(aq)$
    (3) $Na^+(g) + H_2O(l) \longrightarrow Na^+(aq)$
    (4) $Na^+(g) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + H^+(aq)$
    (5) $Na^+(g) + Cl^-(g) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$

20. Which of the following is **not** a step in the chlorination of methane?
    (1) $Cl_2 \xrightarrow{h\upsilon} 2Cl^•$
    (2) $CH_4 + {}^•Cl \longrightarrow {}^•CH_3 + HCl$
    (3) ${}^•CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl^•$
    (4) $CH_3Cl + Cl^• \longrightarrow {}^•CH_2Cl + HCl$
    (5) ${}^•CH_2Cl + HCl \longrightarrow CH_2Cl_2 + H^•$

21. Which of the following statements regarding the critical temperature of a real gas is correct?
    (1) It is the temperature at which the intermolecular forces can be neglected.
    (2) It is the temperature corresponding to the lowest pressure at which the gas can be liquified.
    (3) It is the temperature at which the gas is in equilibrium with its solid.
    (4) It is the highest temperature at which the gas phase and the liquid phase are in equilibrium.
    (5) It is the temperature given by the van der Waals equation at any pressure.

22. In an experiment, Mg metal was made to react with excess N_2 gas and the product obtained was reacted with H_2O. The volume of the gas evolved at standard temperature (273 K) and pressure (1.0 atm) was 672 cm^3. The mass of Mg used in the experiment is,
   (Assume that 1.0 mol of gas occupies a volume of 22.4 dm^3 at 273 K and 1.0 atm.
   Relative atomic mass: Mg = 24)
   (1) 0.24 g   (2) 0.48 g   (3) 0.72 g   (4) 1.08 g   (5) 1.50 g

23. The mean square speed of H_2 at absolute temperature T is equal to the mean square speed of N_2 at absolute temperature T'. Which of the following equations gives the correct relationship between T and T'? (Relative atomic mass: H = 1, N = 14)
   (1) $T = T'$ (2) $T = 14T'$ (3) $T = \dfrac{T'}{4}$ (4) $T = 7T'$ (5) $T = \dfrac{T'}{14}$

24. A buffer solution at constant temperature contains a monobasic weak acid ($K_a = 1.00 \times 10^{-5}$ mol dm^{-3}) and its sodium salt. The concentrations of the weak acid and the sodium salt in the solution are 0.10 mol dm^{-3} each. The volume of 1.00 mol dm^{-3} weak acid that should be added to change the pH of 10.00 cm^3 of this solution by one unit, and the pH value of the solution after the addition of the weak acid are respectively,
   (1) 9.00 cm^3, 4.0   (2) 9.00 cm^3, 6.0   (3) 10.00 cm^3, 4.0
   (4) 10.00 cm^3, 5.0   (5) 11.00 cm^3, 4.0

25. A gaseous discharge/production that contributes to all three environmental issues, namely, global warming, acid rain and photochemical smog is,
   (1) exhaust gas released from fossil fuel burning vehicles.
   (2) exhaust gas released from coal power plants.
   (3) gases released during repair of air conditioners and refrigerators.
   (4) gases produced from the improper discharge of municipal solid waste.
   (5) exhaust gas released from biofuel burning vehicles.

26. Which of the following statements is **incorrect** with regard to element Lithium (Li) and its compounds?
   (1) Among the Group I elements from Li – Cs, lithium has the most negative value for electron gain energy.
   (2) Lithium forms two products when heated in air.
   (3) Considering the gases evolved, upon heating $LiNO_3$(s) produces two gases whereas Li_2CO_3(s) gives only one gas.
   (4) Among Group I elements, lithium has the weakest metallic bonding.
   (5) Lithium gives a red coloured flame in the flame test.

27. The number of moles of $KMnO_4$ that are required to react completely with one mole of $Fe(NO_2)_2$ in acidic medium is,
   (**Note:** Neglect the loss of NO_2^- due to acidic conditions.)
   (1) $\dfrac{3}{5}$ (2) $\dfrac{4}{5}$ (3) 1   (4) $\dfrac{5}{4}$ (5) $\dfrac{5}{3}$

28. Which of the following statements is correct regarding water and aqueous solutions at a given temperature?
   (1) The solubility of a polar gas in water is lower than the solubility of a non polar gas in water.
   (2) Any gas undergoes ionization in an aqueous solution.
   (3) The solubility of a gas in water is proportional to its pressure.
   (4) Boiling point of water decreases with increasing pressure.
   (5) The temperature of the triple point of water increases with increasing pressure.

29. Select the correct statement with regard to chromium (Cr) and its compounds.
    (1) When an aqueous solution of K_2CrO_4 is treated with dilute H_2SO_4, a colour change is not observed.
    (2) The electronegativity of Cr is greater than that of Co.
    (3) An aqueous solution of $Cr(H_2O)_6^{2+}$ when treated with excess NaOH, followed by the addition of H_2O_2 gives a yellow coloured solution.
    (4) Cr_2O_3 shows basic properties.
    (5) When H_2S gas is passed into an acidic solution of $K_2Cr_2O_7$, a clear green coloured solution is observed.

30. Which of the following statements is **incorrect** regarding carboxylic acids?
    (1) The product formed by the reaction of a carboxylic acid with $LiAlH_4$ gives an alcohol upon hydrolysis.
    (2) Carbon dioxide is liberated when carboxylic acids are reacted with aqueous NaOH.
    (3) Carboxylic acids react with PCl_5 to give acid chlorides.
    (4) Methane is liberated when carboxylic acids are reacted with CH_3MgBr.
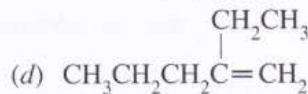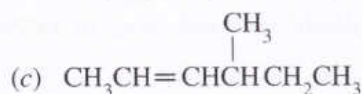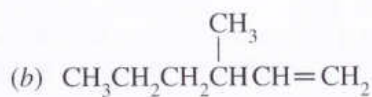   (5) Carboxylic acids are formed when aldehydes are treated with $H^+/K_2Cr_2O_7$.

● For each of the questions **31** to **40**, one or more responses out of the four responses (a), (b), (c) and (d) given is/are correct. Select the correct response/responses. In accordance with the instructions given on your answer sheet, mark
    (1) if only (a) and (b) are correct.
    (2) if only (b) and (c) are correct.
    (3) if only (c) and (d) are correct.
    (4) if only (d) and (a) are correct.
    (5) if **any other** number or combination of responses is correct.

Summary of above Instructions

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	**Any other** number or combination of responses is correct

31. Which of the following give(s) 3-bromo-3-methylhexane as the major product when reacted with HBr?

    (a) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_3$

    (b) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{CH}CH=CH_2$

    (c) $CH_3CH=CH\underset{\underset{CH_3}{|}}{CH}CH_2CH_3$

    (d) $CH_3CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}=CH_2$

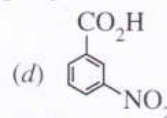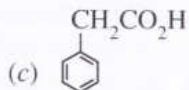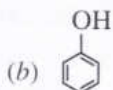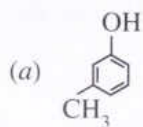32. Which of the following statements is/are correct regarding products related to plant sources?
    (a) Essential oils contain complex mixtures of volatile constituents of plants.
    (b) Biodiesel is produced from volatile plant oils.
    (c) Methanol is not used in the production of biodiesel.
    (d) Ethanol produced by fermentation of plant materials is regarded as a renewable energy source.

33. On which of the following factor/factors does the electrode potential of the electrode $M^{2+}(aq)/M(s)$ depend?
    (a) Surface area of M(s)
    (b) Concentration of $M^{2+}(aq)$
    (c) Temperature
    (d) Volume of $M^{2+}(aq)$ solution

34. Which of the following give(s) CO_2 when treated with aqueous Na_2CO_3?

(a) [structure: benzene ring with OH and CH_3 substituents]

(b) [structure: benzene ring with OH]

(c) [structure: benzene ring with CH_2CO_2H]

(d) [structure: benzene ring with CO_2H and NO_2]

35. Which of the following statements is/are always correct regarding an aqueous solution of a weak electrolyte?
    (a) When conducting an electric current, the fraction of the current carried by the anion is greater than the fraction of the current carried by the cation.
    (b) The conductivity of the anion is greater than the conductivity of the cation.
    (c) Only a small percentage of molecules of the weak electrolyte is dissociated into ions.
    (d) The fraction of molecules of the weak electrolyte dissociated increases with dilution.

36. Which of the following statements is/are correct regarding the relationship between global environmental issues and volatile halogenated hydrocarbons?
    (a) CFC, HCFC and HFC all three contribute to global warming.
    (b) CFC contributes to ozone layer depletion by producing chlorine radicals in the troposphere.
    (c) HFC contributes to ozone layer depletion by producing chlorine radicals in the stratosphere.
    (d) Both CFC and HCFC contribute to ozone layer depletion by producing chlorine radicals in the stratosphere.
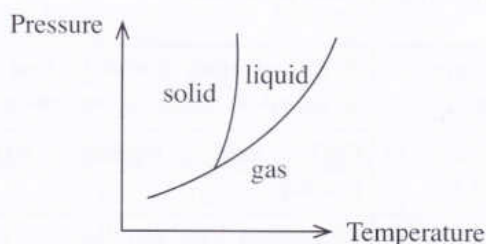
37. Which of the following statements is/are correct with regard to the two allotropes of carbon, namely, graphite and diamond?
    (a) Carbon atoms in diamond are tetrahedrally surrounded by four other carbon atoms to give a three-dimensional lattice.
    (b) Because graphite is composed of two-dimensional layers held together by weak van der Waals forces (secondary interactions), it acts as a good lubricant.
    (c) Diamond is a good conductor of heat and electricity.
    (d) Graphite has a considerably higher melting point than diamond.

38. Which of the following statements is/are correct regarding gases?
    (a) Molecules move at different speeds in a sample of a real gas whereas all the molecules move at the same speed in a sample of an ideal gas.
    (b) Ideal gases can be liquified at extremely high pressures.
    (c) The Maxwell-Boltzmann speed distribution curve of an ideal gas is symmetric about the maximum point.
    (d) The compressibility factor of a real gas depends on pressure.

39. [phase diagram: Pressure vs Temperature showing solid, liquid, gas regions]

Which of the following statements is/are correct regarding the phase diagram of a pure substance given above?
    (a) The number of molecules in a unit volume is always higher in the gas phase than in the liquid phase.
    (b) The liquid phase and the gas phase never co-exist at the same temperature.
    (c) The solid phase and the gas phase never co-exist at the same pressure.
    (d) When the system is at the triple point, the rate at which the gas is converted to the liquid is equal to the rate at which the liquid is converted to the gas.

40. Which of the following statements is/are correct regarding the given industrial processes?
    (a) Sea water can be used directly as a raw material in the extraction of Mg by the Dow process.
    (b) In the production of NaOH, the use of membrane cells is more environmentally friendly than the use of mercury cells.
    (c) The efficiency of the Solvay process used to produce Na_2CO_3 can be increased by cooling the ammonification tower.
    (d) Rh metal is used as a catalyst in the production of H_2SO_4 by the contact process.

● In question Nos. **41** to **50**, two statements are given in respect of each question.
   From the Table given below, select the response, out of the responses (1), (2), (3), (4) and (5), that **best** fits the two statements and mark appropriately on your answer sheet.

Response	First Statement	Second Statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does **not** explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

	First Statement	Second statement
41.	When an acidic solution of MnO_4^- is treated with H_2O_2, it turns colourless with the evolution of O_2, whereas, an acidic solution of Fe^{2+} on treatment with H_2O_2 turns yellow-brown.	H_2O_2 can act as an oxidizing agent as well as a reducing agent in acidic medium.
42.	Energy of a gas in a closed rigid container with thermally insulated walls remains constant.	Both energy and matter of an isolated system do not exchange with the surroundings.
43.	Cl_2 gas undergoes disproportionation on reaction with water giving HOCl(aq) and HCl(aq).	HOCl has the highest oxidizing ability among the oxoacids of chlorine.
44.	When a catalyst is added, the position of equilibrium of a reversible reaction changes.	A catalyst always increases the rate of the forward reaction more than the rate of the reverse reaction.
45.	$RC\equiv CMgBr$ can be prepared by the reaction between $RC\equiv CH$ and methylmagnesium bromide.	The alkyl group of a Grignard reagent can react as a base.
46.	Reaction of HCN with any aldehyde gives a product containing a chiral carbon atom.	A carbon atom joined to four different groups is called a chiral carbon atom.
47.	The main by-product in the production of Na_2CO_3 by the Solvay process is $CaCl_2$.	CaO is used to regenerate NH_3 in the Solvay process.
48.	Benzenediazonium chloride reacts with phenol in the presence of aqueous NaOH to give the following compound. ⬡—N=N—⬡—OH	Diazonium ions can react as electrophiles.
49.	When strong acids are titrated with aqueous ammonia, a neutral solution is not obtained at the equivalence point.	NH_4^+ reacts with water forming H_3O^+.
50.	Atomic oxygen is an essential factor for the formation of ozone in the atmosphere.	Atomic oxygen in the atmosphere is produced only by decomposition of molecular oxygen.

ශ්‍රී ලංකා විභාග දෙපාර්තමේන්තුව

Department of Examinations – Sri Lanka

අ.පො.ස.(උ.පෙළ)විභාගය/G.C.E. (A/L)- 2021 (2022)

විෂයය අංකය Subject No	02	විෂයය Subject	**Chemistry**

ලකුණු දීමේ පටිපාටිය/Marking Scheme
I පත්‍රය/Paper I

ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.
01.	4	11.	3	21.	4	31.	4	41.	1
02.	5	12.	2	22.	4	32.	4	42.	1
03.	2	13.	5	23.	5	33.	2	43.	2
04.	1	14.	4	24.	1	34.	3	44.	5
05.	2	15.	5	25.	1	35.	5	45.	1
06.	3	16.	2	26.	4	36.	4	46.	4
07.	4	17.	2	27.	3	37.	1	47.	1
08.	5	18.	5	28.	3	38.	5	48.	1
09.	3	19.	3	29.	3 OR 4	39.	5	49.	1
	5		5		2		2		3

✪විශේෂ උපදෙස්/**Special Instructions:**

එක් පිළිතුරකට ලකුණු 01 බැගින්/ **01 Mark for each question**

මුළු ලකුණු/**Total Marks**   01 $\times$ 50 = 50

PART A — STRUCTURED ESSAY
*Answer **all four** questions on this paper itself. (Each question carries **100** marks.)*

1. (a) State whether the following statements are **true** or **false** on the dotted lines. Reasons are not required.

(i) Rules related to polarizing power of cations and polarizability of anions predict that the melting point of KBr is higher than that of LiI. ......**True**......

(ii) The electron gain energy of Be is positive. ......**True**......

(iii) The spacing between two adjacent lines in a given series of the atomic spectrum of hydrogen decreases gradually in the direction of decreasing wavelengths. ......**True**......

(iv) The de Broglie wavelength associated with the N_2 molecule is shorter than the de Broglie wavelength of the O_2 molecule when travelling at the same velocity. ......**False**......

(v) The effective nuclear charge (Z_{eff}) felt by a valence electron of C is greater than the effective nuclear charge felt by a valence electron of N. ......**False**......

(vi) All C–O bonds in carbonic acid (H_2CO_3) are equal in length. ......**False**......
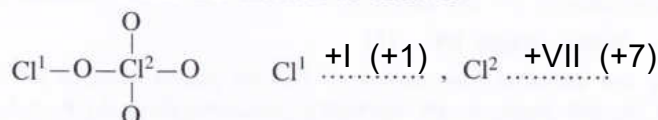
(04 marks x 6 = 24 marks)

1(a): 24 marks

(b) (i) Draw the **most** acceptable Lewis dot-dash structure for the molecule Cl_2O_4. Its skeleton is given below.

(06)
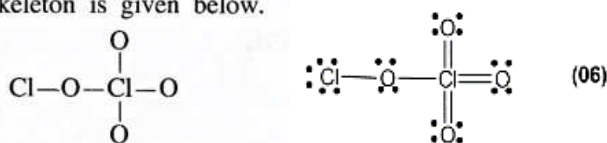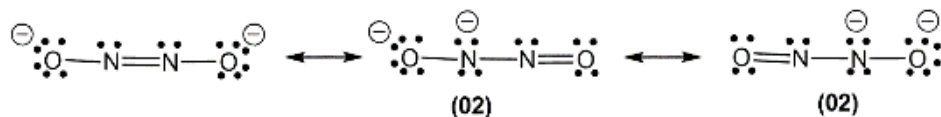
(ii) Give the oxidation states of the two chlorine atoms in the structure drawn in (i) above. The chlorine atoms are labelled as follows.

Cl^1—O—Cl^2—O Cl^1 ...**+I (+1)**..., Cl^2 ...**+VII (+7)**...
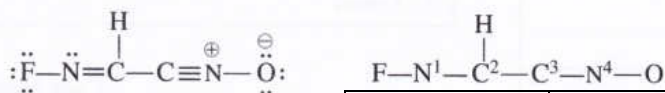
(01 + 01)

(iii) The **most** stable Lewis dot-dash structure for the ion $N_2O_2^{2-}$ is shown below. Draw **two** additional Lewis dot-dash structures (resonance structures) for this ion.

(02)   **(02)**

(iv) Complete the given table based on the Lewis dot-dash structure and its labelled skeleton given below.

F—N^1—C^2—C^3—N^4—O

		N^1	C^2	C^3	N^4
I	VSEPR pairs around the atom	3	3	2	2
II	electron pair geometry around the atom	trigonal planar	trigonal planar	linear	linear
III	shape around the atom	angular/V	trigonal planar	linear	linear
IV	hybridization of the atom	sp^2	sp^2	sp	sp

(01 mark x 16 = 16 marks)

- Parts (v) to (viii) are based on the Lewis dot-dash structure given in part (iv) above. Labelling of atoms is as in part (iv).

(v) Identify the atomic/hybrid orbitals involved in the formation of σ bonds between the two atoms given below.

I. N^1—F N^1 .... sp^2 ....   F .... 2p or sp^3 ....

II. N^1—C^2 N^1 .... sp^2 .... C^2 .... sp^2 ....

III. C^2—H C^2 .... sp^2 ....   H .... 1s ....

IV. C^2—C^3 C^2 .... sp^2 .... C^3 .... sp ....

V. C^3—N^4 C^3 .... sp .... N^4 .... sp ....

VI. N^4—O N^4 .... sp ....   O .... 2p or sp^3 ....

(01 mark x 12 = 12 marks)

(vi) Identify the atomic orbitals involved in the formation of π bonds between the two atoms given below.

I. N^1—C^2 N^1 .... 2p .... C^2 .... 2p ....

II. C^3—N^4 C^3 .... 2p .... N^4 .... 2p ....

C^3 .... 2p .... N^4 .... 2p ....

(01 mark x 6 = 06 marks)

(vii) State the approximate bond angles around N^1, C^2, C^3 and N^4 atoms.

N^1 .... (118° ± 1) ...., C^2 .... (120° ± 1) ...., C^3 .... (180° ± 1) ...., N^4 .... (180° ± 1) ....

(01 mark x 4 = 04 marks)

(viii) Arrange the atoms N^1, C^2, C^3 and N^4 in the **increasing** order of electronegativity.

C^2 < C^3 < N^1 < N^4 **(04)**

1(b): 54 marks

(c) (i) A laser emits photons of wavelength 695 nm.

I. To which region of the electromagnetic spectrum do these photons belong?

Visible region   **(02)**

II. Calculate the energy of a mole of these photons in kJ mol^{-1}.

Velocity of light $c = 3.00 \times 10^8$ m s^{-1} Planck constant $h = 6.63 \times 10^{-34}$ J s

Energy of a photon (E) $= h\nu$

$= h\dfrac{c}{\lambda}$ **(01)**

Energy of a mole of photons $= h\dfrac{c}{\lambda} \times N_A$ **(01)**
(N_A = Avogadro constant)

Therefore, Energy of a mole of photons

$= \dfrac{6.63 \times 10^{-34}\,(\text{J s}) \times 3.00 \times 10^8\,(\text{m s}^{-1}) \times 6.022 \times 10^{23}\,(\text{mol}^{-1})}{695 \times 10^{-9}\,(\text{m})}$ **(03+01)**

$= 172$ kJ mol^{-1} **(02)**

Note: Marks can be awarded for combining steps.
$h = 6.626 \times 10^{-34}$ (J s) is accepted.

(ii) A molecule of formula AX_3 has **three** A−X σ bonds. Here, A and X represent symbols of elements and A is the central atom.

Name the molecular shape(s) possible for AX_3 in I and II given below.

I. if AX_3 is polar   T shape,   trigonal pyramidal   **(02 + 02)**

II. if AX_3 is non-polar ....

III. Give **one** example each, for the shapes stated by you in I and II above.
(**Note:** Molecular formulae are required.)

AX_3 is polar   T shape – ClF_3, BrF_3, IF_3 .... (any one) ..... **(02)**

trigonal pyramidal – NH_3, PH_3, NCl_3, PCl_3 (any one)   **(02)**

AX_3 is non-polar   trigonal planar – BF_3, BCl_3, BBr_3, BI_3 .... (any one) .... **(02)**

1(c): 22 marks

2. The questions [(a) – (d)] given below relate to elements/species designated as **A**, **B**, **C** and **D**.

(a) **A** is a s-block element. It has an atomic number less than 20. It reacts with water vigorously with ignition to give a strongly basic solution, with the evolution of a gas. **A** reacts with excess $O_2(g)$ to give the superoxide. The naturally occurring ore Sylvite contains a compound of **A**.

(i) Write the chemical symbol of **A**. ......K........... **(05)**

(ii) Write the complete electronic configuration of **A**. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(05)**

(iii) Name the gas evolved in the reaction of **A** with water. Hydrogen or H_2 **(05)**

(iv) What is the colour given by **A** in the flame test? ......Lilac (violet)......... **(05)**

(v) Write the balanced chemical equation for the reaction of **A** with excess $O_2(g)$.

$K + O_2 \longrightarrow KO_2$ **(05)**

(vi) Is the first ionization energy of **A** higher or lower than that of the element in the same group and the period above it in the Periodic Table? Briefly explain your answer. **(02)**

Lower

....When going down the group, change in effective nuclear charge
(or Z_{eff}) for the outer most / last electron is negligible. **(01)**
....However, atom size increases.......... **(01)**
Therefore, attraction of outer electron to nucleus decreases. **(01)**

(vii) Give the chemical formula of the compound of **A** in Sylvite. ......KCl........... **(05)**

Note: (vi) Award marks for reasoning only if 'lower' is written.

2(a): 35 marks

(b) **B** is an anion containing only the two elements **X** and **Y**, in the ratio 2:3 respectively. Both **X** and **Y** are p-block elements that belong to the same group in the Periodic Table. The atomic number of each element is less than 20. The electronegativity of **X** is less than the electronegativity of **Y**. When **X** reacts with hot concentrated sulfuric acid, a colourless gas with a pungent smell is evolved as one of the products.

(i) Write the chemical formula, including the charge, of **B**. $S_2O_3^{2-}$ **(05)**

(ii) Draw the Lewis dot-dash structure of **B**.
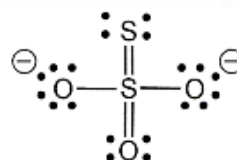
(05)

(iii) Give the oxidation state of the central atom of **B**. ......+4......... **(05)**

(iv) Give a chemical test to identify **B**. (**Note:** Observation(s) is/are also required.)

Test	Observation
1. Add dil. H_2SO_4	Colourless gas with a pungent smell and colloidal sulfur precipitate (or milky solution)
2. Add $Pb(OAc)_2$	White precipitate which turns black on heating
3. Add $AgNO_3$	White precipitate which turns black on standing / heating
Any one of the above.	Test **(02)**, Observation **(03)**

Note: Test must be correct to award marks for observation.

(v) Write the chemical formula for the compound which has **A** as the cation and **B** as the anion.

......$K_2S_2O_3$......... **(05)**

2(b): 25 marks

(c) **C** is an oxidizing agent. It is composed of three elements in the ratio 1:1:3. One of the elements of **C** is **A**. The other two elements belong to the p-block of the Periodic Table. One of these two elements is also present in **B**. The salt formed between Ag^+ and the anion of one of these elements is yellow in colour, and insoluble in concentrated solution. Write the chemical formula of **C**. KIO_3 **(10)**
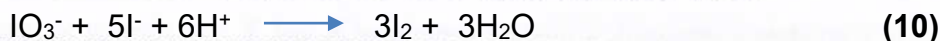
2(c): 10 marks

(d) **D** is a compound composed of two elements. Both these elements are also present in **C**.

(i) When **C**(aq) is mixed with an excess of **D**(aq) in acidic medium, a reddish-brown solution results.

I. Identify **D**.   D = KI   (05)

II. Write the balanced **ionic** equation for the reaction that takes place.

$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ (10)

(ii) On addition of an excess of a solution containing **B**, to the reddish-brown solution obtained in (i) above, the reddish-brown solution becomes colourless. Write the balanced **ionic** equation for the reaction that takes place.

$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$ (05)
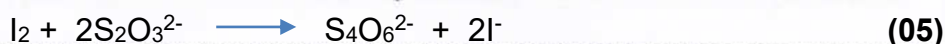
(iii) The concentration of a solution containing **B** can be determined by volumetric analysis utilizing the reactions in (i) and (ii) above. State an indicator which can be used and give the expected colour change at the end point.

Indicator :   Indicator – starch   (05)

Colour change :   Colour change – blue / dark blue/ blue-violet to colourless   (05)

$\boxed{\textbf{2(d): 30 marks}}$

3. (a) **X** and **Y** are two volatile liquids that form an ideal solution. The temperature-composition phase diagram (at a pressure of 1.0×10^5 Pa) for a system containing **X** and **Y** is given below.

● Parts (i) to (v) are based on the given phase diagram.

(i) Indicate the following regions on the phase diagram by writing the letters P, Q, R.

P – region where only the liquid phase is present

Q – region where only the vapour phase is present

R – region where the liquid phase and the vapour phase are in equilibrium

Q or vapour (02)

R or vapour + liquid (02)

P or liquid (02)

(ii) Give the boiling points of pure **X** and pure **Y**.
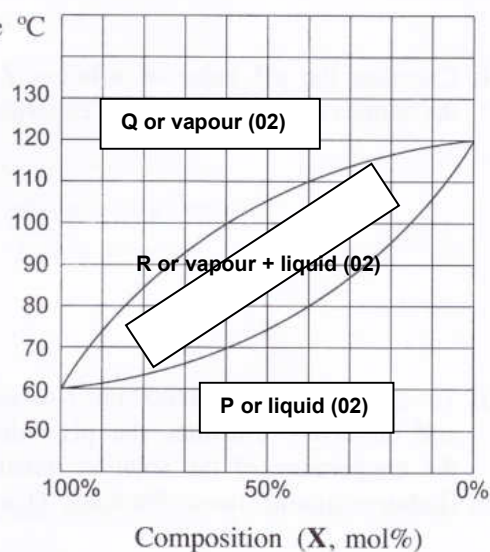
X = 60 ⁰C   Y= 120 ⁰C   (02+01)x2

(iii) What is the temperature at which a liquid mixture of **X** and **Y** containing 40 mol% of **X** begins to boil?

80 ⁰C   (02+01)

(iv) What is the lowest temperature at which a mixture of **X** and **Y** containing 60 mol% of **X** is completely converted to vapour?

100 ⁰C   (02+01)

(v) Calculate the saturated vapour pressure of **X** at the temperature of 100 °C.

$$P_X^g = P_X^0\, x_X^l \qquad \text{(03)}$$

$$P_X^g = P^{total} x_X^g \qquad \text{(03)}$$

Therefore, $P_X^0 = \dfrac{P^{total} x_X^g}{x_X^l}$ \qquad (03)

$$P_X^0 = \dfrac{1\times10^5\,Pa\,\times 60}{15} \qquad \text{(05+01)}$$

$$P_X^0 = 4.0 \times 10^5\,Pa \qquad \text{(04+01)}$$

(vi) In a separate experiment, a mixture containing **X** and **Y** was allowed to reach equilibrium in a **closed rigid** container at temperature T. It was then found that the liquid phase in equilibrium with the vapour phase contained 0.10 mol of **X** and 0.10 mol of **Y**. Saturated vapour pressures of **X** and **Y** at this temperature are 4.0×10^5 Pa and 2.0×10^5 Pa, respectively. Using Raoult law, calculate the partial pressures of **X** and **Y**.

$$P_X = \dfrac{0.1\,mol \times 4.0 \times 10^5\,Pa}{0.1\,mol + 0.1\,mol} \qquad \text{(02+01)}$$

$$P_X = 2.0 \times 10^5 Pa \qquad \text{(02+01)}$$

$$P_Y = \dfrac{0.1\,mol \times 2.0 \times 10^5\,Pa}{0.1\,mol + 0.1\,mol} \qquad \text{(02+01)}$$

$$P_X = 1.0 \times 10^5 Pa \qquad \text{(02+01)}$$
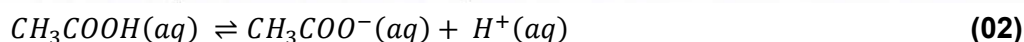
3(a): 50 marks

(b) The concentration of an aqueous solution of acetic acid (solution **Z**) was determined by titrating with an aqueous solution of NaOH. A volume of 12.50 cm³ of solution **Z** required 25.00 cm³ of NaOH solution of concentration 0.050 mol dm⁻³ to reach the end point.

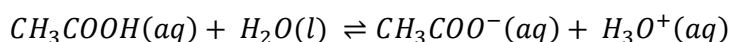(i) Calculate the concentration of acetic acid in solution **Z**.

$$[CH_3COOH(aq)] = \dfrac{25.00\,cm^3 \times 0.05\,mol\,dm^{-3}}{12.50\,cm^3} \qquad \text{(02+01)}$$

$$= 0.10\,mol\,dm^{-3} \qquad \text{(02+01)}$$

(ii) Calculate the pH value of solution **Z**. Acid dissociation constant of acetic acid (K_a) at the temperature at which the experiment was carried out is 1.80×10^{-5} mol dm⁻³.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \qquad \text{(02)}$$

Or

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Initial concentration of acetic acid = C

Fraction dissociated = α (or amount dissociated = x)

[Physical states are required for K_a]

$$K_a = \dfrac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} \; or \; K_a = \dfrac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} \qquad \text{(02)}$$

$$K_a = \dfrac{C\alpha\, C\alpha}{} \quad or \quad K_a = \dfrac{x^2}{} \qquad \text{(02)}$$

[if the equation, $K_a = \dfrac{C\alpha\, C\alpha}{C(1-\alpha)}$ or $K_a = \dfrac{x^2}{C-x}$ is not written
but the calculation is done correctly, award 02 marks for the calculation]

Since α<<1 or x << c \qquad (02)

pH calculation
(Do not deduct marks if physical states are not given)

$$[H^+(aq)] = \sqrt{K_a C}$$
$$[H^+(aq)] = \sqrt{1.80 \times 10^{-5}\ mol\ dm^{-3}\ \times 0.1\ mol\ dm^{-3}}$$ **(02)**

$$[H^+(aq)] = 0.00134\ mol\ dm^{-3}$$ **(02)**

$$pH = -\log\left[\frac{H_3O^+(aq)}{1.0\ mol\ dm^{-3}}\right]\ or\ pH = -\log\left[\frac{H^+(aq)}{1.0\ mol\ dm^{-3}}\right]$$ **(02)**

$$pH = 2.87$$ **(02)**

Alternate answer for pH calculation
Using Henderson equation,
(Do not deduct marks if physical states are not given)
$$-\log[H^+(aq)] = 1/2(-\log(K_a c))$$ **(02)**

$$pH = 1/2(-\log(1.8 \times 10^{-5}\ \times 0.1))$$ **(04)**

$$pH = 2.87$$ **(02)**

(iii) To another portion (100.00 cm³) of solution **Z**, 0.200 g of pure solid NaOH was added and dissolved. Calculate the pH value of this solution assuming that the volume and the temperature of the solution remain unchanged.
[Relative atomic mass: Na = 23, O = 16, H = 1]

Amount of CH_3COOH in 100.00 cm³ of solution = 1.0×10^{-2} mol **(02)**
Amount of NaOH added = 0.005 mol **(02)**
Amount of CH_3COOH left in the medium (after reacting with NaOH) = 5.00×10^{-3} mol **(02)**

Therefore, in solution,
(Do not deduct marks if physical states are not given)
$[CH_3COOH(aq)]$ = 0.05 mol dm⁻³ **(02)**

$[CH_3COONa(aq)]$ = 0.05 mol dm⁻³ **(02)**

----

pH calculation
(Do not deduct marks if physical states are not given)

$$[H^+(aq)] = \frac{K_a\ [CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$ **(02)**

$$[H^+(aq)] = \frac{1.80 \times 10^5 mol\ dm^{-3} \times 0.050\ mol\ dm^{-3}}{0.050\ mol\ dm^{-3}}$$ **(02)**

$$[H^+(aq)] = 1.80 \times 10^{-5}\ mol\ dm^{-3}$$

$$pH = 4.74$$ **(02)**

Alternate answer for pH calculation
(Do not deduct marks if physical states are not given)

$$pH = pK_a + \log\left[\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}\right] \qquad \textbf{(02)}$$

$$pH = -\log(1.8 \times 10^{-5}) + \log\left[\frac{[0.05]}{[0.05]}\right] \qquad \textbf{(02)}$$

$$pH = 4.74 \qquad \textbf{(02)}$$

(iv) Does the solution described in (iii) above behave as a buffer solution? Explain your answer.

The solution in (iii) above behaves as a buffer solution. **(02)**
The solution contains a weak acid and the sodium salt of its conjugate base **(02+02)**

(v) In a separate experiment, 0.800 g of pure solid NaOH was dissolved in a 100.00 cm^3 volume of solution **Z**. Does this solution behave as a buffer solution? Explain your answer using a suitable calculation. Assume that the volume and temperature of the solution remain unchanged.

The amount of CH$_3$COOH in 100.00 cm^3 = 0.01 mol

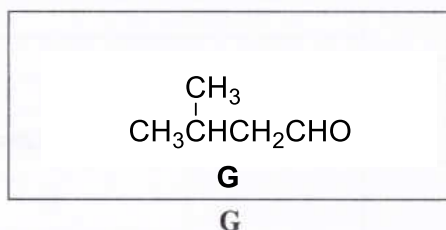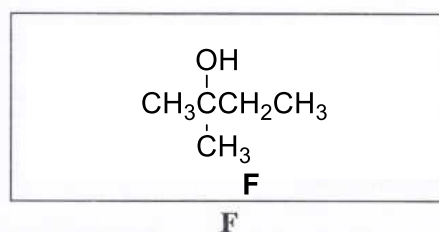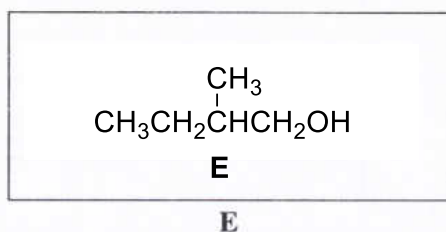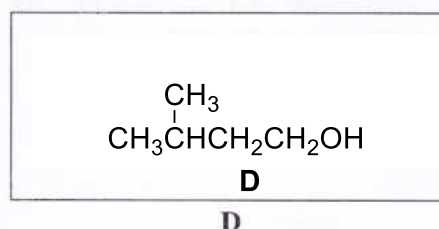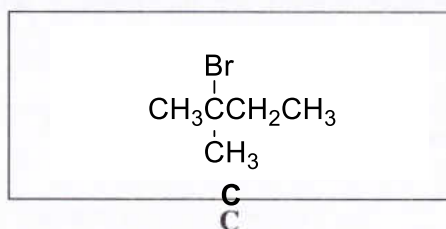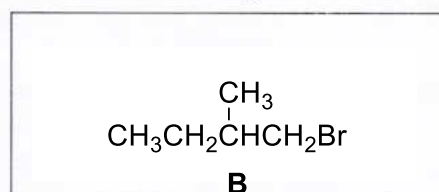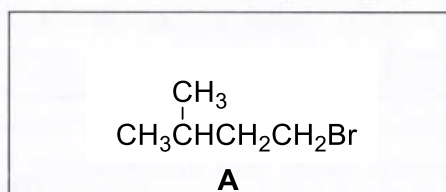The amount of NaOH added = 0.02 mol **(02)**
Solution does not contain CH$_3$COOH (or CH$_3$COOH has reacted completely) **(02)**
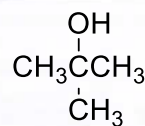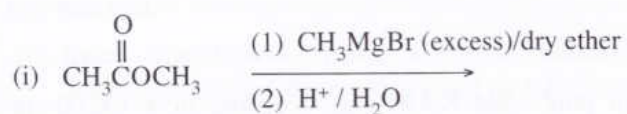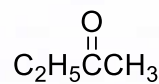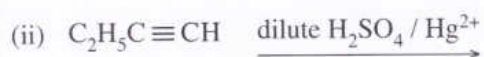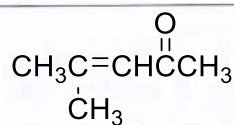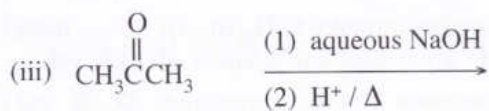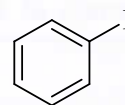Solution does not behave as a buffer solution **(02)**

3(b): 50 marks

4. (*a*) **A, B** and **C** are structural isomers having the molecular formula $C_5H_{11}Br$. Of these three isomers, only **B** exhibits optical isomerism. **A** and **C** are positional isomers of each other. When **A, B** and **C** were reacted separately with aqueous NaOH, compounds **D, E** and **F** having the molecular formula $C_5H_{12}O$ were formed respectively. **D, E** and **F** were treated separately with PCC. **F** did not react with PCC. **D** and **E** reacted with PCC and gave **G** and **H** respectively. Both compounds **G** and **H** gave coloured precipitates with 2,4–dinitrophenylhydrazine (2,4–DNP) and silver mirrors with ammonical $AgNO_3$.

Draw the structures of **A, B, C, D, E, F, G** and **H** in the boxes given below.

|	
CH_3 $CH_3CHCH_2CH_2Br$ **A**	CH_3 $CH_3CH_2CHCH_2Br$ **B**
A	**B**
Br $CH_3CCH_2CH_3$ CH_3 **C**	CH_3 $CH_3CHCH_2CH_2OH$ **D**
C	**D**
CH_3 $CH_3CH_2CHCH_2OH$ **E**	OH $CH_3CCH_2CH_3$ CH_3 **F**
E	**F**
CH_3 CH_3CHCH_2CHO **G**	CH_3 CH_3CH_2CHCHO **H**
G	**H**
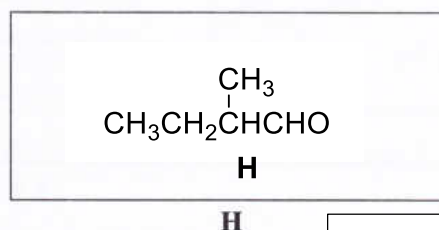
4(a): 07 × 8 = 56

(b) Draw the structures of the products **I**, **J**, **K** and **L** of the following reactions, in the given boxes.

(i) CH_3COCH_3 (with $=O$) $\xrightarrow{\text{(1) } CH_3MgBr \text{ (excess)/dry ether}}{\text{(2) } H^+ / H_2O}$

$$\underset{\overset{|}{CH_3}}{CH_3\overset{\overset{\displaystyle OH}{|}}{C}CH_3}$$

I

(ii) $C_2H_5C \equiv CH$ $\xrightarrow{\text{dilute } H_2SO_4 / Hg^{2+}}$

$$C_2H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

J

(iii) CH_3CCH_3 (with $=O$) $\xrightarrow{\text{(1) aqueous NaOH}}{\text{(2) } H^+ / \Delta}$

$$\underset{\overset{|}{CH_3}}{CH_3C{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3}$$

K

(iv) $N_2^+Cl^-$ (on benzene ring) $\xrightarrow{KI}$

benzene ring with I

L

4(b): 06 × 4 = 24 marks

(c) Give the mechanism and the structure of the product formed for the reaction between $CH_3CH = CHCH_3$ and Br_2/CCl_4.

(02)
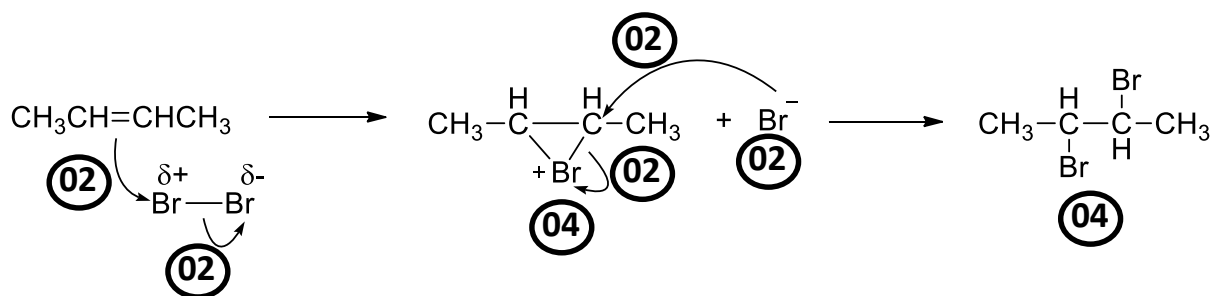
(02) For the polarization of Br

4(c): 20 marks

PART B — ESSAY

Answer two questions only. (Each question carries 150 marks.)

5. (a) (i) A gas mixture containing CH_4, C_2H_6 and excess O_2 was introduced into an evacuated closed rigid container. The volume of the container was 8.314×10^{-3} m³. The pressure of the container at 400 K was 4.80×10^6 Pa. Calculate the total number of moles of gases in the container. Assume that all the gases behave ideally and that there is no reaction at this temperature.

Using pV=nRT, **(05)**

At 400K, $n_1 = \dfrac{4.8 \times 10^6 Pa\ 8.314 \times 10^{-3} m^3}{8.314\ J\ mol^{-1}K^{-1}\ 400K}$ **(04+01)**

$n_1 = 12.0\ mol$ **(04+01)**

(ii) All the hydrocarbons in the container were completely combusted by increasing the temperature of the container to 800 K. The pressure of the container after the combustion reactions at 800 K was 1.00×10^7 Pa. Calculate the total number of moles of gases in the container after combustion. Assume that H_2O is present as a gas under these conditions.

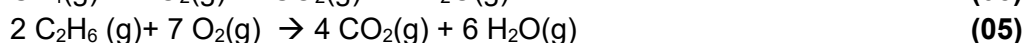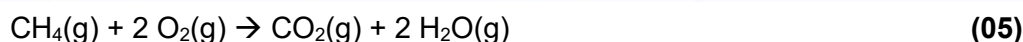At 800K, $n_2 = \dfrac{1.0 \times 10^7 Pa\ 8.314 \times 10^{-3} m^3}{8.314\ J\ mol^{-1}K^{-1}\ 800K}$ **(04+01)**

$n_1 = 12.5\ mol$ **(04+01)**

(iii) Write balanced chemical equations (giving physical states, at 800 K) for the combustion reactions of the gases given below.
   I. $CH_4(g)$
   II. $C_2H_6(g)$

   $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ **(05)**
   $2\ C_2H_6\ (g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(g)$ **(05)**

(iv) Only one of the two hydrocarbons above contributes to the change in the number of moles of gases before and after combustion.
Calculate the number of moles of this hydrocarbon initially introduced into the container.

Hydrocarbon that contributes to the change of the number of moles before and after the combustion is C_2H_6 **(05)**
No. of moles increased after combustion = 0.5 mol
The amount of C_2H_6 introduced initially = 0.5 mol x 2 = 1.0 mol **(04+01)**

(v) The container was then cooled to 300 K and the water was removed. Then the pressure of the container was 2.10×10^6 Pa.
Calculate the following.

Amount (moles) of gases after removing water,
$n_3 = \dfrac{2.1 \times 10^6\ Pa\ 8.314 \times 10^{-3} m^3}{8.314\ J\ mol^{-1}K^{-1}\ 300K}$ **(04+01)**
$n_3 = 7.0\ mol$ **(04+01)**

I. Total number of moles of H_2O produced

The amount of water formed = (12.7 – 7.0) mol = 5.5 mol **(04+01)**

II. Number of moles of H_2O produced from the combustion of C_2H_6

The amount of water generated from the combustion of C_2H_6 = $\dfrac{6.0\ mol \times 3.0\ mol}{2.0\ mol}$
= 3.0 mol **(04+01)**

III. Number of moles of H_2O produced from the combustion of CH_4

The amount of water generated from the combustion of CH_4 = (5.5 – 3.0) mol

= 2.5 mol   **(04+01)**

IV. Number of moles of O_2 introduced initially into the container

The amount of O_2 introduced initially = 12.0 mol – (1.0 mol + amount of CH_4 introduced)

= 12.0 mol – (1.0 + 2.5/2) mol

= 9.75 mol   **(04+01)**

5(a) : 75 marks

Alternate answer for (iv) and (v)

(iv) Hydrocarbon that contributes to the change of the number of moles before and after the combustion is C_2H_6.   **(05)**

Let the number of moles of the species as follows

Initially,

$CH_4 = n_1$ $C_2H_6 = n_2$ and $O_2 = 2n_1 + 7/2n_2 + n_{excess}$

After combustion,

$CO_2 = n_1 + 2n_2$, $H_2O = 2n_1 + 3n_2$ and $O_2 = 2n_1 + 7/2n_2 + n_{excess}$

Before combustion the number of moles in the container => 12.0 mol = $n_1 + n_2 + 2n_1 + 7/2n_2 + n_{excess}$ --(1)

After combustion the number of moles in the container   => 12.5 mol = $n_1 + 2n_2 + 2n_1 + 3n_2 + n_{excess}$ -- (2)

(2)-(1) => 0.5 = 1/2n_2

Amount of C_2H_6 introduced = n_2 = 1.0 mol   **(04+01)**

(v) The total amount of water formed = $2n_1 + 3n_2$

Amount (moles) of gases after removing water,

$$n_1 + 2n_2 + n_{excess} = \frac{2.1 \times 10^6\, Pa\ 8.314 \times 10^{-3} m^3}{8.314\, J\, mol^{-1} K^{-1}\ 300K}$$ **(04+01)**

$n_1 + 2n_2 + n_{excess} = 7.0\ mol$ **(04+01)**

Therefore, from part (iv) equation (2),

n_1 = ½(12.5- ($n_1 + 2n_2 + 3n_2 + n_{excess}$)) = ½(12.5-10.0)mol = 1.25 mol

(I) The total amount of water formed = $2n_1 + 3n_2$ = (2x1.25+3x1.0)mol = 5.5 mol   **(04+01)**

(II) The amount of water formed from C_2H_6 combustion = $3n_2$ = 3.0 mol   **(04+01)**

(III) The amount of water formed from CH_4 combustion = $2n_1$ = 2.5 mol   **(04+01)**

(IV) The amount of O_2 introduced initially = (12.0 –(1.25+1.0))mol = 9.75 mol   **(04+01)**

(b) (i) Using a **thermochemical cycle** and the data given, calculate the standard enthalpy change for the reaction given below.

$$4\,CH_4(g) + O_2(g) \longrightarrow 2\,C_2H_6(g) + 2\,H_2O(g)$$
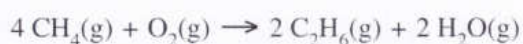
	$\left(\Delta H_f^{o}\right)$ (kJ mol^{-1})	S^{o} (J mol^{-1} K^{-1})
$CH_4(g)$	−74.8	186.3
$C_2H_6(g)$	−84.7	229.6
$CO_2(g)$	−393.5	213.7
$H_2O(g)$	−214.8	188.8
C(s), graphite	0.0	5.7
$O_2(g)$	0.0	205.1
$H_2(g)$	0.0	130.7
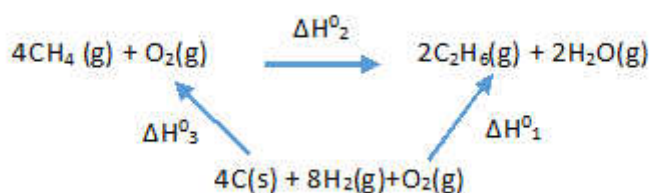
For the thermochemical cycle:
For the correct species, correct stoichiometry and correct physical state

(02 marks x 7 = 14)

$\Delta H^0_2 = \Delta H^0_1 - \Delta H^0_3$ **(03)**
Or

$$\Delta H_2^0 = \sum \Delta H^0(products) - \sum \Delta H^0(reactants)$$

     (06)   **(06)**   **(06)**   **(02)**

$\Delta H_2^0 = [-84.7 \times 2 \ - \ 214.8 \times 2 - (-74.8 \times 4)]$ kJ mol^{-1}

= -299.8 kJ mol^{-1} **(03+01)**

Alternate thermodynamic cycle
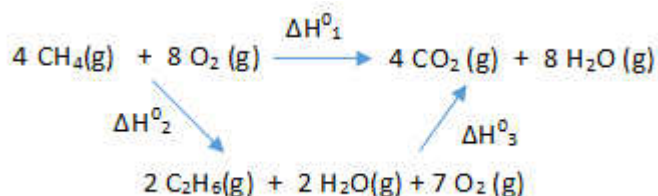
For the thermochemical cycle:
For the correct species, correct stoichiometry and correct physical state

(02 marks x 7 = 14)

     (02)   **(02)**   **(02)**   **(02)**
$\Delta H^0_1 = (-393.5 \times 4 - 214.8 \times 8 - (-74.8 \times 4 + 0 \times 8))$ kJ mol^{-1}
     = -2993.2 kJ mol^{-1}
    (02)   **(02)**   **(02)**   **(02)**   **(02)**   **(02)**

$\Delta H^0_3 = ((-393.5 \times 4 - 214.8 \times 8) - (-84.7 \times 2 - 214.8 \times 2 - 0 \times 7))$ kJ mol^{-1}
     $= -2693.4$ kJ mol^{-1}
$\Delta H^0_2 = \Delta H^0_1 - \Delta H^0_3$ **(03)**
     $= (-2993.2 - (-2693.4))$ kJ mol^{-1}
     $= -299.8$ kJ mol^{-1} **(03+01)**

(ii) Calculate the standard entropy change for the reaction in (b)(i) above.

$\Delta S^0 = \sum S^0(products) - \sum S^0(reactants)$ **(04)**

           (02)   **(02)**   **(02)**   **(02)**   **(01)**
$\Delta S^0 = ((229.6 \times 2 + 188.8 \times 2 - (186.2 \times 4 + 205.1 \times 1))$ J mol^{-1} K^{-1}
     $= -113.5$ J mol^{-1} K^{-1} **(02+01)**

(iii) Calculate the standard Gibbs energy change (ΔG^o) for the reaction in (b)(i) above at 500 K.

$\Delta G^0 = \Delta H^0 - T \Delta S^0$ **(04)**
     $= -299.8$ kJ mol^{-1} $- (500$ K $\times (-113.5 \times 10^{-3})$ kJ mol^{-1} K^{-1})   **(04+01)**
     $= -243.05$ kJ mol^{-1} **(02+01)**

(iv) State, giving reasons, whether increase in temperature favours the reaction in (b)(i) above. Assume that the enthalpy change and entropy change are independent of temperature.

Increasing temperature does not favour the forward reaction.   **(03)**

(Or increasing temperature makes Gibbs energy change less negative)

Because the reaction has a negative change in entropy.   **(03)**

[If the sign of entropy change is incorrect, but prediction agrees with the sign of the entropy change award 06 marks)

5(b) : 75 marks

6. (a) (i) Consider the reversible reaction **a A(aq) ⇌ b B(aq) + c C(aq)** that occurs in the aqueous medium. Considering that both forward and reverse steps are elementary reactions, write expressions for the rate of the forward reaction (R$_1$) and the rate of the reverse reaction (R$_2$). Rate constants for the forward reaction and the reverse reaction are k_1 and k_2, respectively.

$R_1 = k_1 [A(aq)]^a$ **(05+01)**

$R = k [B(aq)]^b [C(aq)]^c$ **(05+01)**

(ii) Write the relationship between R$_1$ and R$_2$ at equilibrium.

At equilibrium, $R_1 = R_2$ **(05)**

(iii) Write down the expression for equilibrium constant K_C. Also give the relationship between K_C, k_1 and k_2.

$$K_c = \frac{[B(aq)]^b [C(aq)]^c}{[A(aq)]^a}$$ 　　　　　　　　　　　　　　　　**(05+01)**

[expression 05 marks, physical states 01 mark]

$$K_C = \frac{k_1}{k_2}$$ 　　　　　　　　　　　　　　　　　　　　　　　　**(05)**

(iv) To study the above equilibrium, three experiments were carried out at a constant temperature. In these experiments, different amounts of A, B and C were mixed, and the system was allowed to reach equilibrium. The following data were obtained at equilibrium.

Experiment Number	Concentration at equilibrium (mol dm^{-3})		
	[A]	[B]	[C]
1	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}
2	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-3}
3	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}

I. Obtain three relationships by substituting the concentrations of A, B and C given in the table for experiments 1, 2 and 3 in the equilibrium constant expression written in (a)(iii) above.

$$K_c = \frac{(1.0 \times 10^{-2})^b (1.0 \times 10^{-3})^c}{(1.0 \times 10^{-1})^a} \quad \text{--(1)}$$ 　　　　**(06)**

$$K_c = \frac{(1.0 \times 10^{-3})^b (1.0 \times 10^{-3})^c}{(1.0 \times 10^{-2})^a} \quad \text{--(2)}$$ 　　　　**(06)**

$$K_c = \frac{(1.0 \times 10^{-2})^b (1.0 \times 10^{-5})^c}{(1.0 \times 10^{-2})^a} \quad \text{--(3)}$$ 　　　　**(06)**

II. Prove that a = b = 2c using these relationships.

From (1)/(2)=> $1 = \frac{10^b}{10^a}$ 　　　　　　　　　　　　　　　　　**(05)**

$10^a = 10^b$

a=b 　　　　　　　　　　　　　　　　　　　　　　　　　　　　　**(05)**

From (2)/(3) => $1 = \frac{10^{2c}}{10^b}$ 　　　　　　　　　　　　　　　　**(05)**

$10^b = 10^{2c}$

Therefore, a = b = 2c

Alternate answer 1 for **(iv) (II)**

Using equation (1), (2) and (3) in (iv)(I)

$K_C = 10^{-2b-3c+a}$ ----------(4)   **(04)**

$K_C = 10^{-3b-3c+2a}$ ---------(5)   **(04)**

$K_C = 10^{-2b-5c+2a}$ ---------(6)   **(04)**

Log K_c = -2b-3c+a   ---------(7)

Log K_c = -3b-3c+2a ---------(8)

Log K_c = -2b-5c+2a ----------(9)

(4)/(5) or (7)-(8) → a = b   **(04)**

(5)/(6) or (8)-(9) → a = 2c   **(04)**

Therefore, a = b = 2c

Alternate answer 2 for **(iv) (II)**

Using equation (1), (2) and (3) in (iv)(I)

$K_C = (0.01)^b (0.001)^c (0.1)^{-a}$ ----------(4)

$K_C = (0.001)^b (0.001)^c (0.01)^{-a}$ --------(5)

$K_C = (0.01)^b (0.00001)^c (0.01)^{-a}$ ------(6)

(1)/(2)→   1 = 10^b x 10^{-a}   **(05)**

          $10^a = 10^b$

            a=b   **(05)**

(1)/(3) →   1 = 10^{2c} x10^{-a}   **(05)**

            a = 2c   **(05)**

Therefore, a = b = 2c

III. Using the smallest integers for the stoichiometric coefficients a, b and c, calculate the value of the equilibrium constant, K_C of the above reaction.

Using the smallest set of integers,

a = 2, b=2, c=1

Calculation of K_C

$$K_C = \frac{(1.0 \times 10^{-2} mol\ dm^{-3})^2 (1.0 \times 10^{-3} mol\ dm^{-3})^1}{(1.0 \times 10^{-1} mol\ dm^{-3})^2}$$ **((02+01)x3=09)**

$$K_C = 1.0 \times 10^{-5} mol\ dm^{-3}$$ **(04+01)**

6(a) : 80 marks

(b) Consider the reaction, **p P(g) ⇌ q Q(g) + r R(g)** that takes place in gas phase.

(i) The enthalpy change and activation energy of the forward reaction, **p P(g) → q Q(g) + r R(g)** are 50.0 kJ mol⁻¹ and 90.0 kJ mol⁻¹, respectively. Draw the labelled energy diagram (the graph of energy vs reaction coordinate) for this reaction. Show the positions of P, Q and R by marking them on the energy diagram. Also, mark the position of the activated complex as 'activated complex' on it.
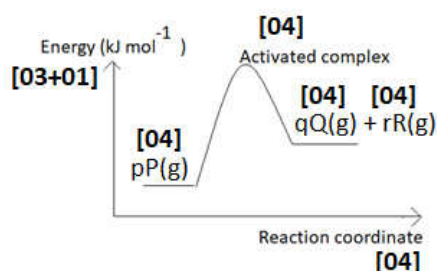
(ii) Calculate the activation energy for the reverse reaction.

Activation energy of the reaction = E_a

E_a = (90.0 – 50.0) kJ mol⁻¹   **(05+01)**

    = 40.0 kJ mol⁻¹   **(04+01]**

(iii) Explain the effect of increasing temperature on the equilibrium constant of this reaction.

When the temperature is increased, the equilibrium constant is increased **(05)** because the reaction has a positive change in enthalpy **(05)**
When the temperature is increased, the rate constant of the forward reaction is increased more than the rate constant of the reverse reaction. **(05)**

(iv) Explain the effect of a catalyst
   I. on the rates of forward and reverse reactions.
   II. on the equilibrium constant.

(I) Increases the rate of forward reaction **(05)**
and the rate of the reverse reaction **(05)**
by the same factor (extent). **(05)**

(II) The value of the equilibrium constant is not changed. **(05)**

Alternate answer

(iv) Addition of a catalyst,

(I) It provides a new pathway for the reaction with higher rate constants for forward and reverse reactions **(05)**. The ratio between the two rate constants does not change **(05)**. Rate constants of the forward and reverse reactions are increased by the same factor (extent). **(05)**

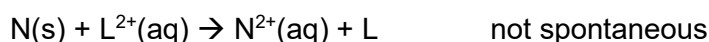(II) The value of the equilibrium constant is not changed. **(05)**

6(b) : 70 marks

7. (a) You are provided with the three metal rods **L**, **M**, **N** and the three solutions L^{2+} (1.0 mol dm^{-3}), M^{2+} (1.0 mol dm^{-3}), N^{2+} (1.0 mol dm^{-3}). When the metal **N** is dipped in the solution of M^{2+} ions, M^{2+} is reduced to **M**, whereas when **N** is dipped in the solution of L^{2+} ions, L^{2+} does not get reduced to **L**.

(i) Giving reasons arrange the three metals, **L**, **M** and **N** in the increasing order of their reducing ability.

$N(s) + M^{2+}(aq) \rightarrow N^{2+}(aq) + M$ is spontaneous
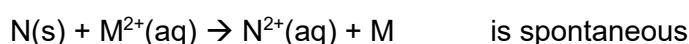
Reducing ability N > M   or $[E^0_{N2+/N} < E^0_{M2+/M}]$ **(05)**

$N(s) + L^{2+}(aq) \rightarrow N^{2+}(aq) + L$ not spontaneous

Reducing ability of L > N   or $[E^0_{L2+/L} < E^0_{N2+/N}]$ **(05)**

Increasing order of reducing ability M<N<L   **(05)**

(Or increasing order of oxidizing ability L<N<M)

(ii) Electromotive forces of the two electrochemical cells prepared using $L^{2+}(aq)/L(s)$ electrode and each of the other two electrodes are +0.30 V and +1.10 V. Using this information and your answer to (i) above, calculate $E^\circ_{M^{2+}(aq)/M(s)}$ and $E^\circ_{N^{2+}(aq)/N(s)}$.

$\left(E^\circ_{L^{2+}(aq)/L(s)} = -0.80 \text{ V} \right)$

Out of the two cells one has E_{cell} = 0.30 V and the other has E_{cell} = 1.10 V

Highest E_{cell} is between $L^{2+}(aq)/L$ electrode and $M^{2+}(aq)/M$ electrode.

The lowest E_{cell} is between $L^{2+}(aq)/L$ electrode and $N^{2+}(aq)/N$ electrode.

$E^0_{M2+(aq)/M} - E^0_{L2+(aq)/L} = 1.10$ V   **(05)**

$E^0_{M2+(aq)/M} = 1.10$ V $- 0.80$ V $= 0.30$ V   **(05)**

And

$E^0_{N2+(aq)/N} - E^0_{L2+(aq)/L} = 0.30$ V   **(05)**

$E^0_{N2+(aq)/N} = 0.30$ V $+ (-0.80$V$) = -0.50$ V   **(05)**

Alternate answer
Based on the order of reducing ability, L^{2+}/L should be the anode in both the cells.

$E^0_{cathode} - E^0_{L2+/L} = 1.10$ V

Therefore $E^0_{cathode} = 1.10$ V $- 0.80$ V $= 0.3$ V **(05)**

$E^0_{cathode} - E^0_{L2+/L} = 0.3$ V

Therefore $E^0_{cathode} = 0.3$ V $- 0.80$ V $= -0.5$ V **(05)**

Therefore,

$E^0_{M2+/M} = 0.3$ V **(05)**

$E^0_{N2+/N} = -0.5$ V **(05)**

(iii) You are provided with the following arrangement, where a potentiometer (**P**) is connected between the metal rods **L** and **N**.
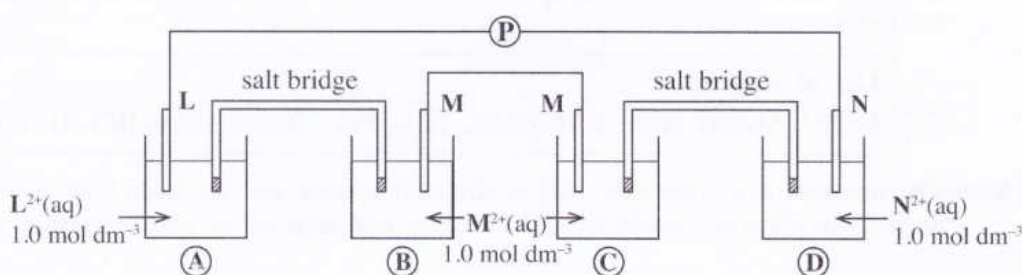
I. Calculate the potentiometer reading.
II. Write the electrode reactions that occur at each of the electrodes Ⓐ, Ⓑ, Ⓒ and Ⓓ separately when the potentiometer is removed and **L** and **N** are connected by a conductor.

Potentiometer reading (P),

$P = E^0_{cell(1)} + E^0_{cell(2)}$ **(05)**

$= (E^0_{M2+(aq)/M} - E^0_{L2+(aq)/L}) + (E^0_{N2+(aq)/N} - E^0_{M2+(aq)/M})$ **(05)**

$= E^0_{N2+(aq)/N} - E^0_{L2+(aq)/L}$ **(05)**

$= -0.50$ V $- (-0.80$ V$)$

$= 0.30$ V **(05)**

II. Write the electrode reactions that occur at each of the electrodes Ⓐ, Ⓑ, Ⓒ and Ⓓ separately when the potentiometer is removed and **L** and **N** are connected by a conductor.

Electrode reactions when a current is drawn.

Electrode (A) $L(s) \rightarrow L^{2+}(aq) + 2e$ **(05)**

Electrode (B) $M^{2+}(aq) + 2e \rightarrow M(s)$ **(05)**

Electrode (D) $N^{2+}(aq) + 2e \rightarrow N(s)$ **(05)**
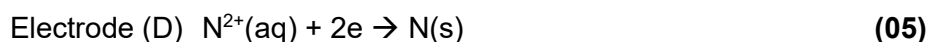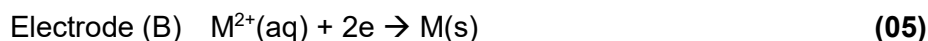
7(a) : 75 marks

(b) The following questions are based on the element manganese (Mn).

(i) Write the complete electronic configuration of Mn.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$ **(03)**

(ii) Write **three** common oxidation states of Mn.

+2, +3, +4, +7   (any three)   **(02 x 3)**

(iii) When $MnSO_4 \cdot H_2O$ is dissolved in water, solution **P** is obtained.

    I. State the colour of solution **P**.

    II. Give the chemical formula and the IUPAC name of the species responsible for this colour.

I. very pale pink/ pale pink/ colourless   **(03)**

II. $[Mn(H_2O)_6]^{2+}$(aq)   **(03)**

   hexaaquamanganese(II) ion   **(03)**

(iv) What would you observe when

    I. dilute NaOH is added to solution **P**?

    II. the mixture from (iv)(I) above is exposed to air?

    III. conc. HCl is added to the mixture from (iv)(I) above?

I. white/cream precipitate   **(03)**
II. brown precipitate or blackish-brown precipitate   **(03)**
III. Yellow / greenish-yellow solution   **(03)**

(v) Give the chemical formulae of **five** oxides of Mn, and write the oxidation state of Mn in each. State the nature of each of the oxides as basic, weakly basic, amphoteric, weakly acidic, acidic.

MnO	+2	basic	**(02 x 3)**
Mn_2O_3	+3	weakly basic	**(02 x 3)**
MnO_2	+4	amphoteric	**(02 x 3)**
MnO_3	+6	weakly acidic	**(02 x 3)**
Mn_2O_7	+7	acidic	**(02 x 3)**

(vi) Give the chemical formula of the most common oxoanion of Mn.

MnO_4^- **(03)**

(vii) Give balanced ionic half equations to indicate how the oxoanion given by you in (vi) above behaves as an oxidizing agent in acidic and basic media.
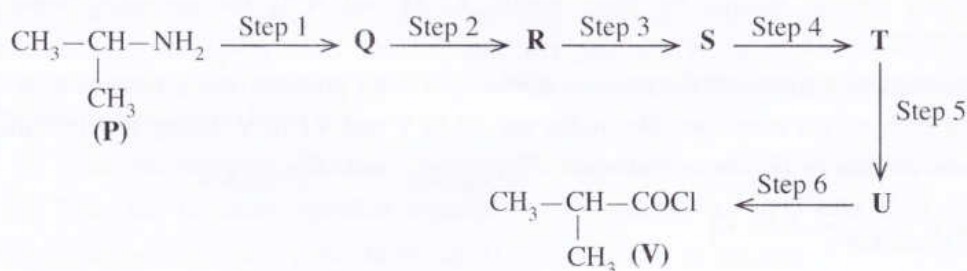
Acidic
MnO_4^-(aq) + $8H^+$(aq) + 5e $\longrightarrow$ Mn^{2+}(aq) + $4H_2O$(l)   **(06)**

Alkaline
MnO_4^-(aq) + $2H_2O$(l) + 3e $\longrightarrow$ MnO_2(s) + $4OH^-$(aq)   **(06)**

(viii) State **one** use of $MnSO_4$ in the analysis of water quality parameters.

Determination of dissolved O_2 in water samples   **(03)**

> **7(b) : 75 marks**
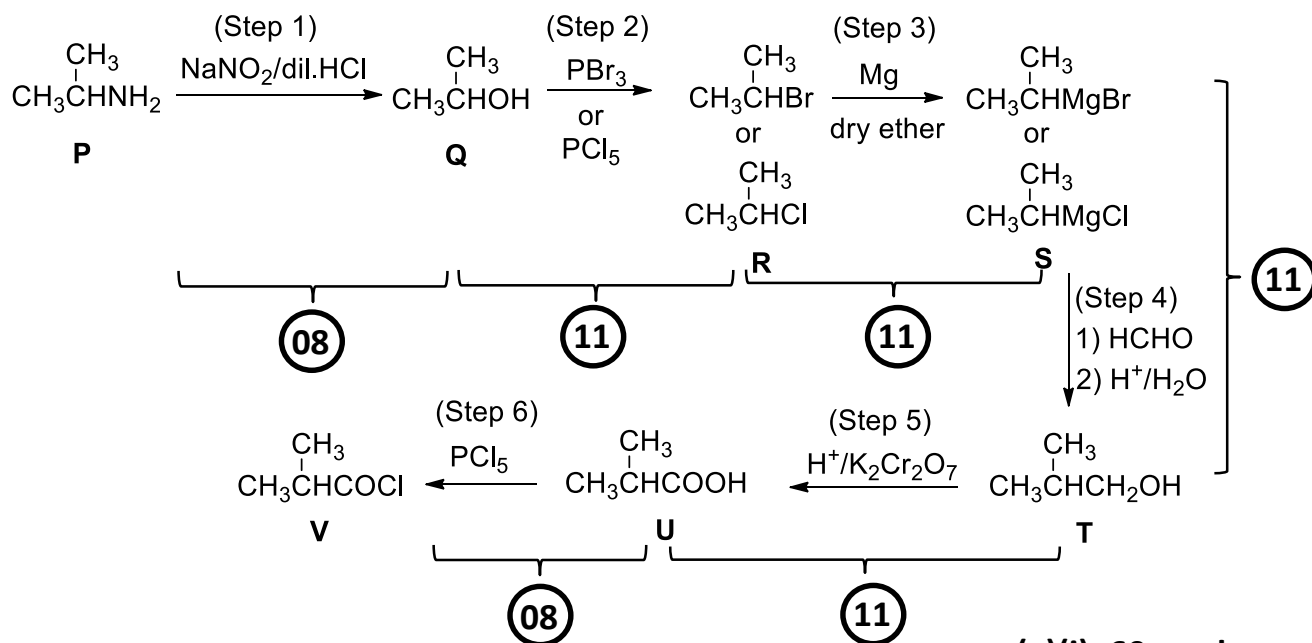
PART C — ESSAY
Answer *two* questions only. (Each question carries **150 marks**.)

8. (*a*) Compound **P** was converted to compound **V** using the reaction scheme given below.

$$CH_3-CH-NH_2 \xrightarrow{\text{Step 1}} Q \xrightarrow{\text{Step 2}} R \xrightarrow{\text{Step 3}} S \xrightarrow{\text{Step 4}} T$$

(with CH_3 on the CH of **P**)

$$T \xrightarrow{\text{Step 5}} U \xrightarrow{\text{Step 6}} CH_3-CH-COCl \;\; (V)$$

(with CH_3 on the CH of **V**)

(i) Complete the above reaction sequence by drawing the structures of compounds **Q**, **R**, **S**, **T** and **U** and writing the reagents for steps 1–6 selected only from those given in the list below.

> **List of reagents**
> HCHO, Mg/dry ether, $H^+/K_2Cr_2O_7$, PCl_5, PBr_3, $NaNO_2$/dilute HCl, H^+/H_2O

(**Note:** The reaction of a compound with a Grignard reagent and the hydrolysis of the resultant magnesium alkoxide should be considered as **one step** in the above reaction sequence.)

(ii) Draw the structure of the product formed when compounds **P** and **V** react with each other.

(i)

$$CH_3CHNH_2 \;(P) \xrightarrow[\text{NaNO}_2/\text{dil.HCl}]{\text{(Step 1)}} CH_3CHOH \;(Q) \xrightarrow[\substack{\text{PBr}_3 \\ \text{or} \\ \text{PCl}_5}]{\text{(Step 2)}} \substack{CH_3CHBr \\ \text{or} \\ CH_3CHCl} \;(R) \xrightarrow[\text{dry ether}]{\text{(Step 3) Mg}} \substack{CH_3CHMgBr \\ \text{or} \\ CH_3CHMgCl} \;(S)$$

(08) (11) (11) — (11)

$$S \xrightarrow[\substack{\text{1) HCHO} \\ \text{2) } H^+/H_2O}]{\text{(Step 4)}} CH_3CHCH_2OH \;(T) \xleftarrow{\text{(Step 5)} \; H^+/K_2Cr_2O_7} CH_3CHCOOH \;(U) \xrightarrow{\text{(Step 6)} \; PCl_5} CH_3CHCOCl \;(V)$$

(11) (08)

(each compound carrying a CH_3 substituent on the CH)

(a)(i): 60 marks

*In Step 4 the student may have misinterpreted the instruction given in the note in the question and written HCHO and H^+/H_2O without showing the sequence 1 and 2.

(ii)
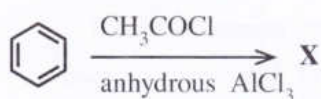
$$CH_3CHCONHCHCH_3$$

(with CH_3 on each CH) (05)
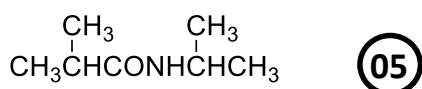
(a) (ii): 05 marks

8(a): 65 marks

(b) (i) Propose a method to prepare a mixture of *o*-nitrobenzoic acid and *p*-nitrobenzoic acid from benzene using not more than **three** (03) steps.
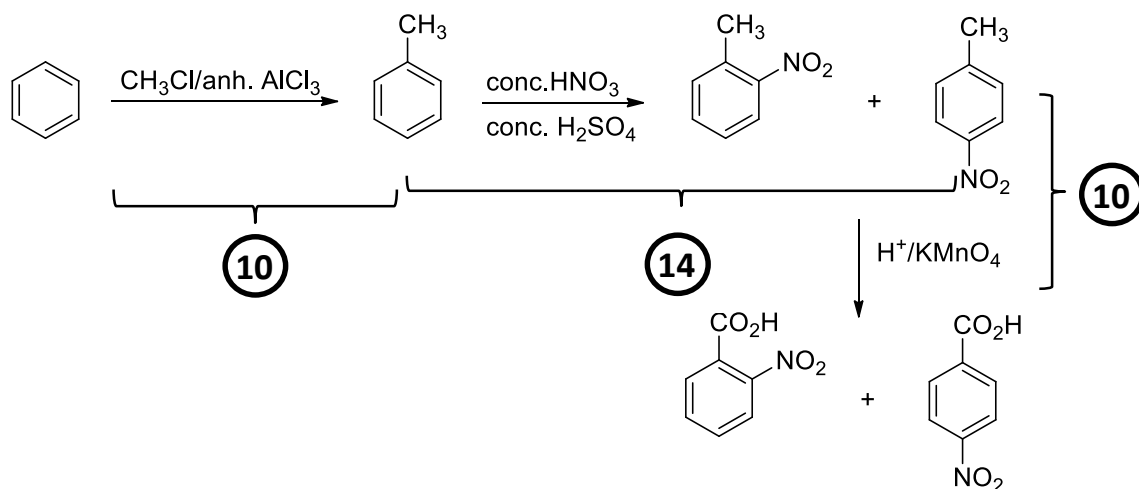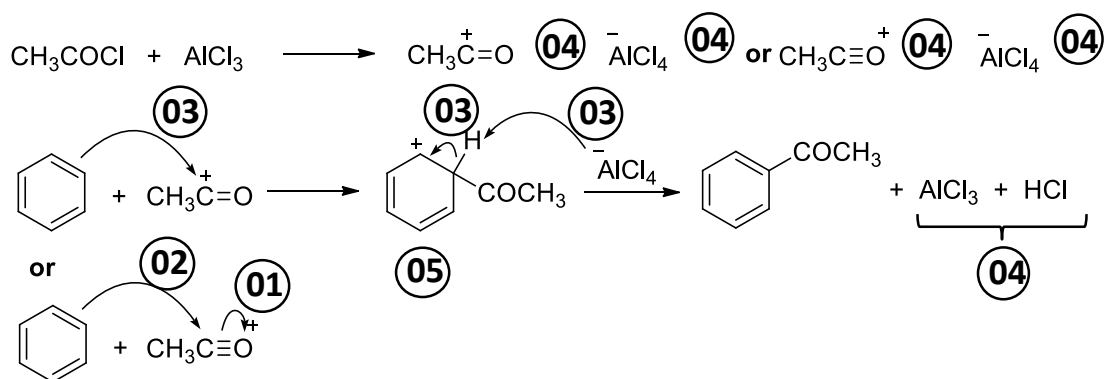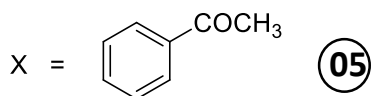

(b)(i): 34 marks

(ii) Give the structure of the product **X** and the mechanism of the following reaction.
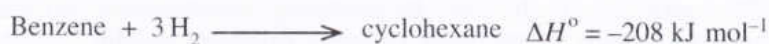

(65 marks)

(b) (ii): 31 marks

8(b): 65 marks

(c) The structure of benzene is represented as the resonance hybrid of the following two hypothetical six membered cyclic structures (cyclohexatriene).

Using the standard enthalpy data of hydrogenation given below, show that benzene is more stable than hypothetical 'cyclohexatriene'.

cyclohexene + H_2 ⟶ cyclohexane $\Delta H° = -120$ kJ mol^{-1}

Benzene + $3H_2$ ⟶ cyclohexane $\Delta H° = -208$ kJ mol^{-1}

(20 marks)

(c) Standard enthalpy of hydrogenation of cyclohexene = -120 kJ mol^{-1}

Expected enthalpy of hydrogenation of hypothetical "cyclohexatriene" = -120 × 3 kJ mol^{-1}

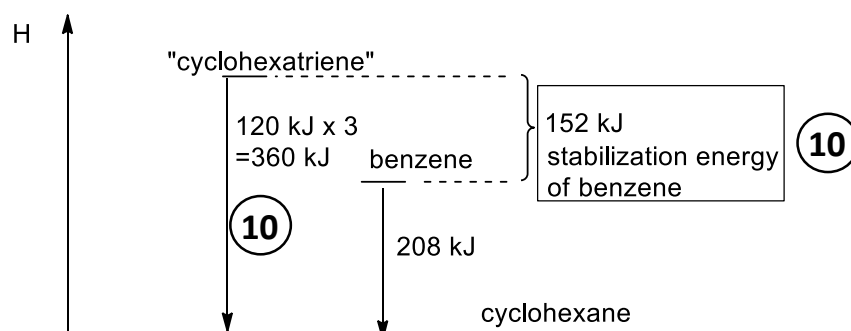= -360 kJ mol^{-1} ⑩

Standard enthalpy of hydrogenation of benzene = -208 kJ mol^{-1}

Stabilization energy of benzene = - 152 kJ mol^{-1} ⑩

OR

NB. **10 marks** for calculating the expected enthalpy of hydrogenation of "cyclohexatriene"
10 Marks for stating or indicating the stabilization of benzene. This **10 marks** can be awarded even if the stabilization energy is not calculated but indicating by a statement such as following.

Hydrogenation of both benzene and "cyclohexatriene" (with 3H$_2$) give cyclohexane. However, benzene

8(c):20 marks

9. (a) The following question is based on the qualitative analysis of cations.
An aqueous solution **Q** contains **four** cations of metals **A**, **B**, **C** and **D**. **Q** is subjected to the reactions given in the scheme below.
The symbols given in the box are used to represent precipitates with solutions, solids and solutions.

(**Note**: RT – room temperature)
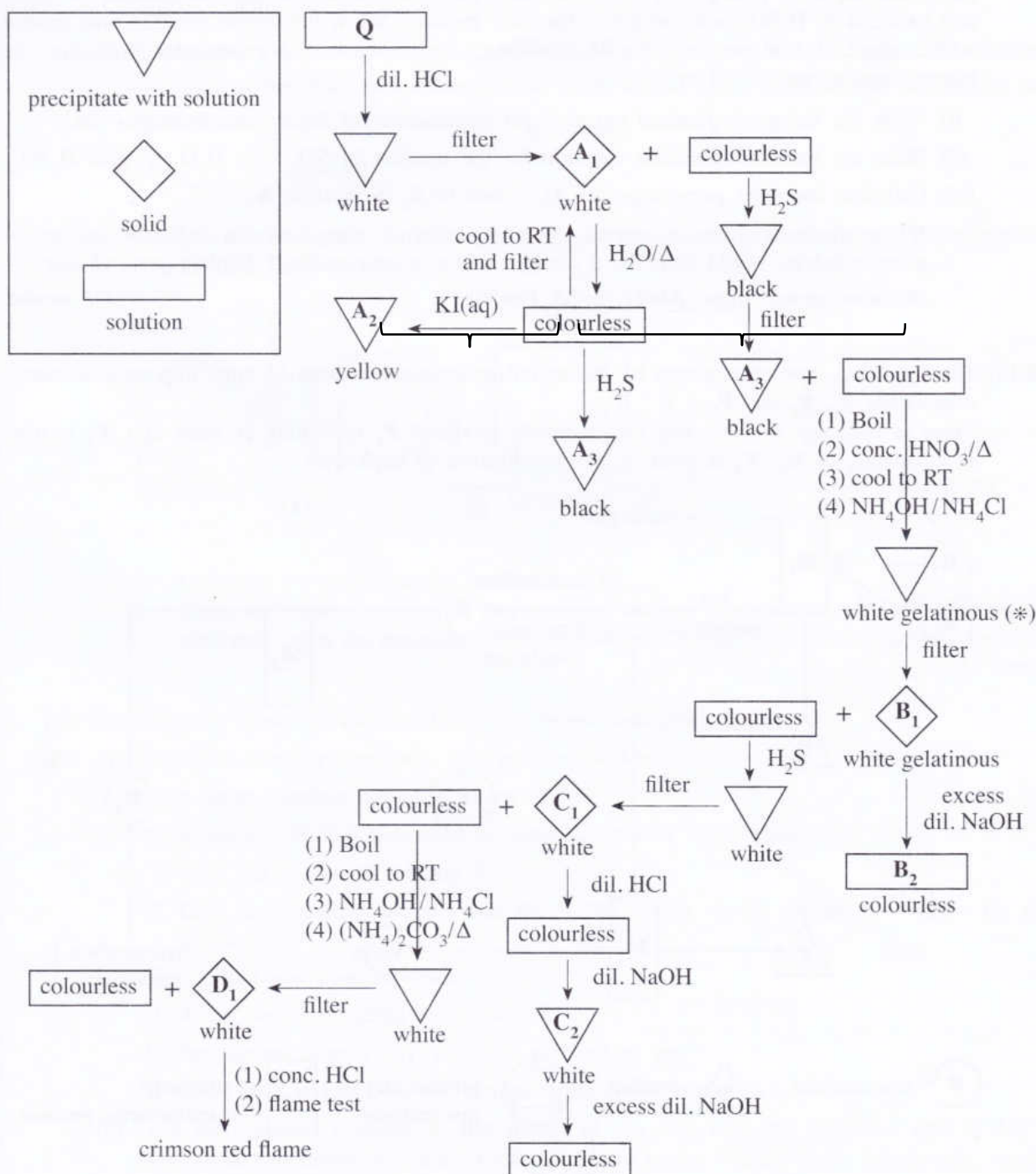
(i) A_1, A_2, A_3, B_1, B_2, C_1, C_2, and D_1 are compounds/species of the four cations **A**, **B**, **C**, and **D**.
Identify A_1, A_2, A_3, B_1, B_2, C_1, C_2, and D_1.
(**Note**: Write **only** chemical formulae. Chemical equations and reasons are **not** required.)

A₁ $PbCl_2$

A₂ PbI_2

A₃ PbS

B₁ $Al(OH)_3$

B₂ $NaAlO_2$ or AlO_2^- or $[Al(OH)_4]^-$ or $Na[Al(OH)_4]$

C₁ ZnS

C₂ $Zn(OH)_2$

D₁ $SrCO_3$

(08 marks x 8 = 64 marks)

(ii) Give a reason for the use of NH_4OH/NH_4Cl as a reagent when obtaining the white gelatinous precipitate (*).   (75 *marks*)

NH_4OH is added to precipitate the Group III ions (Fe^{3+}, Al^{3+} and Cr^{3+})   **(02)**
as hydroxides.
Then, the hydroxides of Group IV metal ions (Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}) **(02)**
may also precipitate together with the hydroxides of Group III metal ions.
NH_4Cl is added to reduce the concentration of OH^- (common ion effect). **(02)**
or
Addition of NH_4Cl shifts the equilibrium position of NH_4OH
$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ and the concentration of
OH^- is reduced
The K_{sp} of hydroxides of Group IV metal ions is greater than   **(02)**
those of the Group III metal ions.
This allows Fe^{3+}, Al^{3+} and Cr^{3+} hydroxides to be precipitated while   **(03)**
the hydroxides of Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} remain in solution.
                                                                    (11 marks)

Alternate Answer
NH_4OH is added to precipitate Al^{3+} as the hydroxide.   **(02)**
However, then both Zn^{2+} and Al^{3+} can be precipitated as   **(02)**
their hydroxides.
NH_4Cl is added to reduce the concentration of OH^- (common ion effect).   **(02)**
or
Addition of NH_4Cl shifts the equilibrium position of NH_4OH
$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ and the concentration of
OH^- is reduced
K_{sp} of $Zn(OH)_2 > Al(OH)_3$ **(02)**
Therefore, precipitation of $Zn(OH)_2$ can be prevented by using   **(03)**
NH_4Cl / NH_4OH
                                                                    (11 marks)

9(a): 75 marks

(b) A mixture **X** contains only aluminium sulfide (Al_2S_3) and ferric sulfide (Fe_2S_3). The following procedure was carried out to calculate the mass percentages of Al_2S_3 and Fe_2S_3 in **X**.

When a mass **m** of mixture **X** was heated at high temperature under H_2 gas, Al_2S_3 remains unchanged but Fe_2S_3 was converted to iron (Fe) metal. The final mass obtained was 0.824 g. When another mass **m** of mixture **X** was heated at high temperature in air, both Al_2S_3 and Fe_2S_3 decomposed, giving SO_2 gas. This SO_2 gas was bubbled through a solution of H_2O_2 and oxidized to H_2SO_4 acid, which is the only product. When this entire solution was titrated with a standard $1.00\ mol\ dm^{-3}$ NaOH solution in the presence of phenolpthalein indicator, the burette reading was $36.00\ cm^3$.
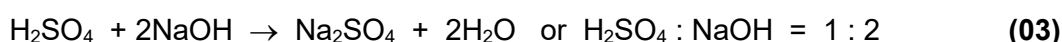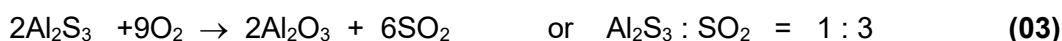
(i) Write the balanced chemical equation for the reaction of Fe_2S_3 with hydrogen gas.

$$Fe_2S_3 + 3H_2 \rightarrow 2Fe + 3H_2S \qquad \textbf{(04)}$$

(ii) Write the balanced chemical equation for the reaction of SO_2 with H_2O_2 to give H_2SO_4.

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \qquad \textbf{(04)}$$

(iii) Calculate the mass percentages of Al_2S_3 and Fe_2S_3 in mixture **X**.

$$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2 \qquad or \quad Al_2S_3 : SO_2 = 1:3 \qquad \textbf{(03)}$$

$$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2 \qquad or \quad Fe_2S_3 : SO_2 = 1:3 \qquad \textbf{(03)}$$

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \quad or \ H_2SO_4 : NaOH = 1:2 \qquad \textbf{(03)}$$

Molar mass of Al_2S_3 = (27x2)+(32x3) = 150 **(02)**

Molar mass of Fe_2S_3 = (56x2)+(32x3) = 218 **(02)**

Assume mass of Al_2S_3 to be m_1 and Fe_2S_3 to be m_2

Mass of Fe from Fe_2S_3 after heating under H_2

$$\frac{m_2}{208} \times 56 \times 2 \qquad \textbf{(04)}$$

Total mass after heating under H_2

$$m_1 + \frac{m_2}{208} \times 56 \times 2 = 0.824g \ \text{------} \qquad [1] \qquad \textbf{(08)}$$

From heating under air

Mols of H_2SO_4 from $Al_2S_3 \quad = \dfrac{m_1}{150} \times 3 \qquad \textbf{(04)}$

Mols of H_2SO_4 from $Fe_2S_3 \quad = \dfrac{m_2}{208} \times 3 \qquad \textbf{(04)}$

Total mols from both Fe_2S_3 and $Al_2S_3 \quad = \dfrac{m_1}{150} \times 3 + \dfrac{m_2}{208} \times 3 \qquad \textbf{(04)}$

Mols of NaOH for titration $\qquad = \dfrac{1}{1000} \times 36 \qquad \textbf{(02)}$

Mols of H_2SO_4 from titration $= \dfrac{1}{1000} \times \dfrac{36}{2} = 18 \times 10^{-3}$ **(02)**

$\dfrac{3m_1}{150} + \dfrac{3m_2}{208} = 18 \times 10^{-3} g \quad \rightarrow [2]$ **(08)**

$m_1 + \dfrac{m_2}{208} \times 112 = 0.824 \, g \quad \rightarrow [1]$

$\dfrac{3m_1}{150} + \dfrac{3m_2}{208} = 18 \times 10^{-3} g \quad \rightarrow [2]$

Solving equations [1] and [2] for m_1 and m_2

$\dfrac{m_1}{50} + \dfrac{3m_2}{208} = 0.018 \quad \rightarrow [3]$

$\dfrac{m_1}{50} + \dfrac{3m_2}{208} = 0.018 \quad \rightarrow [3]$

[3] x 50

$m_1 + \dfrac{150m_2}{208} = 50 \times 0.018 \quad \rightarrow [4]$

[4] - [1]

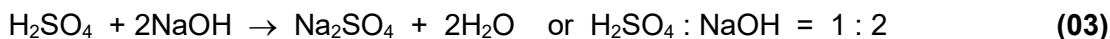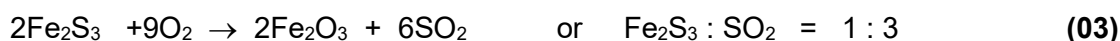$\dfrac{150m_2}{208} - \dfrac{112m_2}{208} = 0.900 \times 0.824$

$m_2 = \quad 0.416 \, g$ **(02)**
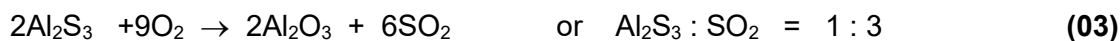
$m_2 = \quad 0.416 \, g$ in eq [1]

$m_1 + \dfrac{0.416 \times 112}{208} = 0.824$

$m_1 = \quad 0.600 \, g$ **(02)**

$\% m_1 = \dfrac{0.600}{0.416 + 0.600} \times 100\% = 59.06\% \quad$ or $\;$ 59 % **(04)**

$\% m_2 = 100 - 59.06 = 40.94\%$

Alternate answer 01 for (iii)

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$ or $Al_2S_3 : SO_2 = 1 : 3$ **(03)**

$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$ or $Fe_2S_3 : SO_2 = 1 : 3$ **(03)**

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ or $H_2SO_4 : NaOH = 1 : 2$ **(03)**

Molar mass of Al_2S_3 = (27x2)+(32x3) = 150   **(02)**

Molar mass of Fe_2S_3 = (56x2)+(32x3) = 218   **(02)**

Assuming mols of Al_2S_3 is n_1 and mols of Fe_2S_3 as n_2

Mols of Fe from Fe_2S_3

$$n_2 \times 56 \times 2$$ **(04)**

Total mass after heating under H_2

$$150n_1 + 112n_2 = 0.824 \quad \rightarrow \quad \underline{[1]}$$ **(08)**

Mols of NaOH for titration $= \dfrac{1}{1000} \times 36$ **(02)**

Mols of H_2SO_4 from titration $= \dfrac{1}{1000} \times \dfrac{36}{2} = 18 \times 10^{-3}$ **(02)**

Mols of H_2SO_4 from Al_2S_3 = $3n_1$ **(04)**

Mols of H_2SO_4 from Fe_2S_3 = $3n_2$ **(04)**

Total mols of H_2SO_4 = $3n_1 + 3n_2$ **(04)**

Therefore,

$$3n_1 + 3n_2 = 0.018 \quad \rightarrow [2]$$ **(08)**

Solving equation [1]and [2] for n_1 and n_2

[2] x 50 $150n_1 + 150n_2 = 0.9 \quad \rightarrow [3]$

[3] –[1] $38n_2 = 0.076$

                      $^{-3}$ mol   **(02)**

Substituting n_2 in [2]

$$3n_1 + 3 \times 0.002 = 0.018$$

$$n_1 = 0.004 \text{ mol}$$ **(02)**

Mass of Al_2S_3 = 0.004 mols x 150 gmol^{-1} = 0.600 g

Mass of Fe_2S_3 = 0.002 mols x 208 gmol^{-1} = 0.416 g

% mass of Al_2S_3 = $\dfrac{0.600}{0.600 + 0.416} \times 100\% = 59.06$ or 59 % **(04)**

% mass of Fe_2S_3 = $100 - 59.06 = 40.94$ or 41 % **(04)**

Alternate answer 02 for (iii)

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$ or $Al_2S_3 : SO_2$ = 1 : 3 **(03)**

$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$ or $Fe_2S_3 : SO_2$ = 1 : 3 **(03)**

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ or $H_2SO_4 : NaOH$ = 1 : 2 **(03)**
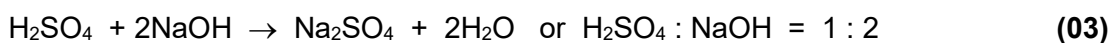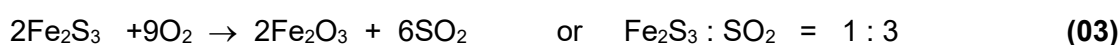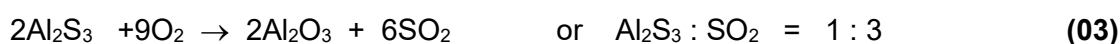
Molar mass of Al_2S_3 = (27x2)+(32x3) = 150 g mol^{-1} **(02)**

Molar mass of Fe_2S_3 = (56x2)+(32x3) = 218 g mol^{-1} **(02)**

Assume mass of Al_2S_3 in the mass of 0.824 g is as m

$n_{Fe} = \dfrac{(0.824 - m)}{56} \, mol$ **(06)**

$n_{Fe_2S_3} = \dfrac{1}{2} \dfrac{(0.824 - m)}{56} \, mol$ ———— **[1]** **(06)**

$n_{SO_2} = 3 \times \dfrac{m}{150} + 3 \times \dfrac{1}{2} \dfrac{(0.824 - m)}{56} \, mol$ **(10)**

Mols of NaOH for titration $= \dfrac{1}{1000} \times 36 \, mol$ **(02)**

Mols of H_2SO_4 from titration $= \dfrac{1}{1000} \times \dfrac{36}{2} = 18 \times 10^{-3} \, mol$ **(02)**

Therefore, $n_{SO_2} = 0.018 \, mol$

$n_{SO} = 3 \times \dfrac{m}{} + 3 \times \dfrac{1}{} \dfrac{(0.824 - m)}{} = 0.018$ ——— **[2]** **(10)**

Solving equation [2] for m

$\dfrac{m}{150} + \dfrac{(0.824 - m)}{112} = 0.006$

$112 m + 150(0.824 - m) = 0.006 \times 150 \times 112$

$$38m = 22.8$$

$$m = m_{Al_2S_3} = 0.60\,g \qquad\qquad \textbf{(02)}$$

Substituting m= 0.60 g in equation [1]

$$n_{Fe_2S_3} = \frac{1}{2}\frac{(0.824 - 0.60)}{56}\,mol = 0.002\,mol$$

$$m_{Fe_2S_3} = 0.002 \times 208\,gmol^{-1} = 0.416\,g \qquad\qquad \textbf{(02)}$$

Therefore

% mass of $Al_2S_3 = \dfrac{0.600}{0.600 + 0.416} \times 100\% = 59.06\%$ or 59 % $\qquad$ **(04)**

% mass of $Fe_2S_3 = 100\% - 59.06\% = 40.94\%$ or 41% $\qquad$ **(04)**

(iv) If the above titration is carried out using methyl orange as the indicator instead of phenolpthalein, would there be a change in the burette reading? Explain your answer.
(Relative atomic mass: Al=27, S=32, Fe=56) *(75 marks)*

No $\qquad\qquad$ **(02)**

Because this is a strong acid- strong base titration $\qquad\qquad$ **(02)**

So the color change pH interval of methyl orange and phenolphthalein both falls into vertical region of the titration curve. $\qquad\qquad$ **(02)**

9(b): 75 marks

10. (a) The following flow chart shows the industrial extraction/production of three important elements/ compounds P_1, P_2 and P_3.
There is evidence to show that our ancestors produced P_1 thousands of years ago. P_1 is used as a catalyst in M_2. P_3 is used in the manufacture of explosives.
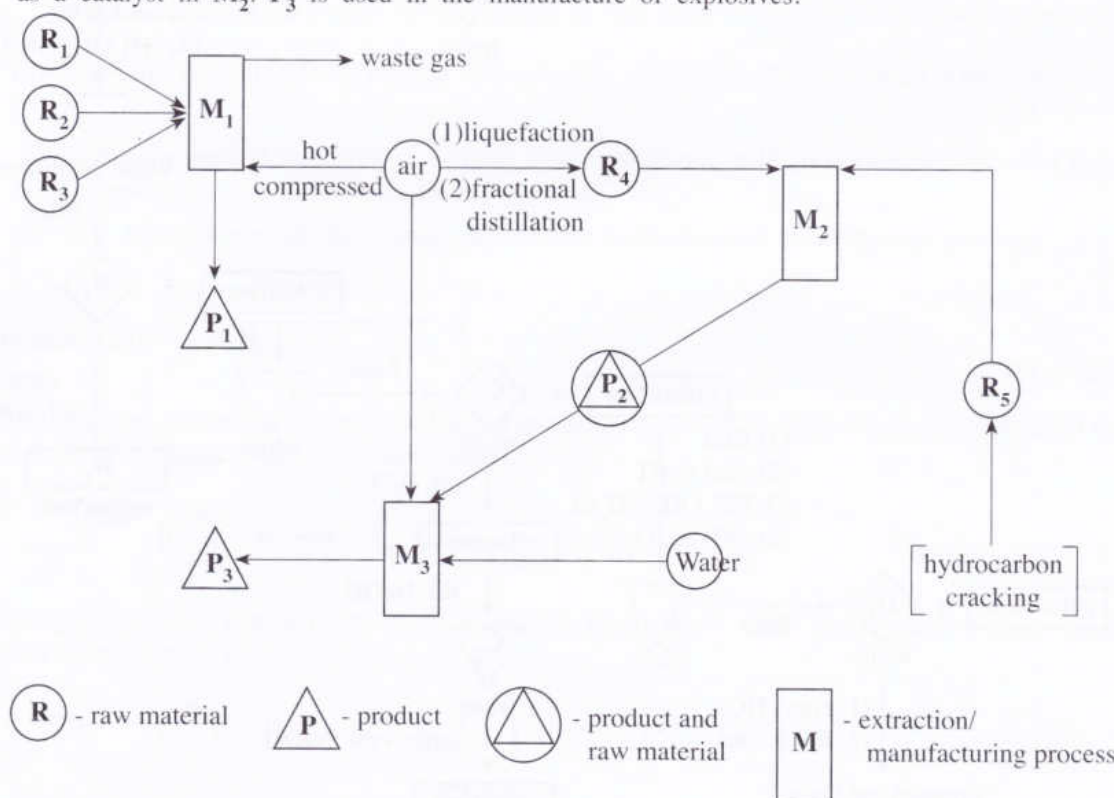
(i) Name the manufacturing processes M_2 and M_3. (e.g.: Manufacture of Na_2CO_3 is named as Solvay process.)

M_2 - Manufacture of NH_3 by Haber Process   (02)
M_3 – Manufacture of HNO_3 by Ostwald Process   (02)

(ii) Identify the process M_1 and name the main constituent of its waste gas.

M_1 – extraction of Fe   (02)
N_2 gas   (02)

(iii) Give the common names of the raw materials R_1, R_2 and R_3 used in M_1.

R_1 – coke   (02)
R_2 – iron ore   / hematite   (02)
R_3 – limestone   (02)

(iv) Write a balanced chemical equation for the role of R_1 as a reducing agent in M_1 process.

As a reducing agent: $FeO(s) + C(s) \rightarrow Fe(l) + CO(g)$ (02)
Or
$CO_2(g) + C(s) \rightarrow 2CO(g)$
Or
$2FeO(s) + C(s) \rightarrow 2Fe(l) + CO_2(g)$
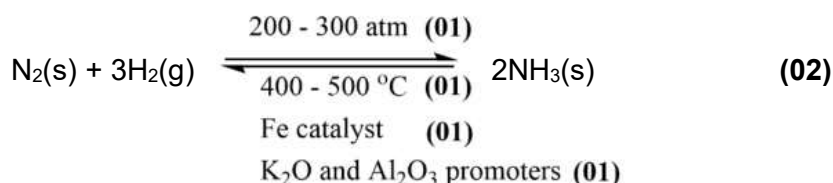
(v) Identify R_4 and R_5.

$R4$ – $N_2(g)$ (02)
$R5$ – $H_2(g)$ (02)

(vi) Give balanced chemical equations for reactions taking place in the processes M_1, M_2 and M_3. Appropriate conditions (temperature, pressure, catalysts, etc.) must be stated as required. (**Note:** For the M_1 process, give only the reactions showing the conversion of R_2 to P_1.)
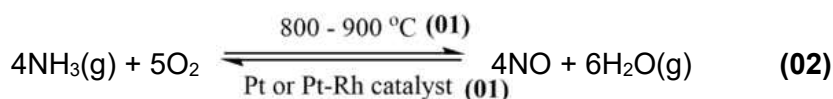
M1: $3Fe_2O_3 + CO \rightarrow Fe_3O_4 + CO_2$ **(02)**

$Fe_3O_4(s) + CO \rightarrow 3FeO(s) + CO_2(g)$ **(02)**

$FeO(s) + CO(s) \rightarrow Fe(l) + CO_2(g)$ -----(A)

$2FeO(s) + C(s) \rightarrow 2Fe(l) + CO_2(g)$ -----(B)

Either (A) or (B)   **(02)**

M2:

$$N_2(s) + 3H_2(g) \underset{\overset{\displaystyle \text{400 - 500 °C } \textbf{(01)}}{\longleftarrow}}{\overset{\displaystyle \text{200 - 300 atm } \textbf{(01)}}{\longrightarrow}} 2NH_3(s) \quad \textbf{(02)}$$

Fe catalyst   **(01)**

K_2O and Al_2O_3 promoters **(01)**
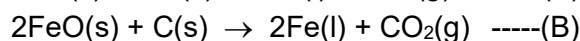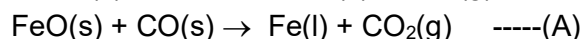
(Any pressure between 200 – 300 atm and any temperature between 400 – 500 °C accepted)

M3:

$$4NH_3(g) + 5O_2 \underset{\overset{\displaystyle \text{Pt or Pt-Rh catalyst } \textbf{(01)}}{\longleftarrow}}{\overset{\displaystyle \text{800 - 900 °C } \textbf{(01)}}{\longrightarrow}} 4NO + 6H_2O(g) \quad \textbf{(02)}$$

$2NO(g) + O_2 \rightarrow 2NO_2$ **(02)**

$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3$ **(02)**

(vii) Give **two** uses each of P_1, P_2 and P_3 (**other than** what is indicated in the flow chart or given in the question).

P1 – to make alloy steel / construction industry to provide strength
to structures / in machinery and tool manufacture   **(01 x 2)**

P2 – production of fertilizers / production of nylon /
in petroleum industry to neurtralize acide in crude oil constituents /
water and waste water treatment / as refrigerant / to prevent
coagulation of rubber   **(01 x 2)**

P3 – manufacture of fertilizer / in industries which require nitrates
such as KNO_3 in explosive manufacture and $AgNO_3$ in
photography / to clean surfaces when welding metals /
aqua regia   **(01 x 2)**

(viii) State whether the M_2 process would be favoured at very high temperatures. Explain your answer using ΔH, ΔS and ΔG.
(50 marks)

Reaction is exothermic. ΔH is (-ve)
No of gaseous moles decrease. ΔS decreases (-ve)   **(01)**
According to $\Delta G = \Delta H - T\Delta S$
When ΔS is negative, $-T\Delta S$ term is +ve.   **(01)**
As temperature increases, +ve term overrides -ve term, making ΔG +ve.   **(01)**
Therefore not favoured at high temperature.   **(01)**

10(a): 50 marks

(b) The following questions are based on photochemical smog and water pollution.

   (i) State the major types of gaseous chemical pollutants and conditions that are required for the formation of photochemical smog.

NO_x (NO or NO_2), Volatile hydrocarbon (VOC), sunlight/solar radiation,

temperature above 15 °C   **(02 x 4)**

   (ii) State why the strength of photochemical smog is low in the morning and evening.

The intensity of solar radiation is low during morning and evening.   **(03)**

Therefore photochemical smog is weak in the morning and evening.

   (iii) Using balanced chemical equations, explain how ozone is formed in the lower atmosphere due to photochemical smog.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

$NO_2(g) \rightarrow NO(g) + O(g)$

$O(g) + O_2(g) \rightarrow O_3(g)$
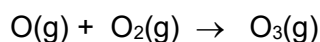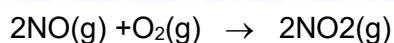
           (03 x 3)

   (iv) State **four** major products (excluding ozone) of photochemical smog.

PAN (peroxy acetyl nitrate)

PBN (peroxy benzoyl nitrate)

Short chain(volatile) aldehydes

Particles (particulate matter)

           (02 x 4)

   (v) State **three** free radicals produced during the formation of photochemical smog.

$OH^{\bullet}$ (hydroxyl radical), $ROO^{\bullet}$ (peroxy radical), $R^{\bullet}$ (alkyl radical**)**, $RO^{\bullet}$ (Alkoxy radical), $O^{\bullet}$ (oxygen radical), NO

           (02 x 3)

   (vi) Many countries now promote the use of electric vehicles. State how the use of electric vehicles affect the formation of photochemical smog.

Electric vehicles do not release ingredients for photochemical smog.   **(02)**

Therefore, electric vehicles contribute for the reduction of photochemical smog/ no

   (vii) State an environmental problem, other than photochemical smog, that could ease due to the use of electric vehicles.

Global warming/acid rain   **(03)**

(viii) A ship carrying the following chemicals sank in the sea.

Na_2HPO_4, HNO_3, $Pb(CH_3COO)_2$
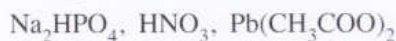
State an effect from each chemical on the water quality parameters of the water surrounding the ship, by the release of the above chemicals. (50 *marks*)

PO_4^{3-}, NO_3^-, Reduction of dissolved oxygen level.
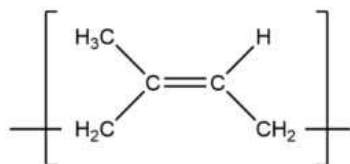HNO_3 Increases the acidity/decreases pH
Pb^{2+} -Increases the heavy metal level of sea water /Increases the lead level of water

(03 x 3)

10(b): 50 marks

(c) The following questions are based on natural rubber and additives used for polymer related products.

(i) Sketch the repeating unit of natural rubber.

(10)

(ii) Give a compound that can be used to prevent coagulation of natural rubber latex.

NH_3 solution (04)

(iii) State a compound that can be used to coagulate natural rubber latex and explain how it acts.

Acids such as acetic/formic acid. (04)
H+ can neutralize the COO- groups, making the surface of
rubber particles   neutral. Particles can then combine together and
become as a mass.

(02 x 4 = 08)

(iv) Briefly state how the 'vulcanization' of natural rubber is carried out.

rubber is heated with 1-3% sulfur (03 x 3 = 09)

(v) State **two** types of substances used to increase the efficiency of vulcanization.

Organic catalysts
Catalyst promoters or ZnO (03 x 2 = 06)

(vi) Give **three** properties, which can be enhanced by adding additives to polymer products.

Increase flexibility
Decrease flammability

Increase mechanical and/or physical strength   (Any three)   (03 x 3 = 09)

10(c): 50 marks