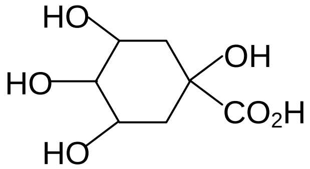
Victoria Junior College
2015 H2 Chemistry Prelim Exam 9647/2
Suggested Answers

1 Planning

You are provided with 5 unlabelled bottles containing pure natural acids from the extracts of roasted coffee.

Each bottle contains one of the following natural acids:

lactic acid,	$CH_3CH(OH)CO_2H$
maleic acid,	$HO_2CCH{=}CHCO_2H$
oxalacetic acid,	$HO_2CCOCH_2CO_2H$
pyruvic acid,	CH_3COCO_2H
quinic acid,	

All the acids above are soluble in water.

You are also provided with any other common laboratory reagents and apparatus.

(a) All natural acids contain one or more carboxylic acid functional groups. Other than the carboxylic acid functional group, what other functional groups are also present in these natural acids?

lactic acid: **secondary alcohol**

maleic acid: **alkene**

oxalacetic acid: **ketone**

pyruvic acid: **ketone**

quinic acid: **Secondary alcohol and tertiary alcohol**

[2]

(b) Two of these natural acids are colourless liquids and the rest are white crystalline solids.

Using relevant chemical knowledge, identify the two liquids. Explain your choices.

The two liquids are **lactic acid and pyruvic acid.**

Explanation: **These two compounds have a relatively smaller M_r and thus weaker dispersion forces between their respective molecules than the other 3 compounds (due to smaller number of electrons present).**

[2]

(c) Suggest a reagent that could be used to carry out a test-tube experiment to distinguish the two liquids.

Reagent: **Brady's reagent [or 2,4-dinitrophenylhydrazine]**

Describe what would be observed for each compound in the experiment.

Observation: **Pyruvic acid will give an orange ppt. but lactic acid will not.**

[2]

(d) Outline a logical sequence of chemical tests that would enable you to identify the remaining 3 solids. You should aim for a minimum number of reactions.

Your plan should include

- a positive test to confirm the identity of each compound;
- detailed procedure (including quantities of chemicals and conditions used);
- expected observations for each compound in each test.

Step 1: Prepare aqueous solutions of each of the 3 solid samples by dissolving 1-cm depth of solid in about 5 cm depth of deionised water in each test-tube.

Step 2: To 1-cm depth of each of the 3 samples in separate test-tubes, add equal volume of Brady's reagent.
Oxalacetic acid will give an orange ppt. while the other 2 samples will not.

Step 3: To 1-cm depth of each of the 2 remaining samples in separate test-tubes, add a few drops of Br_2(aq).
Maleic acid will decolourise reddish-brown Br_2 while the remaining sample will not.

Step 4: To 1-cm depth of the last sample in a test-tube, add a few drops of acidified $KMnO_4$(aq). Heat the mixture in a hot water-bath. Quinic acid will turn purple $KMnO_4$ colourless.

[2]

(e) How would you ensure the reliability of the test result for quinic acid?

To ensure a colour change for $KMnO_4$, the acidified $KMnO_4(aq)$ must be added slowly and dropwise. It should not be added in excess. The mixture must also be heated to prevent incomplete reduction to black MnO_2 solid.

[Or hydrochloric acid cannot be used to acidify $KMnO_4$ as the chloride ions can be oxidised by $KMnO_4$. As a result, there may be a colour change of $KMnO_4$ due to oxidation of chloride to Cl_2.]

[1]

(f) Suggest a safety measure that you would consider in carrying out your plan.

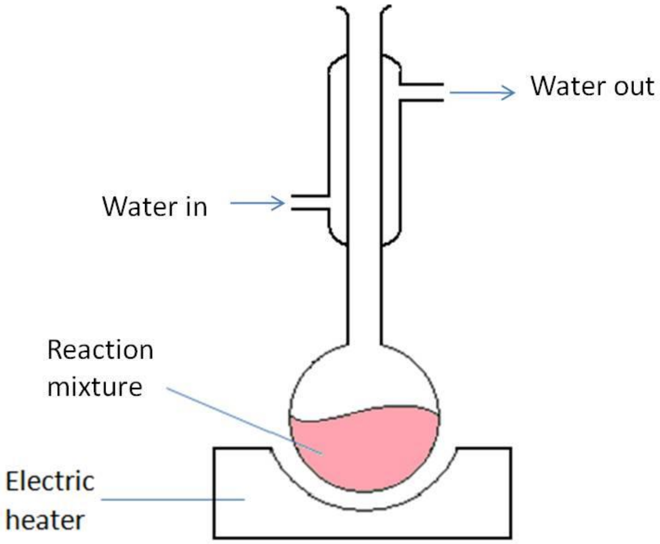
Use a hot water bath for heating instead of using a direct naked flame from the bunsen burner as most organic compounds are highly flammable.

[1]

(g) Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid. State the required reagents and conditions.

Reagents and conditions: **$KMnO_4(aq)$ / $H_2SO_4(aq)$, reflux**

[OR $K_2Cr_2O_7(aq)$ / $H_2SO_4(aq)$, reflux]



[2]

[Total: 12]

2 *Use of the Data Booklet* is required for this question.

(a) A 2.85 g sample of haematite iron ore, Fe_2O_3, was dissolved in hydrochloric acid and the solution diluted to 250 cm^3 in a standard flask. A 25.0 cm^3 of this solution was completely reduced with excess tin (II) chloride to form a solution of iron(II) ions.

After the remaining tin(II) ions were removed with a suitable reagent, the solution of iron(II) ions was titrated against an acidified solution of 0.020 mol dm^{-3} potassium dichromate(VI) and required 26.40 cm^3 for complete oxidation back to iron(III) ions.

(i) Give the balanced equation for the reaction between iron(II) and dichromate(VI) ions.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

[1]

(ii) Calculate the percentage of iron(III) oxide, Fe_2O_3, in the ore.

Amount of $Cr_2O_7^{2-}$ used = $0.0200 \times \frac{26.40}{1000}$ = 5.28×10^{-4} mol

Amount of Fe^{2+} present in 25.0 cm^3 solution = $6 \times 5.28 \times 10^{-4}$ mol

Total amount of Fe^{2+} present = $6 \times 5.28 \times 10^{-4} \times \frac{250}{25}$ = 3.168×10^{-2} mol

Hence amount of Fe_2O_3 present = $3.168 \times 10^{-2} \times \frac{1}{2}$ mol

Mass of Fe_2O_3 present = $3.168 \times 10^{-2} \times \frac{1}{2} \times 159.6 = 2.528$ g

% of Fe_2O_3 present = $\frac{2.528}{2.85} \times 100 = 88.7\%$

[3]

(b) **(i)** Suggest whether the acidified potassium dichromate(VI) can be replaced by potassium manganate(VII) for oxidising iron(II) back to iron(III). Explain your answer.

$KMnO_4$ cannot be used as it is a stronger oxidising agent than $K_2Cr_2O_7$ (more positive $E^\ominus$). Thus chloride ions in both hydrochloric acid and $SnCl_2$ would also be oxidised leading to inaccurate titration results.

[2]

(ii) Explain why the excess tin(II) ions have to be removed before titration with potassium dichromate(VI).

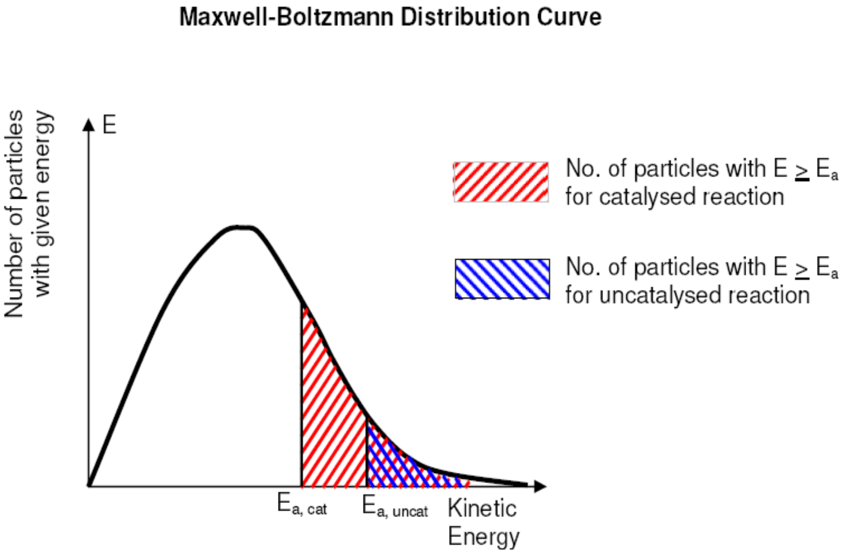
The excess tin(II) ions would also be oxidised to tin(IV) by $Cr_2O_7^{2-}$ ions hence again leading to inaccurate titration results.

[1]

(c) The compounds of manganese catalyse a wide variety of reactions, one instance being manganese dioxide, MnO_2, which catalyses the decomposition of hydrogen peroxide:

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

(i) With the aid of a sketch of the Boltzmann distribution curve, explain how the presence of a catalyst increases the rate of reaction.



Correct shape of Boltzman distribution curve and axis labels

When a catalyst is used in a reaction, it provides an alternative reaction pathway with lower activation energy. Hence, number of reacting particles with energy ≥ E_a increases as shown by the shaded area. This leads to higher frequency of effective collisions, thereby increasing the rate of reaction.

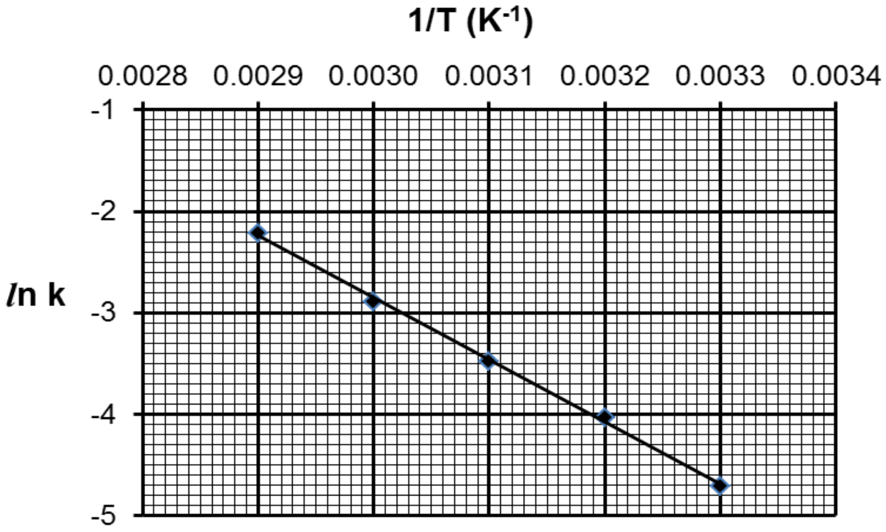
[2]

(ii) The relationship between the rate constant and temperature is generally governed by the Arrhenius equation:

$$k = Ae^{-E_a/(RT)}$$

where
k = rate constant
A = Arrhenius constant
E_a = activation energy in J mol^{-1}
R = molar gas constant = = 8.31 J K^{-1} mol^{-1}
T = temperature in K

To determine the activation energy of the above reaction, the rate constant was determined at various temperatures and the experimental results were then processed by plotting a graph of *l*n *k* vs 1/*T* (K^{-1}):



Use the given information to determine a value for the activation energy of the reaction.

Taking *l*n on both sides of the Arrhenius equation gives:

$\ln k = \ln A - (E_a / R) \times (1/T)$

Hence in the graph of ln k vs 1/T, gradient = $- E_a / R$

Gradient $= \dfrac{-2.2 - (-4.7)}{0.0029 - 0.0033}$

$= -6250$

$-6250 = -E_a / R$

$E_a = 6250 \times 8.31$
$= 51900$ J mol^{-1}

[2]

(d) Manganese compounds are also involved in many redox reactions. For example, MnO_4^- ions oxidize $C_2O_4^{2-}$ ions in an acidic medium according to the following equation:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

A student decided to investigate the rate of the above reaction. He placed the reaction flask in a thermostatically controlled water bath to keep the temperature constant and measured how the conductivity of the solution changed with time.

He observed that the conductivity changes slowly at first but in the course of time, the conductivity changes at a progressively faster rate. Towards the end of the reaction, the conductivity is again detected to change slowly.

(i) Deduce whether the conductivity readings increased or decreased as the reaction progressed.

Since the reaction results in less number of ions formed, the conductivity should have decreased.

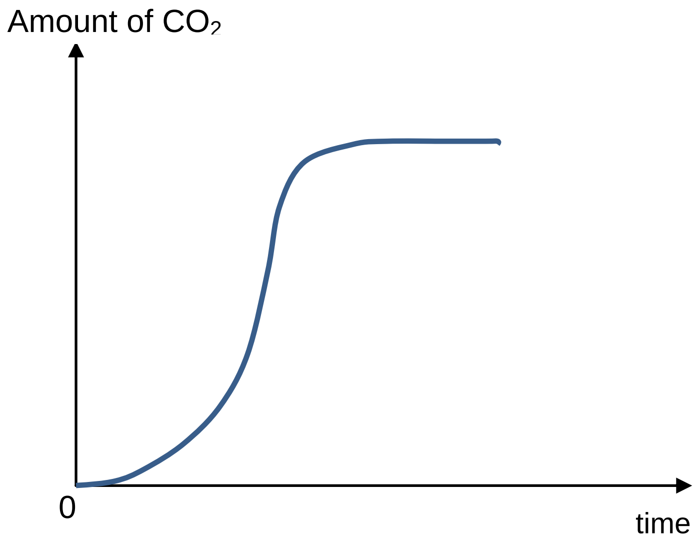
[1]

(ii) Suggest reasons why the conductivity changes at different rates as observed by the student.

The reaction is slow initially as it has a high activation energy. As time progresses, Mn^{2+}, the autocatalyst, is formed in increasing amounts, hence reaction speeds up. Towards the end, reactant concentration is low, hence rate decreases again.

[2]

(iii) Sketch on the axes below to show how the amount of CO_2 formed varies with time.



Sketch [-½ m for each mistake]

- **start from origin**
- **gradient increases then decreases**
- **constant max volume reached at the end**

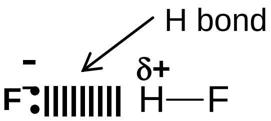
[1]
[Total: 15]

3 Hydrogen halides (or hydrohalic acids) are inorganic compounds with the formula H*X* where *X* is one of the halogens. The hydrogen halides are colourless gases at s.t.p., except for hydrogen fluoride, which boils at 19°C.

(a) The hydrogen halides are diatomic molecules with no tendency to ionize in the gas phase. However, in the liquid state, HF exhibits both the Bronsted-Lowry properties of an acid and a base. The conjugate base that is formed is especially stable in liquid HF.

(i) Write an equation to show how HF can act both as a Bronsted-Lowry acid and base in the liquid phase. Hence, explain with a diagram why the conjugate base that is formed is especially stable in liquid HF.

$\mathbf{HF + HF \rightarrow F^- + H_2F^+}$



In liquid HF, as HF has H bonded to highly electronegative F, hence, H is very electron deficient and it acquires a partial positive charge. It is therefore bonded to the lone pair electrons on F⁻ through a hydrogen bond. Hence, this makes the conjugate base formed, F⁻, especially stable in liquid HF.

[3]

(ii) HF is a weak acid in aqueous solution with a pK_a > 1 whereas the pK_a values become increasingly negative from HC*l* to HI. Explain briefly why the pK_a values become increasingly negative from HC*l* to HI.

Down the group, size of halogen atoms increases. Hence, the extent of overlapping of atomic orbitals between that of H and halogen (X) atoms decreases, H-X bond strength decreases. It is therefore easier to break the H-X bond to dissociate H^+ and halide ions in aqueous solution. Acid strength increases from HC*l* to HI, K_a values therefore increases numerically and pK_a decreases numerically (or becomes increasingly negative).

[2]

(iii) A 20.0 cm^3 solution of 0.10 mol dm^{-3} NaOH(aq) is titrated with 0.15 mol dm^{-3} HF(aq). When 20.0 cm^3 of HF(aq) is added, the pH of the solution is 3.44. Determine the pK_a of HF.

$NaOH + HF \rightarrow NaF + H_2O$
Excess HF and NaF formed make up a weak acid buffer with pH of 3.44.
[HF] left = (20x0.15 – 20x0.10) / 40 = 0.0250 mol dm^{-3}
[F$^-$] formed = 20x0.10 / 40 = 0.0500 mol dm^{-3}
$K_a = [H^+][F^-]/[HF] = (10^{-3.44})(0.050) / 0.025 = 7.26 \times 10^{-4}$ mol dm^{-3}
pK_a = −log K_a = 3.14

[2]

(iv) Suggest a suitable indicator for the titration of NaF(aq) with HI(aq). Explain your choice.

As NaF is a weak base while HI is a strong acid, pH < 7 at equivalence point. Suitable indicator is methyl orange.

[1]

(b) Hydrogen and chlorine are both obtained by electrolyzing concentrated sodium chloride solution. The direct reaction of hydrogen with chlorine gives hydrogen chloride. However, hydrogen chloride is produced industrially by treatment of halide salts with sulfuric acid. On the other hand, the least stable hydrogen halide, HI, is produced by the reaction of iodine with hydrogen sulfide or with hydrazine.

(i) Explain briefly why it is not industrially viable to produce HC*l* through the direct reaction of hydrogen with chlorine.

Reaction of hydrogen and chlorine is explosive to handle.

[1]

(ii) Write a balanced equation showing the formation of HI from iodine and hydrogen sulfide. Hence, with reference to the *Data Booklet*, explain why the reaction is thermodynamically spontaneous.

(Given that the $E^\ominus = +0.14$ V for $S + 2H^+ + 2e^- \rightleftharpoons H_2S$)

$I_2 + H_2S \rightarrow 2HI + S$

$S + 2H^+ + 2e^- \rightleftharpoons H_2S \qquad E^\ominus = +0.14\ V$

$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\ominus = +0.54\ V$

$E^\ominus_{cell} = E^\ominus_{Red} - E^\ominus_{Ox} = 0.54 - 0.14 = +0.40\ V$

Since $E^\ominus_{cell} > 0$, the redox reaction is thermodynamically feasible under standard conditions.

[3]

(iii) Determine the amount of time that is needed to produce 1.0 dm^3 of chlorine gas from electrolyzing concentrated sodium chloride solution with a current of 5.0 A at r.t.p.

At anode, $2Cl^- \rightarrow Cl_2 + 2e^-$
No. of moles of electrons transferred = 2 x 1000/24000 = 0.0833 mol
Quantity of charge transferred = 0.0833 x 96500 = 8.04×10^3 C
Hence, Q = I x t
$8.04 \times 10^3 = 5.0 \times t$
$t = 1.61 \times 10^3$ s (or 26.8 min)

[2]

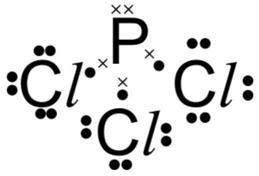
(iv) In addition to hydrogen and chlorine, state an important by-product that is produced during the electrolysis of concentrated sodium chloride solution.

sodium hydroxide

[1]
[Total: 15]

4 **(a)** Phosphorus trichloride, PCl_3, is a colourless fuming liquid which boils at 76°C.

(i) Draw a 'dot-and-cross' diagram of PCl_3.



[1]

(ii) Hence, suggest the hybridisation state of phosphorus in PCl_3.

sp^3 (because four electron domains around phosphorus)

[1]

(b) Ethanol and PCl_3 reacts via the nucleophilic substitution mechanism, whereby PCl_3 is reacting as an electrophile.

By studying the structure of PCl_3, explain why PCl_3 is able to react as an electrophile.

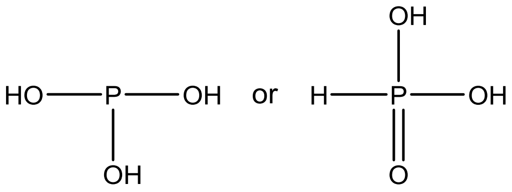
Phosphorus is bonded to three electronegative chlorine atoms making the former electron deficient and susceptible to attack by nucleophile (lone pair of electron on oxygen in ethanol)

[1]

(c) Phosphonic acid, H_3PO_3, is most commonly used in the production of phosphites. It is produced when PCl_3 is reacted with steam according to the equation below:

$$PCl_3(g) + 3H_2O(g) \rightarrow H_3PO_3(l) + 3HCl(g)$$

(i) Two possible structures can be drawn for phosphonic acid.



Make use of the following bond energies to suggest which structure is more likely to be formed.

bond	bond energy /kJ mol^{-1}
O–H	460
P–H	322
P–O	335
P=O	544

Total bond energy in (structure on left)
= 3 × 460 + 3 × 335
= 2385 kJ mol^{-1}

Total bond energy in (structure on right)
= 2 × 460 + 2 × 335 + 322 + 544
= 2456 kJ mol^{-1}

Structure on right is more likely to be formed since its formation will lead to a <u>greater decrease in enthalpy</u> (and, therefore, leading to greater stability) for the chemical system.

[3]

(ii) 10.0 cm^3 of 0.50 mol dm^{-3} H_3PO_3(aq) was mixed with 10.0 cm^3 of excess NaOH(aq). It was found that the temperature of the solution after mixing rose by 6.4°C.
Specific heat capacity of water = 4.2 J g^{-1} K^{-1}; density of water = 1.0 g cm^{-3}.
Calculate the enthalpy change of reaction per mole of H_3PO_3(aq).

No. of moles of H_3PO_3 used = 5.0 × 10^{-3} mol

$\Delta Q = mc\Delta T = 20.0 \text{ g} \times 4.2 \text{ J g}^{-1} \text{ K}^{-1} \times 6.4 \text{ K} = 537.6 \text{ J}$

Enthalpy of reaction $= -\dfrac{537.6}{5.0\times10^{-3}} = -108 \text{ kJ mol}^{-1}$

[2]

(iii) Given that the enthalpy change of neutralization of HC*l*(aq) by NaOH(aq) is −55.8 kJ mol^{-1}; comment on how the answer in **(c)(ii)** confirms the structure of H_3PO_3 that you determined previously in **(c)(i)**.

The enthalpy change of reaction per mole of phosphonic acid is about <u>twice that of hydrochloric acid</u> (monoprotic acid) which means that the former is a <u>diprotic acid</u> and this confirms the structure determined previously.

[1]

(d) PCl_5 can be formed from the reaction between PCl_3 and Cl_2.

Below 163°C, PCl_5 condenses directly from the gaseous phase to the solid phase. In the process, a chloride ion is transferred from one of the PCl_5 molecule to the other, leaving a positive ion, $[PCl_4]^+$ and negative ion, $[PCl_6]^-$ which gives rise to strong electrostatic forces of attraction between the oppositely charged ions.

State the shapes of $[PCl_4]^+$ and $[PCl_6]^-$.

(i) $[PCl_4]^+$ **tetrahedral**

(ii) $[PCl_6]^-$ **octahedral**

[2]

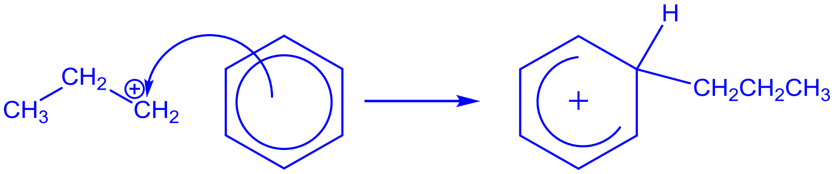
(e) **(i)** Name and describe the mechanism of the reaction between benzene and 1-chloropropane, $CH_3CH_2CH_2Cl$, in the presence of $AlCl_3$. Your answer should include curly arrows showing the movement of electrons and all charges.

Name of mechanism: <u>electrophilic subsititution</u>

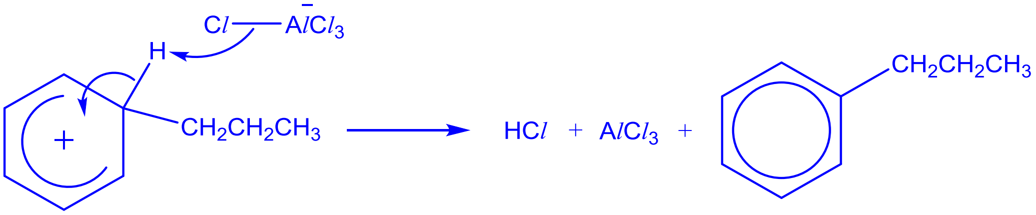
<u>Generation of electrophile</u>

$$AlCl_3 + CH_3CH_2CH_2Cl \longrightarrow AlCl_4^- + CH_3CH_2CH_2^+$$

<u>Electrophilic attack on benzene ring by carbocation</u>

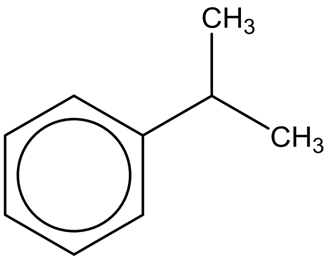


<u>Restoration of resonance in benzene ring by proton abstraction</u>



[2]

(ii) In the reaction between benzene and 1-chloropropane, (1-methylethyl)benzene is formed as a by-product of the reaction.



(1-methylethyl)benzene

Carefully examine the structure and *stability* of the reactive carbocation intermediate in your mechanism.

Hence, explain the formation of (1-methylethyl)benzene from the reaction between benzene and 1-chloropropane.

In the original mechanism, the carbocation is a primary carbocation whereas to form (1-methylethyl)benzene, the carbocation is a <u>secondary carbocation</u>.
The original carbocation was transformed/rearranged to give the secondary carbocation which is <u>more stable</u> than the primary carbocation.

[1]

(iii) Explain why $BeCl_2$ can be used in place of $AlCl_3$ as the catalyst in the formation of chlorobenzene from benzene.

Beryllium in $BeCl_2$ is electron-deficient and can react as a halogen carrier (or form a bond with chlorine atom).

[1]

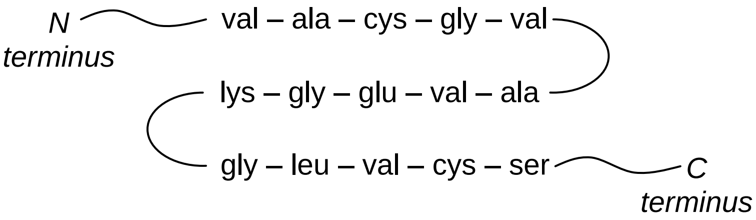
[Total: 15]

5 Bovine serum albumin (BSA) is a protein derived from cows.

The common amino acid residues in BSA are listed below:

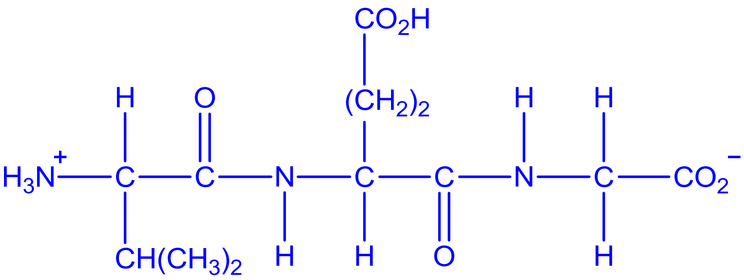
amino acid	**3-letter abbreviation**	**formula of side chain**
alanine	ala	$-CH_3$
cysteine	cys	$-CH_2SH$
glutamic acid	glu	$-(CH_2)_2CO_2H$
glycine	gly	$-H$
leucine	leu	$-CH_2CH(CH_3)_2$
lysine	lys	$-(CH_2)_4NH_2$
serine	ser	$-CH_2OH$
valine	val	$-CH(CH_3)_2$

(a) The following shows part of the sequence of amino acids in BSA.



A proteolytic enzyme **Z** is capable of hydrolysing peptide bonds at the carboxylic end of glycine and the amino end of valine.

Draw the structural formula of the tripeptide formed when enzyme **Z** is added to the sequence of amino acids in BSA.

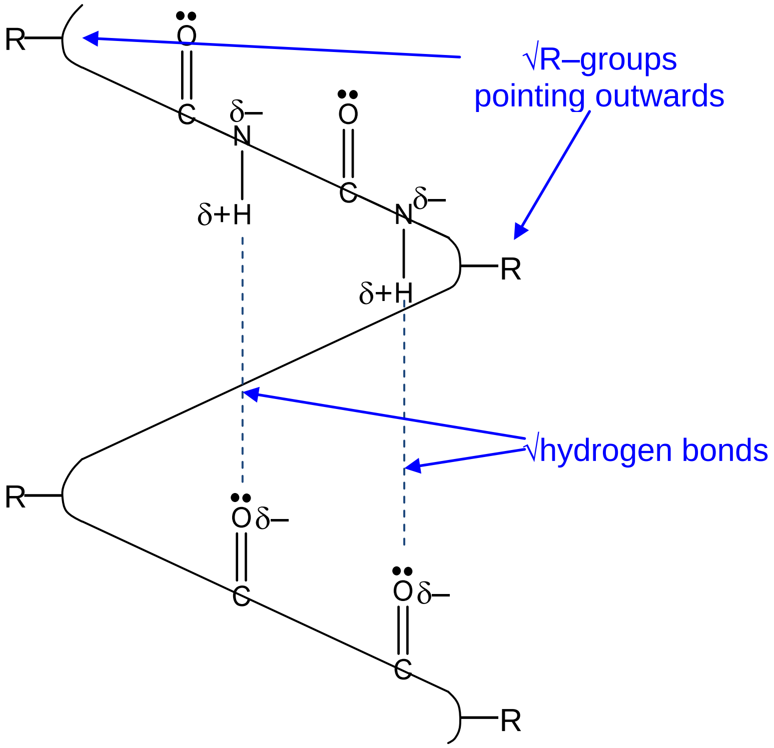


$$H_3N^+CH(CH(CH_3)_2)CONHCH((CH_2)_2CO_2H)CONHCH_2CO_2^-$$

[2]

(b) By considering the R–groups of common amino acids present in BSA, suggest the predominant secondary protein structure present in BSA. Draw a diagram to illustrate the secondary structure.

The R–groups are generally **non–bulky**. Thus, **alpha helix** is likely to be the predominant secondary protein structure.



√R–groups pointing outwards

√hydrogen bonds

[3]

(c) The interactions of small anions, such as halides, with proteins have important significance in the transportation and distribution process of biological systems.

A solution containing excess Br^- of known concentration is added to a fixed concentration of BSA, forming a BSA complex at equilibrium as shown:

$$\text{BSA} + \text{Br}^- \rightleftharpoons \text{BSA complex}$$

The concentration of Br^- that binds to BSA is calculated by finding the difference between the original concentration of Br^- and the concentration of free Br^- at equilibrium. The affinity for binding is then reflected in the value of the binding equilibrium constant, *K*, calculated.

The data obtained at three different temperatures are given below:

T / K	***K* for Br^-**
288	1.85
298	2.62
308	3.82

(i) Account for the trend in binding constants in terms of the structural changes that BSA undergo at elevated temperatures.

As temperature increases, **binding constant increases**. Disruption of dispersion forces, hydrogen bonds, ionic interactions and disulfide linkages results in the **denaturation of 2°, 3°, and 4° structures**. The unfolding of the protein results in **more (positively charged) regions for the Br^- to bind to**.

[2]

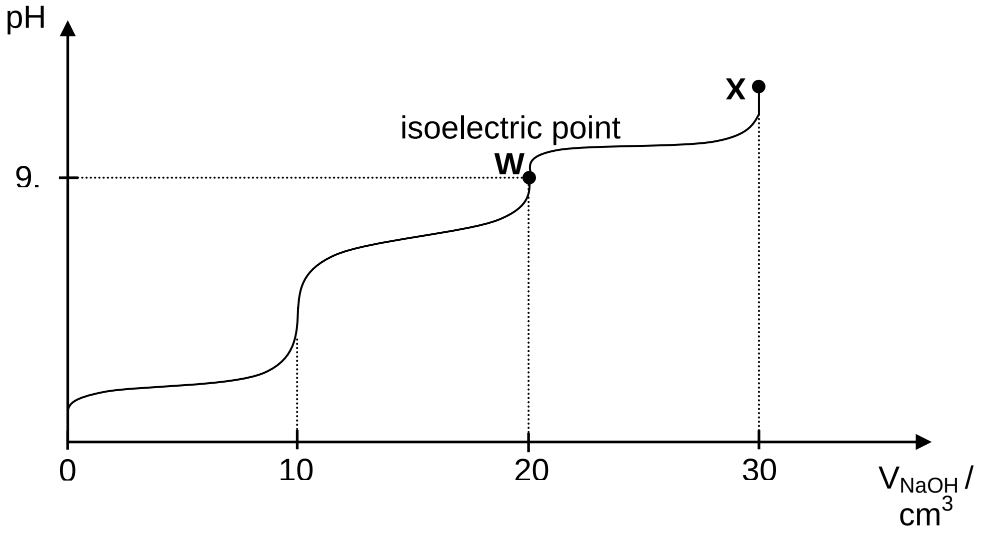
(ii) A student suggested measuring the concentration of free Br^- by adding a known excess of aqueous silver nitrate, and measuring the mass of the precipitate formed. With reference to the types of side chain given in the question, explain why this suggestion is **not** feasible.

Ag^+ from $AgNO_3$ will disrupt **ionic interactions between glutamic acid and lysine residues** as well as **disulfide linkages between cysteine residues**, resulting in the denaturation of **3° and 4°** structures. This will not only result in **less AgBr formed**, but also result in the **probable precipitation of BSA**.

Hence suggestion is **not** feasible.

[2]

(d) When 10 cm^3 of 0.100 mol dm^{-3} of a fully protonated amino acid in BSA is completely neutralised with 0.100 mol dm^{-3} of aqueous sodium hydroxide, the following pH curve is obtained

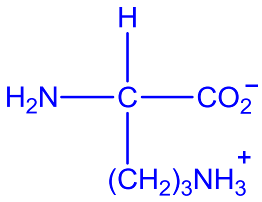


(i) Identify, with reasoning, the amino acid.

3 points of neutralisation means that the amino acid have **3 acidic groups** in its fully protonated form. pI > 7 means that that amino acid has **more NH_2 groups compared to CO_2H groups**. Hence amino acid is **lysine**.

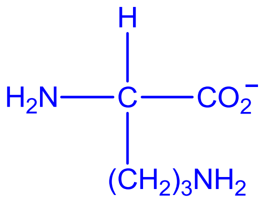
[2]

(ii) Draw the structures of the amino acid at point **W** and **X**.



$H_2N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_3NH_3^+}{C}}-CO_2^-$

W



$H_2N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_3NH_2}{C}}-CO_2^-$

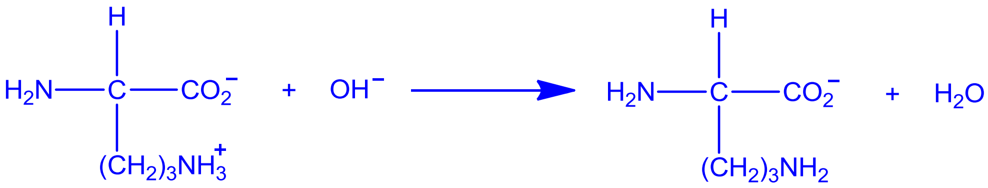
X

[2]

(iii) Using a relevant equation, account for the relatively small change in pH in the region between **W** and **X**.

The region between **W** and **X** is a **buffer region**.

When **small amount of base** is added, the large reservoir of **W** will remove the additional amount of OH⁻ added. Thus pH remains relatively constant.



$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_3NH_3^+}{C}}-CO_2^- + OH^- \longrightarrow H_2N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_3NH_2}{C}}-CO_2^- + H_2O$$

[2]

[Total: 15]