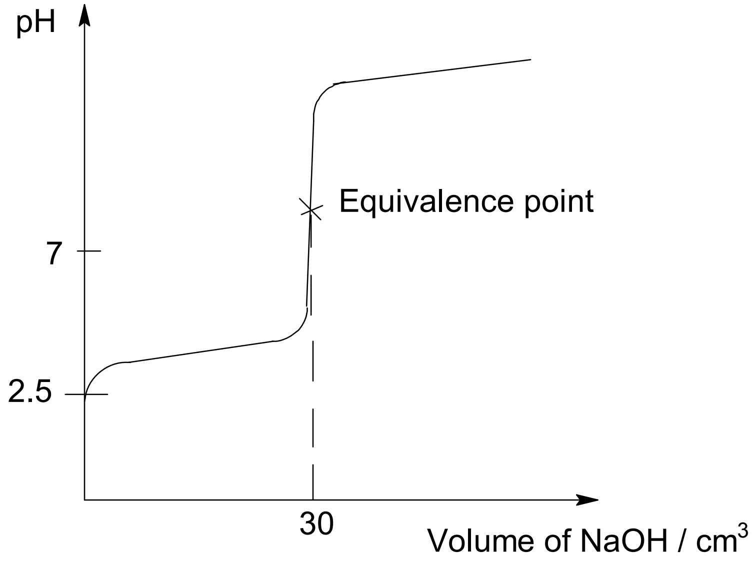
Answer **all** questions

1(a) Pyruvic acid, $CH_3COCOOH$, occurs naturally in the body and is an end product of the metabolism of sugar.
When 10.0 cm^3 of a solution of pyruvic acid were titrated against 0.01 mol dm^{-3} sodium hydroxide, with a data logger, the following curve was obtained.



(i) Suggest a suitable indicator, if the titration were to be repeated without the use of a data logger. Explain your reasoning.

Phenolphthalein. The pH transition range of the indicator **lies within** the sharp pH change over its **equivalence point**.

(ii) Calculate the value of K_a for pyruvic acid.

No. of mol of NaOH = $\frac{30}{1000} \times 0.01$

$= 3 \times 10^{-4}$

No. of mol of pyruvic acid = 3×10^{-4}

[pyruvic acid] = $\frac{3 \times 10^{-4}}{\frac{10}{1000}}$ = 0.03 mol dm^{-3}

From graph, pH = 2.5

Hence $[H^+] = 10^{-2.5} = 3.162 \times 10^{-3}$

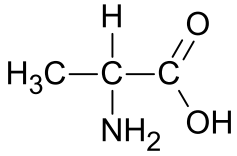
$$K_a = \frac{[H^+]^2}{[pyruvic\_acid]} = \frac{(3.162 \times 10^{-3})^2}{0.03 - 3.162 \times 10^{-3}} = 3.73 \times 10^{-4} \text{ mol dm}^{-3}$$

(iii) Explain, with the aid of an appropriate equation, why the pH at equivalence point is greater than 7.

[7]

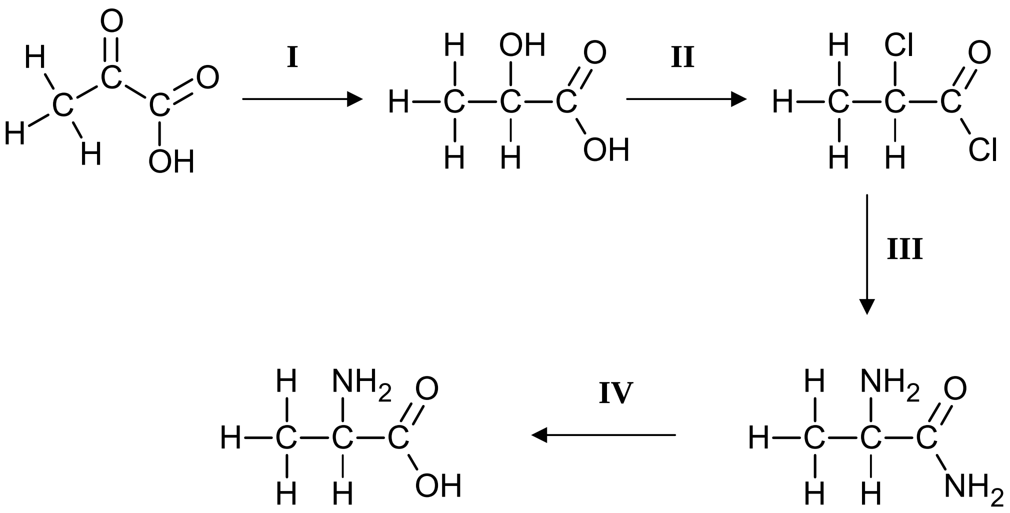
CH_3COCOO^- (aq) + H_2O (l) $\rightleftharpoons$ $CH_3COCOOH$ (aq) + OH^- (aq)
CH_3COCOO^- undergoes **salt hydrolysis**.
[OH] > [H$^{\pm}$].

(b) Pyruvic acid is converted to the amino acid, alanine, in just one single step in the body by the enzyme alanine transaminase. However, to achieve the same conversion in a laboratory, multiple steps are required. Given the chemical structure of alanine below, show how pyruvic acid can be converted to alanine in not more than 4 steps. Indicate the reagents, conditions and all intermediates in your answer. The alanine formed from your suggested synthesis steps may be in its cationic, anionic or zwitterionic forms.



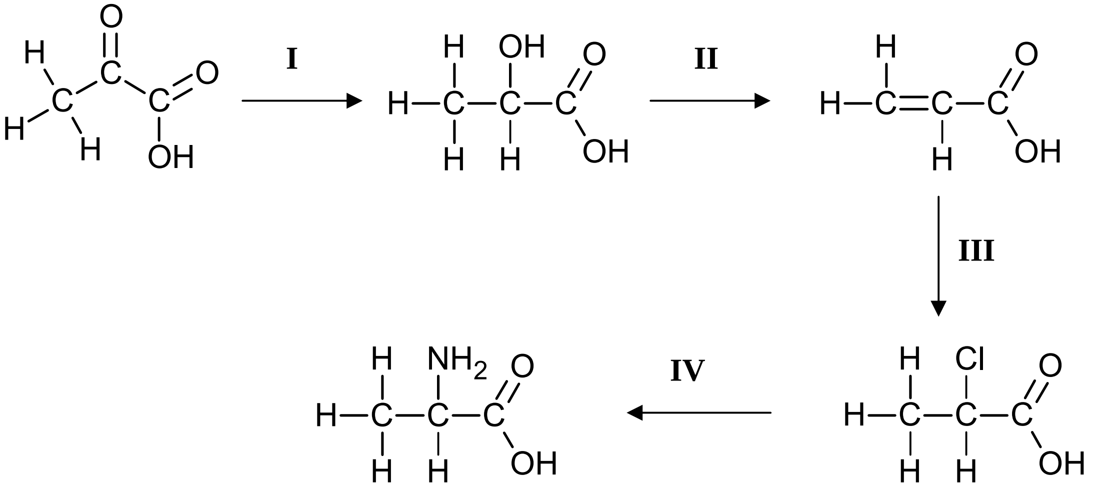
Alanine

[5]



I : H_2 with Ni, heat OR $NaBH_4$ in ethanol / methanol (room temp) ($LiAlH_4$ not acceptable)
II: PCl_5, room temperature
III: NH_3 in sealed tube, heat.
IV: HCl / H_2SO_4, heat OR NaOH, heat

Alternative answer:



I : H_2 with Ni, heat OR $NaBH_4$ in ethanol / methanol (room temp) ($LiAlH_4$ not acceptable)
II: concentrated H_2SO_4, 170 °C
III: HC*l* (g)
IV: NH_3 in sealed tube, heat.

(c) Alanine, together with the 19 other standard amino acids are the building blocks of proteins. State the two factors that cause protein denaturation and explain how the two stated factors denature the protein. [4]

Any 2 of the following

1. Addition of heavy metal ions.
   Heavy metal form salt or complex ions, thereby **breaking / interfering with the ionic interactions** heavy metals **break disulphide links**.

2. Extremes of temperature / High temperature / Heating
   Heat breaks the weak **van der waals's forces** and **hydrogen bonds** holding together the quartenary, tertiary and secondary structure of the protein, resulting in a change in the original conformation of the protein.

3. Extreme pH changes
   Adding H^+ or OH^- **protonate** or **deprotonate** the ionic R groups, disrupting the **ionic or hydrogen bonds** holding together the quarternary and tertiary structure of the protein.

(d) When 0.200g of alanine is subjected to complete combustion, carbon dioxide, nitrogen dioxide and water is formed. These gases are absorbed by 20 cm^3 of 1.5 mol dm^{-3} NaOH. The resultant solution is then titrated with 0.3 mol dm^{-3} H_2SO_4. Calculate the volume of H_2SO_4 required to reach equivalence point. [4]

Hint: $2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O$

$C_3H_7NO_2 + 19/4O_2 \rightarrow 3CO_2 + 7/2H_2O + NO_2$

No. of mol of alanine = $\frac{0.2}{3 \times 12 + 7 + 14 + 16 \times 2}$ = 0.002247

No. of mol of CO_2 = 3 x 0.002247 = 0.006741

No. of mol of NO_2 = 0.002247

$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$

No. of mol of NaOH that reacted with CO_2 = 2 x 0.006741 = 0.01348

$NO_2 \equiv NaOH$

No. of mol of NaOH that reacted with NO_2 = 0.002247

No. of mol of original NaOH = $\frac{20}{1000} \times 1.5$ = 0.03

No. of mol of NaOH remaining = 0.03 – 0.01348 – 0.002247
= 0.01427

$2NaOH \equiv H_2SO_4$

No. of mol of H_2SO_4 required = ½ x 0.01427 = 7.136×10^{-3}

Volume of H_2SO_4 required = $\frac{7.136 \times 10^{-3}}{0.3}$ = 0.0238 dm^3 or 23.8 cm^3

[Total: 20]

2(a) Hydrogen chloride gas and ammonia gas react to form ammonium chloride.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

(i) By constructing a Hess' Law Cycle, calculate the standard enthalpy change of the reaction, given the following information:

$$\Delta H^{\theta}_{f(NH_3)} = -46.1 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{f(HCl)} = -92.3 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{f(NH_4Cl)} = -314.4 \text{ kJ mol}^{-1}$$

$$\begin{tikzcd}
NH_3(g) + HCl(g) \arrow[rr] & & NH_4Cl(s) \\
& \tfrac{1}{2} N_2(g) + 2H_2(g) + \tfrac{1}{2} Cl_2(g) \arrow[ul, "\Delta H^{\theta}_{f(NH_3)}"] \arrow[ul, bend right, "\Delta H^{\theta}_{f(HCl)}"'] \arrow[ur, "\Delta H^{\theta}_{f(NH_4Cl)}"'] &
\end{tikzcd}$$

$$\Delta H^{\theta}_{rxn} + \Delta H^{\theta}_{f(NH_3)} + \Delta H^{\theta}_{f(HCl)} = \Delta H^{\theta}_{f(NH_4Cl)}$$
$$\Delta H^{\theta}_{rxn} = \Delta H^{\theta}_{f(NH_4Cl)} - \Delta H^{\theta}_{f(NH_3)} - \Delta H^{\theta}_{f(HCl)}$$
$$= -314.4 - (-46.1) - (-92.3)$$
$$= -176 \text{ kJ mol}^{-1}$$

(ii) The standard entropy change of the reaction is –284 J $K^{-1}mol^{-1}$. Explain why this value is negative.

There is a **decrease in entropy** due to the **decrease in total number of mol of gases** from 2 to 0.

(iii) State and explain whether the reaction is spontaneous at high or low temperature.

Reaction is spontaneous at **low** temperature.
For $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$**,** since $\underline{\Delta S^{\theta}}$ **and** $\underline{\Delta H^{\theta}}$ **are both negative**, the value of T needs to be low enough such that $\underline{|T\Delta S^{\theta}| < |\Delta H^{\theta}|}$, in order that $\underline{\Delta G^{\theta}}$ **is negative**.

(iv) Calculate the temperature for which the reaction is spontaneous.

[6]

For reaction to be spontaneous, $\Delta G^{\ominus} < 0$
Hence $\Delta H^{\ominus} - T\Delta S^{\ominus} < 0$
$(-176) - T(-284 \times 10^{-3}) < 0$
$T(-284 \times 10^{-3}) > -176$
$T < 618K$

(b) When hydrogen chloride gas is added to organic compound **P**, C_6H_{12}, two products **Q** and **R**, which are isomers of each other, $C_6H_{13}Cl$, are formed in unequal proportion. When **Q** and **R** are separately boiled with aqueous sodium hydroxide, **S** is formed from **Q**, while **T** is formed from **R**. **S** and **T** are also isomers of each other, with the same molecular formula, $C_6H_{14}O$. When **S** and **T** are separately boiled with acidified potassium manganate(VII), no decolourisation is observed in the test tube containing **S**; while decolourisation is observed in the test tube containing **T** which results in the formation of **U**, $C_6H_{12}O_2$. When some sodium carbonate powder is added to **U**, effervescence of carbon dioxide gas is observed. When **P** is boiled with acidified potassium manganate (VII), compound **V**, $C_5H_{10}O$ and CO_2 are formed. **V** gives an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. When **V** is heated with lithium aluminium hydride in dry ether, **W**, $C_5H_{12}O$, which does **not** exhibit optical activity, is formed.

Deduce the structures for each lettered compound, **P** to **W**. Explain the chemistry of the reactions involved. Balanced equations are not required. [12]

The **carbon to hydrogen ratio** of **P** is **1 : 2.**
P does not contain benzene ring, but could contain **alkene** group.

P undergoes **electrophilic addition** with hydrogen chloride gas to form **Q** and **R** in unequal proportion.

P is an **unsymmetrical alkene**. **Q** and **R** are **halogenoalkanes**.

Q and **R** undergo **nucleophilic substitution** with sodium hydroxide to form **S** and **T** respectively.

S and **T** are **alcohols**.

S is **not oxidized** by acidified potassium manganate (VII).
S is a **tertiary alcohol**.

T is **oxidized** by acidified potassium manganate (VII) to form **U**.
T is a **primary or secondary alcohol**. **U** could be **carboxylic acid or ketone**.

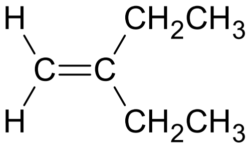
U undergoes **neutralisation / acid – base reaction** with sodium carbonate to liberate carbon dioxide gas.
U is a **carboxylic acid,** hence **T** is a **primary alcohol**.

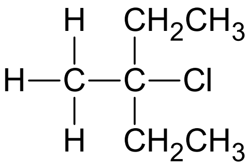
P undergoes **(strong) oxidation** with acidified potassium manganate (VII) to form **V,** $C_5H_{10}O$**, which has only one oxygen atom,** and carbon dioxide.
P has a **terminal alkene** group. **V** is a **ketone**.

V undergoes **condensation** with 2,4-dinitrophenylhydrazine to form an orange precipitate.
V is a **ketone / carbonyl compound**.

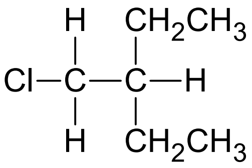
V undergoes **reduction** with lithium aluminium hydride to form **W**, which does not exhibit optical activity.

W is a **secondary alcohol** and is a **symmetrical** molecule.

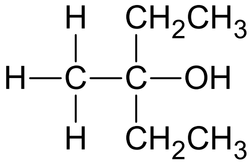

P


$H-\overset{H}{\underset{H}{C}}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-Cl$

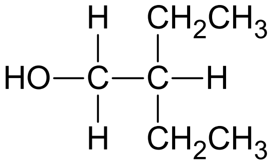
Q


$Cl-\overset{H}{\underset{H}{C}}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-H$

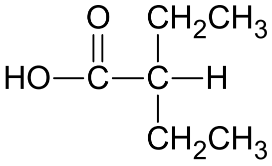
R


$H-\overset{H}{\underset{H}{C}}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-OH$

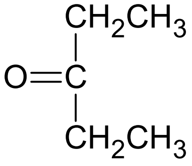
S


$HO-\overset{H}{\underset{H}{C}}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-H$

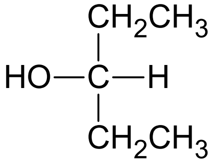
T


$HO-\overset{O}{\overset{\|}{C}}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-H$

U


$O=\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}$

V


$HO-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-H$

W

(c) Using relevant information from the *Data Booklet*, compare and explain the relative acid strength of HC*l* and HF. [2]

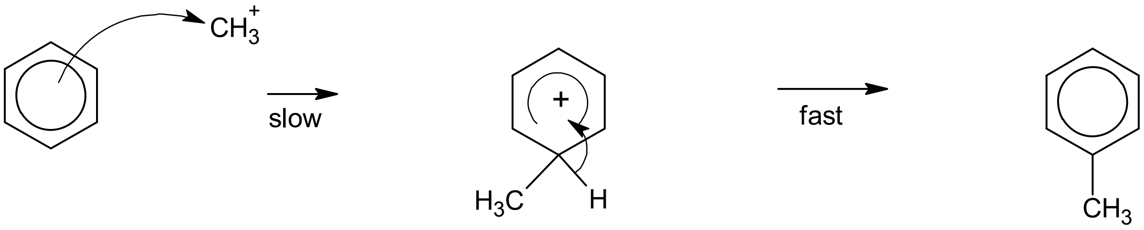
From data booklet,
Bond energy of H – C*l* = 431 kJ mol^{-1}
Bond energy of H – F = 562 kJ mol^{-1}

Covalent bond strength: HF > HC*l*
Bond energy: HF > HC*l*
Acid strength: HF < HC*l*

[Total: 20]

3 $AlCl_3$ is a compound of aluminium and chlorine. The solid has a low melting and boiling point and it is covalently bonded. It finds widespread application in the chemical industry as the classic catalyst for the Friedel-Crafts alkylation reaction. Typically, $AlCl_3$ can be used to catalyse the reaction between benzene and chloromethane.

(a) Describe the mechanism for the reaction between benzene and chloromethane. [3]



Two electrons from the **<u>delocalised pi electron system</u>** are used **<u>to form a new bond with the CH_3^+ ion</u>**. **<u>Loss of proton, H^+, from the carbocation intermediate</u>** to form a stable product.

(b) $C_6H_5CH_2Cl$ can be obtained by reacting $C_6H_5CH_3$ with Cl_2 via a free radical substitution.

(i) By making use of relevant bond energies from the *Data Booklet*, calculate the enthalpy change of this reaction.

From the Data Booklet,

C – Cl bond energy = 340 kJ mol^{-1}
C – H bond energy = 410 kJ mol^{-1}
Cl – Cl bond energy = 244 kJ mol^{-1}
H – Cl bond energy = 431 kJ mol^{-1}

Using Bond Energy method,

$\Delta H^{\theta}_{rxn} = 410 + 244 - 340 - 431 = \underline{\mathbf{-117\ kJ\ mol^{-1}}}$

(ii) Give two reasons why the actual enthalpy change of this reaction deviates from the above value.

[4]

The bond energy values from Data Booklet are an <u>**average**</u> of a particular bond present in many different types of compounds.

Methylbenzene and chloromethylbenzene are <u>**liquids under standard conditions**</u>.

(c) Another metal chloride **A**, which has the formula MCl_x cannot be used to catalyse the reaction between benzene and chloromethane.

When 1.0 x 10^{-3} moles of sodium hydroxide is reacted completely with 0.5 x 10^{-3} moles of **A**, 0.0292 g of a white precipitate, **B** is formed. When **B** is heated, water is lost leaving a white residue **C**. **C** is of high melting point and it is very slightly soluble in cold water.

(i) Deduce the identities of **A**, **B** and **C**. Write equations wherever applicable.

2 moles of OH^- reacts with 1 mole of MCl_x to give **A**. Therefore, M must be a Group II element. Since M is in Group II, formula of **A** must be MCl_2.

$NaOH + MCl_2 \rightarrow M(OH)_2 + 2\ NaCl$

No. of moles of **A** = 0.5 x 10^{-3}
No. of moles of **B** = 0.5 x 10^{-3}
Molar mass of **B** = 0.0292 / 0.5 x 10^{-3}
= 58.4 g mol^{-1}
$\Rightarrow$ molar mass of M = 58.4 – (2 x 17.0)
= 24.4 g mol^{-1}
$\therefore$ M is Mg.

A is $MgCl_2$.
B is $Mg(OH)_2$.
C is MgO.

$NaOH + MgCl_2 \rightarrow MgOH)_2 + 2\ NaCl$
$Mg(OH)_2 \rightarrow MgO + H_2O$

(ii) Predict the pH of the solution formed when **A** is dissolved in water.

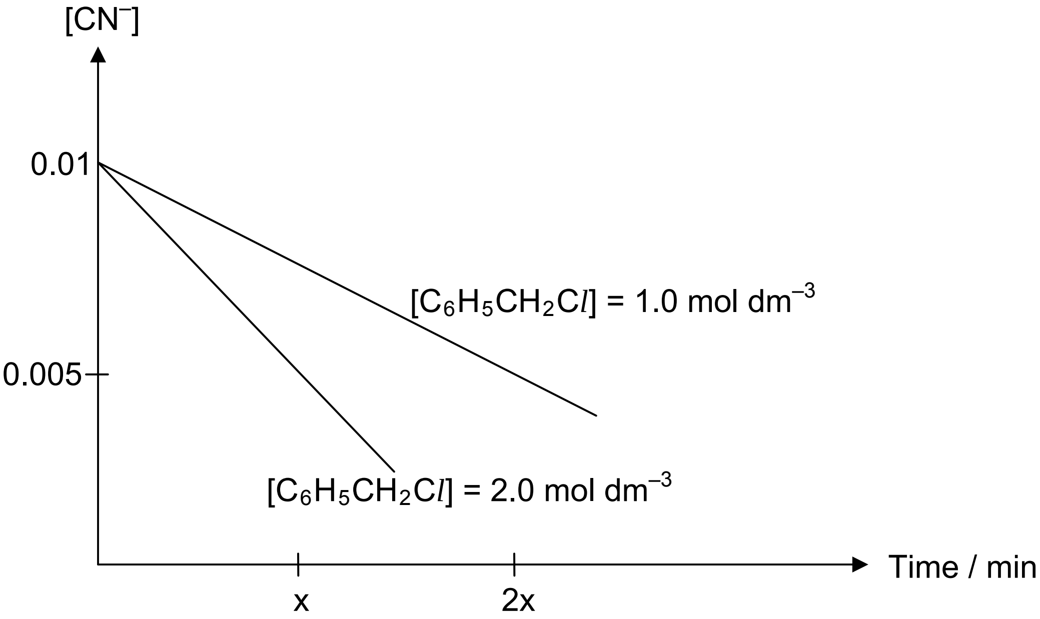
[6]

pH = 6.0 - 6.5

(d) The reaction below is an example of nucleophilic substitution.

$C_6H_5CH_2Cl + CN^- \rightarrow C_6H_5CH_2CN + Cl^-$

The reaction kinetics of this reaction is determined by monitoring the change in the concentration of CN^- with time. The results are shown below:

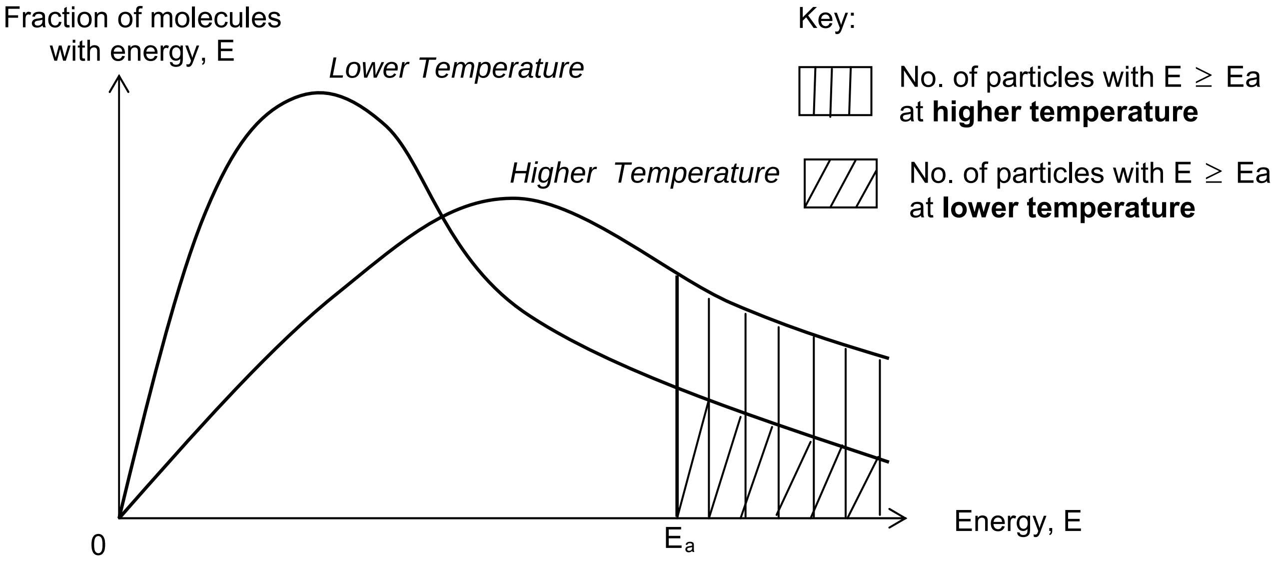


(i) Determine the rate equation for the above reaction.

Order of reaction with respect to $[CN^-]$ = 0
Order of reaction with respect to $[C_6H_5CH_2Cl]$ = 1
Rate = $k[C_6H_5CH_2Cl]$

(ii) With the aid of Maxwell-Boltzmann distribution curve, predict and explain the effect on the rate of this reaction when the reaction temperature is decreased.

[7]



When temperature of the reaction **decreases**,

✓ **average kinetic energy** of the reacting molecules **decreases**.

✓ **number** of **effective collisions with $E \geq E_a$** taking place in the reaction **decreases**.

✓ rate of reaction is **proportional** to the **frequency of effective collisions**.

✓ **rate of reaction decreases**

[Total: 20]

4 The oldest church in Paris named Saint-Germain l'Auxerrois, is well-known for its splendid stained glass.

The components of the stained glass used in the church windows is known to contain lead(II) oxide, silicon(IV) oxide and traces of a chromium-containing oxide.

(a) Explain why transition metals are denser than s-block elements. [3]

They have relatively **smaller atomic radius** and **higher relative atomic mass**. Hence, they have a **close-packed structure**.

(b) Describe the bonding in the following substances and explain why it contributes to the specified property in glass:

substance	property
(i) silicon (IV) oxide	hardness
(ii) lead (IV) oxide	Electrical conductivity (if any)

[4]

SiO_2 has a **giant molecular structure** with **extensive covalent bonding** in a giant three-dimensional structure.

PbO_2 has a **giant ionic structure**. In the solid state, the ions can only **vibrate about fixed positions**.

(c) The window frames enclosing the stained glass is made of aluminium due to its low density and high melting point.

Account for the high melting point of aluminium. [2]

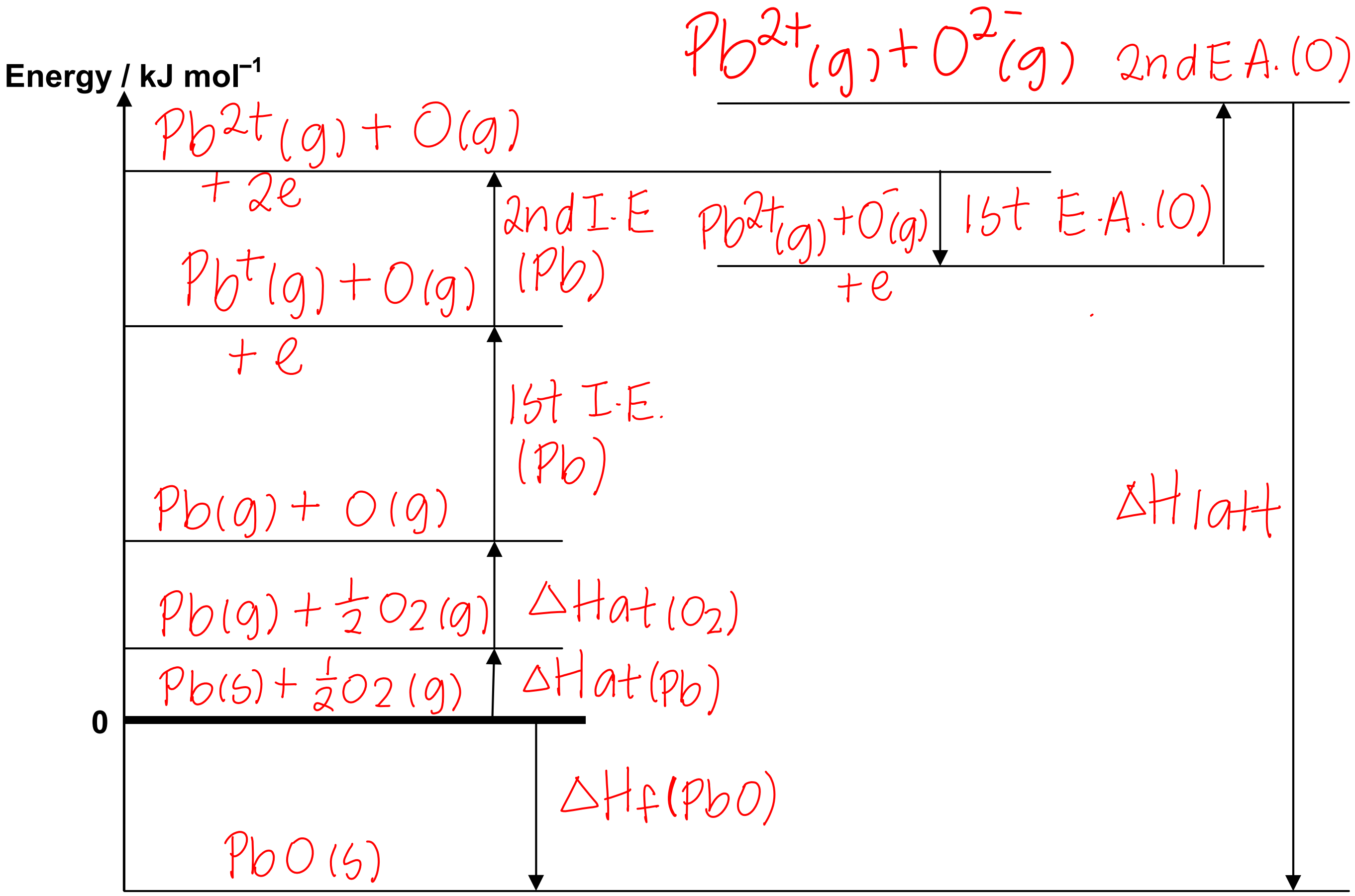
High amount of energy is required to overcome the **strong electrostatic forces of attraction between the cations and sea of delocalised electrons**.

(d) Construct a Born-Haber cycle for the formation of lead(II) oxide from its elements.

Use the relevant data from the table below as well as from the *Data Booklet,* calculate the lattice energy of lead(II) oxide.

enthalpy term	ΔH / kJ mol^{-1}
standard enthalpy change of formation of PbO	–219
standard enthalpy change of atomisation of Pb	+196
first electron affinity of oxygen	–141
second electron affinity of oxygen	+790

[6]



By Hess' law:
ΔH_{latt} = **–3478 kJ mol^{-1}** **OR** **–3.48 x 10^3 kJ mol^{-1}**

(e) It is found that a famous painting brought to an art gallery for cleaning and restoration before being hung in the St Germain church, has darkened because of the formation of lead(II) sulfide, PbS. Gentle treatment of the darkened areas of the painting with a dilute solution of hydrogen peroxide restores the original bright colours. The hydrogen peroxide converts the black lead(II) sulfide to white lead(II) sulfate. $E^{\theta}_{PbSO4/PbS}$ in acidic medium has a value of + 0.45 V.

(i) With the aid of the *Data Booklet* or otherwise, construct an overall equation for the reaction of hydrogen peroxide with lead(II) sulfide and calculate the overall electrode potential for the reaction.

From the *Data Booklet*,

$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \qquad E^{\theta} = +1.77\ V$

Reduction: $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$

Oxidation: $4\ H_2O + S^{2-} \rightarrow SO_4^{2-} + 8H^+ + 8e$

Overall Equation: $PbS\ (s) + 4H_2O_2\ (aq) \rightarrow PbSO_4\ (aq) + 4H_2O\ (l)$

$E^{\theta}_{cell} = +1.77 - 0.45 =$ **<u>+1.32 V</u>**

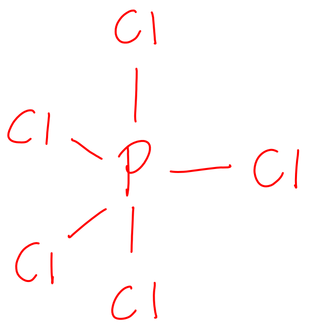
(ii) State the role of hydrogen peroxide.

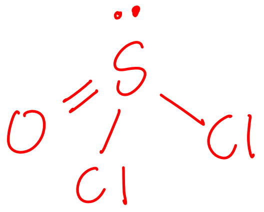
Hydrogen peroxide acts as an **<u>oxidising agent</u>**.

[Total: 20]

5 This question is about compounds commonly used as chlorinating agents in organic synthesis such as PCl_3, PCl_5 and $SOCl_2$.

(a) Draw the Lewis structures of PCl_5 and $SOCl_2$ and state their shapes. [4]





Trigonal bipyramidal

Trigonal pyramidal

(b) Predict the solubility of PCl_5 in tetrachloromethane. Support your prediction with appropriate reasons. [3]

PCl_5 is **soluble** in tetrachloromethane. The weak Van der Waal's forces between PCl_5 molecules are **similar in strength** to the weak Van der Waal's forces of attraction between tetrachloromethane molecules. Tetrachloromethane can penetrate the PCl_5 crystal and solvate it via **salvation**.

(c) PCl_5 can be produced by reacting PCl_3 with chlorine gas. When a mixture containing 1:1 ratio of PCl_3 and Cl_2 at a total initial pressure of 3.8 atm is allowed to react at 700 K, the partial pressure of PCl_5 formed at equilibrium is found to be 1.68 atm.

(i) Calculate the equilibrium partial pressures of PCl_3 and Cl_2.

Initial partial pressure of PCl_3 = 1.9 atm
Initial partial pressure of Cl_2 = 1.9 atm

	PCl_3 (g) + Cl_2 (g) $\rightleftharpoons$ PCl_5 (g)		
initial partial pressure / atm	1.9	1.9	0
Δ in partial pressure / atm	– 1.68	– 1.68	+ 1.68
eq^m partial pressure / atm	0.220	0.220	1.68

Equilibrium partial pressure of PCl_3 = **0.220 atm**
Equilibrium partial pressure of Cl_2 = **0.220 atm**

(ii) Hence, determine the percentage conversion of $\mathrm{PC}l_3$ and the equilibrium constant, K_p.

% conversion of $\mathrm{PC}l_3$ = 1.68 / 1.9 x 100% = **88.4%**

$$K_p = \frac{P_{PCl_5}}{(PCl_3)(P_{Cl_2})} = \frac{1.68}{0.22^2} = 34.7\ atm^{-1}$$

(iii) Using Le Chatelier's Principle, predict the effect on the yield of $\mathrm{PC}l_5$ when the temperature is increased.

When the temperature is increased, the system will try to **absorb the heat** by Le Chatelier's Principle and hence, favouring an endothermic reaction. The position of equilibrium shifts to the left and therefore, the yield of $\mathrm{PC}l_5$ will **decrease**.

(d) Adipic acid, $\mathrm{HOOC(CH_2)_4COOH}$ which is the most important dicarboxylic acid used in the industrial production of nylon, can be converted into its acid chloride by treatment with thionyl chloride, $\mathrm{SOC}l_2$.

(i) A solution of adipic acid has a pH value of 4.4. Suggest a possible pH value of its acid chloride, giving your reason.

pH of acid chloride = 1.0 (accept any value < 4.4)
Acid chloride dissolves in water to give HC*l* which is a strong acid.

(ii) Suggest a suitable chemical test to distinguish between adipic acid and hexamethylenediamine.

[6]

Add **$\mathrm{PC}l_5$** at **room temperature** to both compounds.

For adipic acid, **white fumes** will be observed.

For hexamethylenediamine, **no white fumes** will be observed.

[Total: 20]