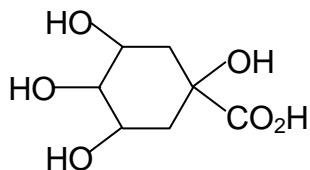


1 Planning

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, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$
- maleic acid, $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$
- oxalacetic acid, $\text{HO}_2\text{CCOCH}_2\text{CO}_2\text{H}$
- pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$
- 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:

maleic acid:

oxalacetic acid:

pyruvic acid:

quinic acid:

[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

Explanation:

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[2]

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

Reagent:

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

Observation:

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[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.

[2]

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

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[1]

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

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[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:

Diagram of the set-up:

[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.

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[1]

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

[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.

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[2]

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

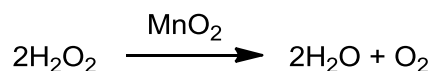
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[1]

- (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:



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

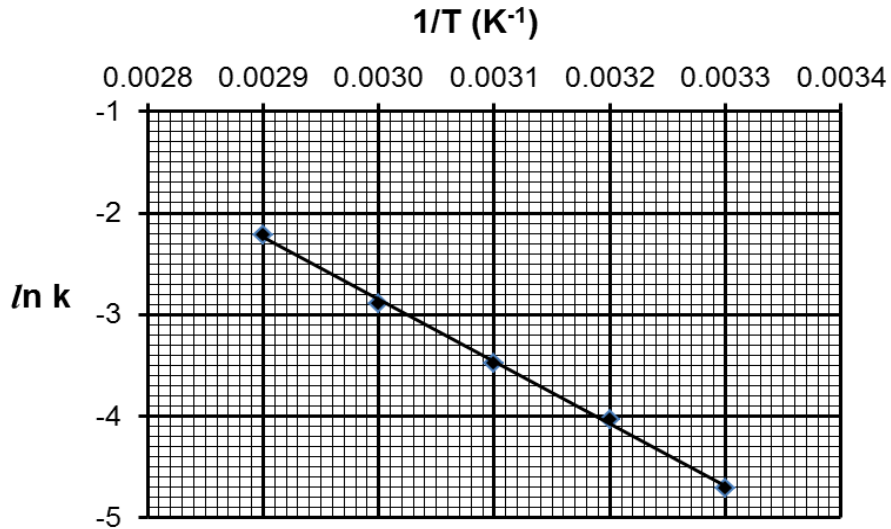
A = Arrhenius constant

E_a = activation energy in J mol^{-1}

R = molar gas constant = $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

T = temperature in K

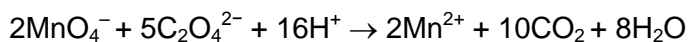
To determine the activation energy of the above reaction, the rate constant was determined at various temperatures and the experimental results were then processed by plotting a graph of $\ln k$ vs $1/T$ (K^{-1}):



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

[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:



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.

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[1]

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

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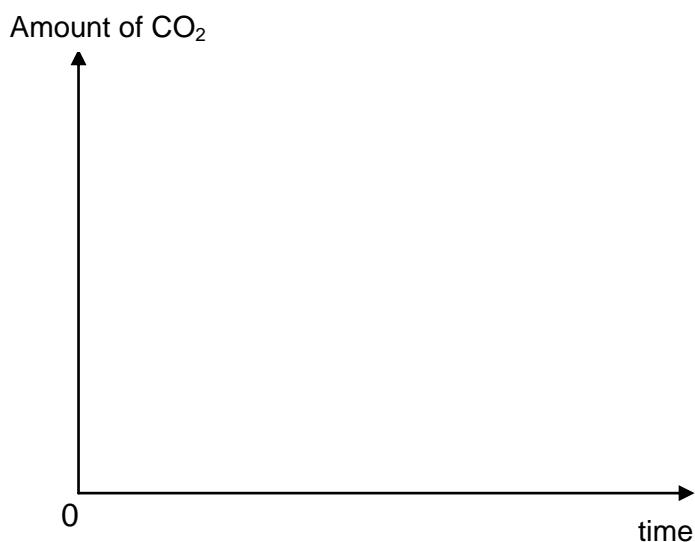
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[2]

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



[1]

[Total: 15]

- 3 Hydrogen halides (or hydrohalic acids) are inorganic compounds with the formula HX 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 .

[3]

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

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[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 $\text{p}K_{\text{a}}$ of HF.

[2]

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

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[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 HCl through the direct reaction of hydrogen with chlorine.

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[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 $E^\ominus = +0.14 \text{ V}$ for $\text{S} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{S}$)

[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.

[2]

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

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[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 .

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[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.

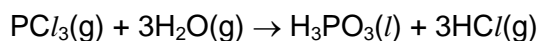
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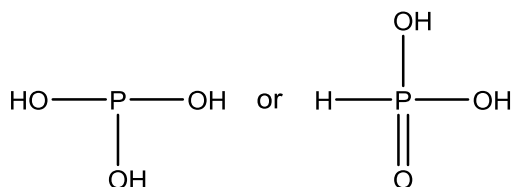
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[1]

- (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:



(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

[3]

- (ii) 10.0 cm³ of 0.50 mol dm⁻³ H₃PO₃(aq) was mixed with 10.0 cm³ 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 neutralisation per mole of H₃PO₃(aq).

[2]

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

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[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, $[\text{PCl}_4]^+$ and negative ion, $[\text{PCl}_6]^-$ which gives rise to strong electrostatic forces of attraction between the oppositely charged ions.

State the shapes of $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$.

- (i) $[\text{PCl}_4]^+$
- (ii) $[\text{PCl}_6]^-$

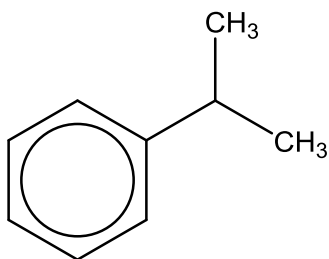
[2]

- (e) (i) Name and describe the mechanism of the reaction between benzene and 1-chloropropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, in the presence of AlCl_3 . Your answer should include curly arrows showing the movement of electrons and all charges.

Name of mechanism:

[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.

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[1]

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

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[1]

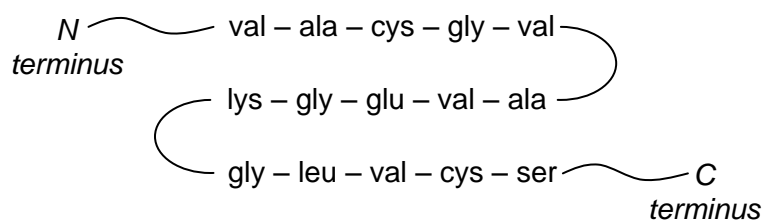
[Total: 15]

- 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	$-\text{CH}_3$
cysteine	cys	$-\text{CH}_2\text{SH}$
glutamic acid	glu	$-(\text{CH}_2)_2\text{CO}_2\text{H}$
glycine	gly	$-\text{H}$
leucine	leu	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$
lysine	lys	$-(\text{CH}_2)_4\text{NH}_2$
serine	ser	$-\text{CH}_2\text{OH}$
valine	val	$-\text{CH}(\text{CH}_3)_2$

- (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.

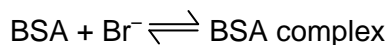
[2]

- (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.

[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:



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.

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[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.

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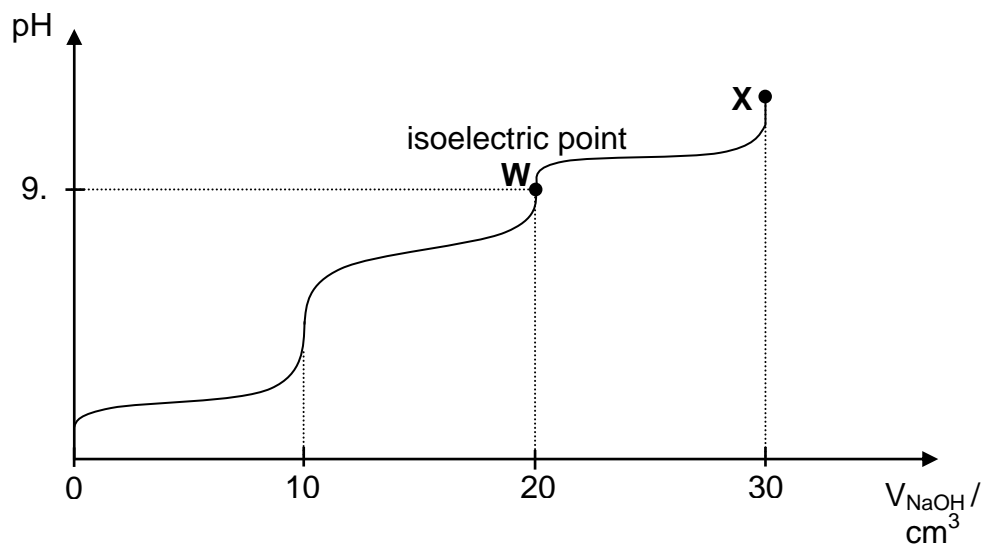
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[2]

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



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

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[2]

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

[2]

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

[2]

[Total: 15]