



**Chemical Equilibria**

**CAIE A Level**

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Q1.

- 2 (a) Barium ions are poisonous. Patients with digestive tract problems are sometimes given an X-ray after they have swallowed a 'barium meal', consisting of a suspension of  $\text{BaSO}_4$  in water. The  $[\text{Ba}^{2+}(\text{aq})]$  in a saturated solution of  $\text{BaSO}_4$  is too low to cause problems of toxicity.

(i) Write an expression for the solubility product,  $K_{\text{sp}}$ , for  $\text{BaSO}_4$ , including its units.

.....

(ii) The numerical value of  $K_{\text{sp}}$  is  $1.30 \times 10^{-10}$ . Calculate  $[\text{Ba}^{2+}(\text{aq})]$  in a saturated solution of  $\text{BaSO}_4$ .

.....

.....

(iii) The numerical value of  $K_{\text{sp}}$  for  $\text{BaCO}_3$  ( $5 \times 10^{-10}$ ) is not significantly higher than that for  $\text{BaSO}_4$ , but barium carbonate is **very** poisonous if ingested. Suggest a reason why this might be so.

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[3]

- (b) A useful commercial source of magnesium is sea water, where  $[\text{Mg}^{2+}(\text{aq})]$  is  $0.054 \text{ mol dm}^{-3}$ . The magnesium is precipitated from solution by adding calcium hydroxide.



(i) Write an expression for the  $K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$ , including its units.

.....

(ii) The numerical value for  $K_{\text{sp}}$  is  $2.00 \times 10^{-11}$ . Calculate  $[\text{Mg}^{2+}(\text{aq})]$  in a saturated solution of  $\text{Mg}(\text{OH})_2$ .

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- (iii) Hence calculate the maximum percentage of the original magnesium in the seawater that this method can extract.

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 [5]

- (c) The magnesium ions in seawater are mainly associated with chloride ions.

- (i) Use the following  $\Delta H_f^\ominus$  values to calculate a value for the  $\Delta H^\ominus$  of the following reaction.



species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{MgCl}_2(\text{s})$	-641
$\text{Mg}^{2+}(\text{aq})$	-467
$\text{Cl}^{-}(\text{aq})$	-167

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- (ii) Use your answer to explain why  $\text{MgCl}_2$  is very soluble in water.

.....  
 [2]

- (d) All the chlorides of Group II elements are soluble in water. The same is not true of their sulphates. These become less soluble as the group is descended.

Explain qualitatively the variation in solubility of the sulphates of the elements in Group II down the Group from magnesium to barium.

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 ..... [2]

[Total : 12]

Q2.

- 5 (a) Give an expression for  $K_a$  as applied to the weak acid  $\text{RCO}_2\text{H}$ .

.....  
 ..... [1]

- (b) The  $K_a$  values for three carboxylic acids are listed in the table below.

acid	$K_a / \text{mol dm}^{-3}$
$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5}$
$\text{ClCH}_2\text{CO}_2\text{H}$	$1.4 \times 10^{-3}$
$\text{Cl}_2\text{CHCO}_2\text{H}$	$5.5 \times 10^{-2}$

- (i) Describe and explain the trend in acid strength illustrated by these values.

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- (ii) Calculate the pH of a  $0.100 \text{ mol dm}^{-3}$  solution of  $\text{ClCH}_2\text{CO}_2\text{H}$ .

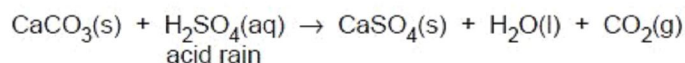
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- (iii) Calculate the  $\text{p}K_a$  value for  $\text{Cl}_2\text{CHCO}_2\text{H}$ .

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 ..... [5]

Q3.

- 2 Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are suffering erosion by acid rain. The carbonate stone is converted by the acid rain into the relatively more soluble sulphate.



- (a) (i) Write an expression for the solubility product,  $K_{\text{sp}}$ , of  $\text{CaSO}_4$ , stating its units.

.....

- (ii) The  $K_{\text{sp}}$  of  $\text{CaSO}_4$  has a numerical value of  $3 \times 10^{-5}$ . Use your expression in (i) to calculate  $[\text{CaSO}_4]$  in a saturated solution.

.....

- (iii) Hence calculate the maximum loss in mass of a small statue if  $100 \text{ dm}^3$  of acid rain falls on it. Assume the statue is made of pure calcium carbonate, and that the acid rain becomes saturated with  $\text{CaSO}_4$ .

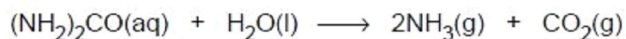
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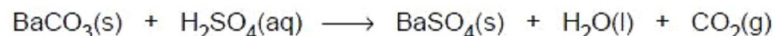
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[5]

- (b) The life of such monuments is now being extended by treating them with a mixture of urea and barium hydroxide solutions. After soaking into the pores of the carbonate rock, the urea gradually decomposes to ammonia and carbon dioxide. The carbon dioxide then reacts with the barium hydroxide to form barium carbonate.



Acid rain then converts the barium carbonate to its sulphate.



Barium sulphate is much less soluble than calcium sulphate. A saturated solution contains  $[\text{Ba}^{2+}] = 9.0 \times 10^{-6} \text{ mol dm}^{-3}$ .

- (i) Explain why barium sulphate is less soluble than calcium sulphate.

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- (ii) Write an expression for the  $K_{sp}$  of barium sulphate and use the data to calculate its value.

Use

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[4]

- (c) (i) Explain what is meant by the term *lattice energy*.

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- (ii) Predict, with a reason, how the lattice energy of  $BaSO_4$  might compare with that of  $MgSO_4$ .

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[3]

[Total: 12]

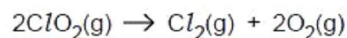
**Q4.**

- 2 This question is about the properties and reactions of the oxides of some elements in their +4 oxidation state.

Use

- (a) Chlorine dioxide,  $ClO_2$ , is an important industrial chemical, used to bleach wood pulp for making paper, and to kill bacteria in water supplies.

However, it is unstable and decomposes into its elements as follows.



- (i) The chlorine atom is in the middle of the  $ClO_2$  molecule. Using the chlorine-oxygen bond energy as  $278 \text{ kJ mol}^{-1}$ , and other values from the *Data Booklet*, calculate  $\Delta H$  for the above reaction.

$\Delta H = \dots\dots\dots \text{ kJ mol}^{-1}$

- (ii) Assuming the Cl-O bonds in chlorine dioxide are double bonds, predict the shape of the  $\text{ClO}_2$  molecule. Explain your answer.

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.....

- (iii)  $\text{ClO}_2$  can be made in the laboratory by reacting  $\text{KClO}_3$  with concentrated  $\text{H}_2\text{SO}_4$ . Other products are  $\text{K}_2\text{SO}_4$ ,  $\text{KClO}_4$  and  $\text{H}_2\text{O}$ .

Construct a balanced equation for this reaction. You may find the use of oxidation numbers helpful.

.....

[5]

- (b) Sulphur dioxide is an atmospheric pollutant.

- (i) State **two** sources of atmospheric  $\text{SO}_2$  that arise from human activity.

.....  
.....

- (ii) Explain why  $\text{SO}_2$  is a pollutant, and state an environmental consequence of this pollution.

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[3]

Fahad H. Ahmad

(c) All the oxides of the elements in Group IV in their +4 oxidation state are high melting point solids except  $\text{CO}_2$ .

(i) Explain this observation by describing the bonding in  $\text{CO}_2$ ,  $\text{SiO}_2$  and  $\text{SnO}_2$ .

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(ii) State the difference in the thermal stabilities of  $\text{SnO}_2$  and  $\text{PbO}_2$ . Illustrate your answer with an equation.

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.....

$\text{CO}_2$  dissolves in water to form a weakly acidic solution containing the hydrogencarbonate ion.

(iii) Write an equation for the reaction of  $\text{CO}_2$  with water, and write an expression for the equilibrium constant,  $K_c$ .

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(iv) Explain the role of the hydrogencarbonate ion in controlling the pH of blood, illustrating your answer with relevant equations.

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[7]

[Total: 15]

Q5.



- 1 (a) Explain what is meant by the *Bronsted-Lowry* theory of acids and bases.

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..... [2]

- (b) The  $K_a$  values for some organic acids are listed below.

acid	$K_a/\text{mol dm}^{-3}$
$\text{CH}_3\text{CO}_2\text{H}$	$1.7 \times 10^{-5}$
$\text{ClCH}_2\text{CO}_2\text{H}$	$1.3 \times 10^{-3}$
$\text{Cl}_2\text{CHCO}_2\text{H}$	$5.0 \times 10^{-2}$

- (i) Explain the trend in  $K_a$  values in terms of the structures of these acids.

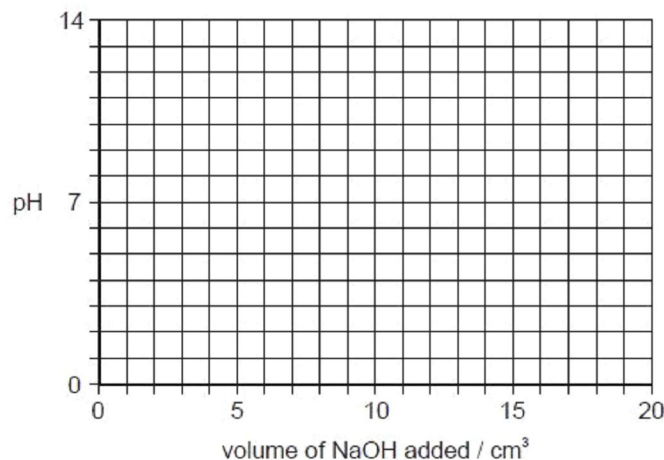
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- (ii) Calculate the pH of a  $0.10 \text{ mol dm}^{-3}$  solution of  $\text{ClCH}_2\text{CO}_2\text{H}$ .

pH = .....

- (iii) Use the following axes to sketch the titration curve you would obtain when  $20 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  NaOH is added gradually to  $10 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$   $\text{ClCH}_2\text{CO}_2\text{H}$ .

For  
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Use



[8]

- (c) (i) Write suitable equations to show how a mixture of ethanoic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , and sodium ethanoate acts as a buffer solution to control the pH when either an acid or an alkali is added.

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- (ii) Calculate the pH of a buffer solution containing  $0.10 \text{ mol dm}^{-3}$  ethanoic acid and  $0.20 \text{ mol dm}^{-3}$  sodium ethanoate.

pH = .....  
[4]

[Total: 14]

Q6.

2 (a) State briefly what is meant by the following terms.

(i) reversible reaction

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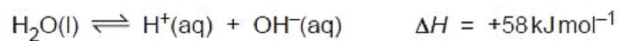
(ii) dynamic equilibrium

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[2]

(b) Water ionises to a small extent as follows.



(i) Write an expression for  $K_c$  for this reaction.

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(ii) Write down the expression for  $K_w$ , the ionic product of water, and explain how this can be derived from your  $K_c$  expression in (i).

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(iii) State and explain how the value of  $K_w$  for hot water will differ from its value for cold water.

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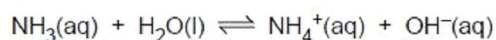
[3]

(c)  $K_w$  can be used to calculate the pH of solutions of strong and weak bases.

(i) Use the value of  $K_w$  in the *Data Booklet* to calculate the pH of  $0.050 \text{ mol dm}^{-3}$  NaOH.

pH = .....

Ammonia ionises slightly in water as follows.



The following expression applies to this equilibrium.

$$[\text{H}_2\text{O}] \times K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

- (ii) Calculate  $[\text{OH}^-(\text{aq})]$  in a  $0.050 \text{ mol dm}^{-3}$  solution of  $\text{NH}_3$ . You may assume that only a small fraction of the  $\text{NH}_3$  ionises, so that  $[\text{NH}_3]$  at equilibrium remains at  $0.050 \text{ mol dm}^{-3}$ .

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$$[\text{OH}^-(\text{aq})] = \dots\dots\dots$$

- (iii) Use the value of  $K_w$  in the *Data Booklet*, and your answer in (ii), to calculate  $[\text{H}^+(\text{aq})]$  in  $0.050 \text{ mol dm}^{-3} \text{ NH}_3(\text{aq})$ .

$$[\text{H}^+(\text{aq})] = \dots\dots\dots$$

- (iv) Calculate the pH of this solution.

$$\text{pH} = \dots\dots\dots$$

[6]

[Total: 11]

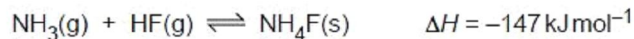
**Q7.**

- 1 (a) Hydrogen fluoride, HF, behaves as a weak acid in water, with  $K_a = 5.6 \times 10^{-4} \text{ mol dm}^{-3}$ .

Calculate the pH of a  $0.050 \text{ mol dm}^{-3}$  solution of HF.

$$\text{pH} = \dots\dots\dots [2]$$

- (b) Gaseous ammonia and hydrogen fluoride react together to give solid ionic ammonium fluoride.



- (i) What *type of reaction* is this?

.....

- (ii) Draw dot-and-cross diagrams (outer shells only) describing the bonding in the three compounds involved in this reaction.



- (iii) There are **three** types of bonding in  $\text{NH}_4\text{F}$ .  
Give the names of each of the three types, and state where in the compound each type occurs.

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.....

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- (iv) The reaction between  $\text{NH}_3$  and  $\text{HF}$  is reversible. What conditions of temperature and pressure would favour the **reverse** reaction, i.e. the dissociation of  $\text{NH}_4\text{F}$ ? Explain your answer.

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[9]

- (c) Many commercial copper and brass polishes contain ammonia. The tarnish that forms on the surface of copper is often copper sulfide,  $\text{CuS}$ . In the presence of  $\text{O}_2$  from the air,  $\text{NH}_3$  can combine with this copper sulfide to produce the soluble cuprammonium sulfate,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ .

- (i) Construct an equation for this reaction.

.....

- (ii) State the colour of cuprammonium sulfate solution.

.....

- (iii) Describe what you would see if a solution of cuprammonium sulfate was diluted with water. Explain your answer.

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[3]

- (d) When sulfuric acid is added to  $\text{Cu}^{2+}(\text{aq})$ , no colour change occurs, but when concentrated hydrochloric acid is added to  $\text{Cu}^{2+}(\text{aq})$ , the solution turns yellow-green. The solution reverts to its original colour when it is diluted with water.

Suggest the type of reaction occurring with  $\text{HCl}(\text{aq})$ , suggest what is formed during the reaction, and write an equation for the change.

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[3]

[Total: 17]

Q8.

1 (a) What is meant by the term *standard electrode potential*, SEP?

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[2]

(b) Draw a fully labelled diagram of the apparatus you could use to measure the SEP of the Fe<sup>3+</sup>/Fe<sup>2+</sup> electrode.

[5]

(c) The reaction between Fe<sup>3+</sup> ions and I<sup>-</sup> ions is an equilibrium reaction.



(i) Use the *Data Booklet* to calculate the  $E_{\text{cell}}^{\circ}$  for this reaction.

.....

(ii) Hence state, with a reason, whether there will be more products or more reactants at equilibrium.

.....  
.....

(iii) Write the expression for  $K_c$  for this reaction, and state its units.

$K_c =$

units .....

An experiment was carried out using solutions of  $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}^{-}(\text{aq})$  of equal concentrations.  $100 \text{ cm}^3$  of each solution were mixed together, and allowed to reach equilibrium.

*For  
Examiner  
Use*

The concentrations at equilibrium of  $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}_2(\text{aq})$  were as follows.

$$[\text{Fe}^{3+}(\text{aq})] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}_2(\text{aq})] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

- (iv) Use these data, together with the equation given in (c), to calculate the concentrations of  $\text{Fe}^{2+}(\text{aq})$  and  $\text{I}^{-}(\text{aq})$  at equilibrium.

$$[\text{Fe}^{2+}(\text{aq})] = \dots\dots\dots \text{ mol dm}^{-3}$$

$$[\text{I}^{-}(\text{aq})] = \dots\dots\dots \text{ mol dm}^{-3}$$

- (v) Calculate the  $K_c$  for this reaction.

$$K_c = \dots\dots\dots [8]$$

[Total: 15]

**Q9.**



- (b) A buffer solution is to be made using  $1.00 \text{ mol dm}^{-3}$  ethanoic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , and  $1.00 \text{ mol dm}^{-3}$  sodium ethanoate,  $\text{CH}_3\text{CO}_2\text{Na}$ . Calculate to the nearest  $1 \text{ cm}^3$  the volumes of each solution that would be required to make  $100 \text{ cm}^3$  of a buffer solution with  $\text{pH} 5.50$ . Clearly show all steps in your working.  
 $K_a(\text{CH}_3\text{CO}_2\text{H}) = 1.79 \times 10^{-5} \text{ mol dm}^{-3}$

volume of  $1.00 \text{ mol dm}^{-3} \text{ CH}_3\text{CO}_2\text{H} = \dots\dots\dots \text{ cm}^3$

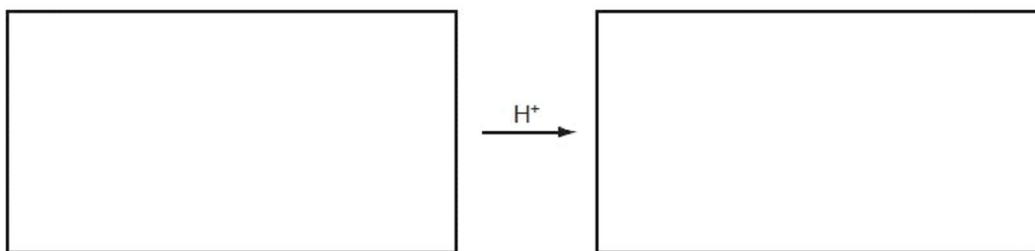
volume of  $1.00 \text{ mol dm}^{-3} \text{ CH}_3\text{CO}_2\text{Na} = \dots\dots\dots \text{ cm}^3$   
[4]

- (c) Write an equation to show the reaction of this buffer solution with each of the following.

(i) added  $\text{HCl}$  .....

(ii) added  $\text{NaOH}$  .....  
[2]

- (d) Choose **one** reaction in organic chemistry that is catalysed by an acid, and write the structural formulae of the reactants and products in the boxes below.



[3]

Q10.

2 (a) Methanoic acid,  $\text{HCO}_2\text{H}$ , is a weak acid, with  $K_a = 1.77 \times 10^{-4} \text{ mol dm}^{-3}$ .

(i) Write an expression for the  $K_a$  of methanoic acid.

.....

(ii) Use your expression to calculate the  $[\text{H}^+]$  in a  $0.0500 \text{ mol dm}^{-3}$  solution of methanoic acid.

.....

(iii) Calculate the percentage of  $\text{HCO}_2\text{H}$  molecules that are ionised in this solution.

(iv) Calculate the pH of this solution.

.....

[4]

- (b) Calculate the pH of a  $0.0500 \text{ mol dm}^{-3}$  solution of the strong acid  $\text{HCl}$ .

.....[1]

- (c) Both  $\text{HCO}_2\text{H}$  and  $\text{HCl}$  react with powdered magnesium metal, giving off hydrogen gas. For a fixed amount of magnesium, the rate equation for the reaction is as follows.

$$\text{rate} = k[\text{H}^+(\text{aq})]$$

- (i) Write an equation for the reaction between  $\text{HCO}_2\text{H}$  and  $\text{Mg}$ .

.....

When  $20.0 \text{ cm}^3$  of a  $0.0500 \text{ mol dm}^{-3}$  solution of either acid is reacted with an excess of powdered magnesium, the same volume of hydrogen is given off, but the methanoic acid solution reacts much more slowly than the hydrochloric acid.

- (ii) Calculate the volume of hydrogen given off.

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- (iii) Explain why the hydrogen is evolved more slowly from the methanoic acid solution.

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- (iv) Explain why, eventually, the methanoic acid solution produces just as much hydrogen as the hydrochloric acid solution.

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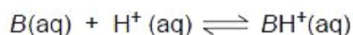
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Q11.

- 1 Sulphuric acid is a strong dibasic acid, which ionises in solution as follows.

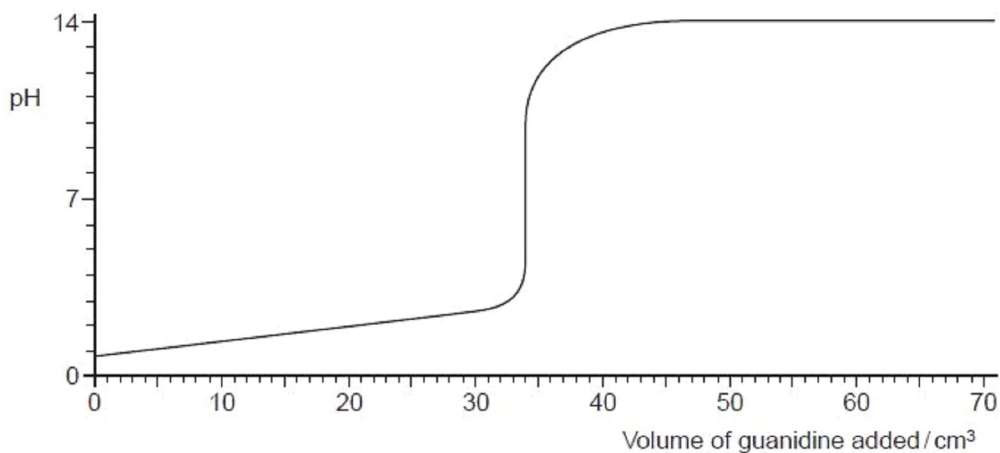


- (a) The organic base guanidine contains carbon, nitrogen and hydrogen. Its reaction with acids can be represented as follows.



where *B* represents the molecule of guanidine.

When a 25.0 cm<sup>3</sup> sample of dilute sulphuric acid was titrated against a solution of guanidine, the following titration curve was obtained.



Use this curve to answer the following questions.

- (i) Is guanidine a strong or a weak base? Explain your answer.

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 .....

- (ii) The pH at the start of the titration was 0.70. Calculate the [H<sup>+</sup>], and hence the concentration of sulphuric acid, at the start of the titration.

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(iii) Calculate the concentration of guanidine in the solution in mol dm<sup>-3</sup>.

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(iv) The guanidine solution contained 8.68 g of the base per dm<sup>3</sup>. Use your answer to (iii) calculate the  $M_r$  of guanidine.

..... [6]

(b) One of the major industrial uses of sulphuric acid is to convert phosphate rock (calcium fluorophosphate(V)) into 'superphosphate' for use as a fertiliser. The process can be represented by the following partially balanced equation.

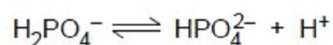


(i) Balance the above equation.

(ii) Use your balanced equation to calculate the mass of H<sub>2</sub>SO<sub>4</sub> required to manufacture 1.0 kg of superphosphate fertiliser.

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..... [4]

- (c) Solutions of hydrogenphosphates make useful buffers for biochemical experiments.



- (i) Explain what is meant by the term *buffer solution*.

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- (ii) Calculate the pH of a buffer solution that contains  $0.20 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$  and  $0.10 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4$ . [ $K_a(\text{H}_2\text{PO}_4^-) = 6.3 \times 10^{-8} \text{ mol dm}^{-3}$ ]

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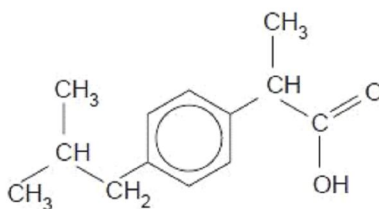
[3]

[Total: 13]

## Q12.

- 2 Ibuprofen is one of the most commonly used non-steroidal anti-inflammatory drugs, used to treat chronic arthritic pain caused by inflammation of the joints.

Use



ibuprofen

- (a) (i) Draw a circle around any chiral centre(s) in the above structure.

- (ii) Write down the molecular formula of ibuprofen.

.....

- (iii) Calculate the  $M_r$  of ibuprofen and use it to calculate how many grams are needed to make  $100 \text{ cm}^3$  of a  $0.15 \text{ mol dm}^{-3}$  solution.

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- (iv) Vigorous oxidation of ibuprofen produces a dibasic acid **A**. A solution containing 0.10 g of **A** required 12.0 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> NaOH for neutralisation.

Suggest a structure for **A**, showing your working.

..... [7]

- (b) The  $K_a$  value for ibuprofen is  $6.3 \times 10^{-6}$  mol dm<sup>-3</sup>.

(i) Write an expression for  $K_a$ .

.....

- (ii) Use the  $K_a$  value to calculate the pH of a 0.15 mol dm<sup>-3</sup> solution of ibuprofen.

.....

..... [3]

- (c) To avoid problems with digestive irritation over a long period of use, research is being carried out into ways of administering ibuprofen using skin patches. For this use the compound is dissolved in a hydrophilic gel which acts as a buffer.

Use

(i) What do you understand by the term *buffer*?

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.....

The buffer used in the pharmaceutical preparation is a solution containing Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. These salts contain the HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions respectively.

(ii) Write equations to show how this buffer reacts with

H<sup>+</sup> ions, .....

OH<sup>-</sup> ions. ....

- (iii) A buffer solution containing equal concentrations of the two sodium phosphate salts has a pH of 7.20.

Calculate the pH of a pharmaceutical preparation containing  $0.002 \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{HPO}_4$  and  $0.005 \text{ mol dm}^{-3}$  of  $\text{NaH}_2\text{PO}_4$ .

[5]

[Total: 15]

### Q13.

- 1 (a) Use the general formula of a carboxylic acid,  $\text{RCO}_2\text{H}$ , to write equations to explain the following terms.

(i)  $K_a$  .....

(ii)  $\text{p}K_a$  .....

[2]

- (b) The  $\text{p}K_a$  values of four carboxylic acids are listed in the table below.

acid	formula of acid	$\text{p}K_a$
1	$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	4.9
2	$\text{CH}_3\text{CHClCO}_2\text{H}$	2.8
3	$\text{CH}_3\text{CCl}_2\text{CO}_2\text{H}$	1.4
4	$\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$	4.1

- (i) Describe and explain the trend in acid strength shown by acids 1, 2 and 3.

.....

.....

.....

.....



(ii) Suggest an explanation for the difference in the  $pK_a$  values for acids 2 and 4.

.....  
.....

(iii) Calculate the pH of a  $0.010 \text{ mol dm}^{-3}$  solution of propanoic acid (acid 1).

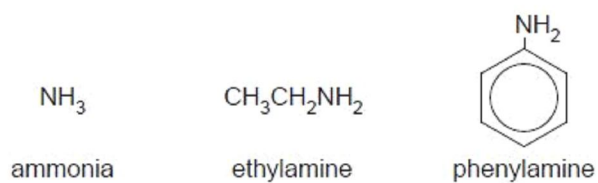
.....  
.....  
.....

[6]

### Q14.

2 (a) Describe and explain how the basicities of ammonia, ethylamine and phenylamine differ.

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U



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.....  
.....  
.....

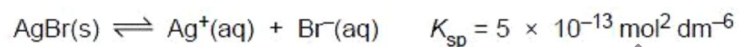
[3]

- (b) Describe how the use of aqueous silver nitrate and aqueous ammonia can distinguish between aqueous solutions containing chloride, bromide or iodide ions by filling in the following table.

halide	observation when $\text{AgNO}_3(\text{aq})$ is added	observation when dilute $\text{NH}_3(\text{aq})$ is added	observation when concentrated $\text{NH}_3(\text{aq})$ is added
chloride			
bromide			
iodide			

[3]

- (c) Silver bromide is sparingly soluble in water.



- (i) Calculate  $[\text{Ag}^+(\text{aq})]$  in a saturated aqueous solution of AgBr.

$$[\text{Ag}^+(\text{aq})] = \dots \text{ mol dm}^{-3}$$

- (ii) State and explain whether AgBr will be less or more soluble in  $0.1 \text{ mol dm}^{-3}$  KBr than it is in pure water.

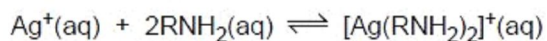
.....

.....

[2]

Fahad H. Ahmad

(d) Silver ions form complexes with ammonia and with amines.



Exar  
L

(i) Write an expression for the  $K_c$  for this reaction, and state its units.

$K_c =$  ..... units .....

$K_c$  has the numerical value of  $1.7 \times 10^7$  when  $R = \text{H}$ .

(ii) Using your expression for  $K_c$  calculate the  $[\text{NH}_3(\text{aq})]$  needed to change the  $[\text{Ag}^+(\text{aq})]$  in a  $0.10 \text{ mol dm}^{-3}$  solution of silver nitrate to the value that you calculated in (c)(i).

$[\text{NH}_3(\text{aq})] =$  .....  $\text{mol dm}^{-3}$

(iii) Explain whether you would expect the  $K_c$  for the reaction where  $R = \text{C}_2\text{H}_5$  to be greater or less than that for the reaction where  $R = \text{H}$ .

.....  
.....

[5]

[Total: 13]

Q15.

- 7 When an aqueous solution of compound **G**,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , is titrated with  $\text{HCl}(\text{aq})$ , two successive acid-base reactions take place.

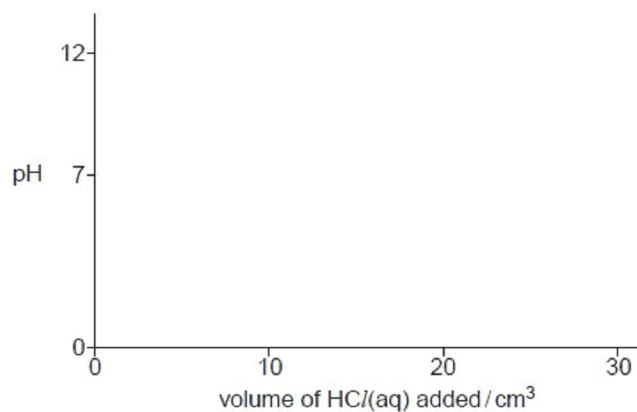
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- (a) Write equations for these two acid-base reactions.

.....

..... [2]

- (b) A  $0.10 \text{ mol dm}^{-3}$  solution of **G** has a pH of 11.3. When  $30 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$   $\text{HCl}$  is added to  $10 \text{ cm}^3$  of a  $0.10 \text{ mol dm}^{-3}$  solution of **G**, the final pH is 1.6. Using the following axes, sketch the pH changes that occur during this addition of  $\text{HCl}(\text{aq})$ .



[2]

[Total: 4]

Q16.

- 4 (a) (i) Write the equation for a reaction in which ethylamine,  $C_2H_5NH_2$ , acts as a Brønsted-Lowry base.

.....

- (ii) Ammonia, ethylamine and phenylamine,  $C_6H_5NH_2$ , are three nitrogen-containing bases.

Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

- (iii) Explain why you have placed the three compounds in this order.

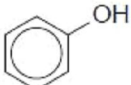
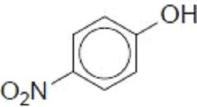
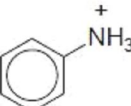
.....  
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[4]

- (b) (i) Write an equation for a reaction in which phenol,  $C_6H_5OH$ , acts as a Brønsted-Lowry acid.

.....

The  $pK_a$  values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

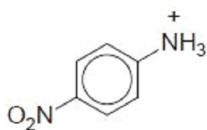
compound	$pK_a$
	10.0
	7.2
	4.6

- (ii) Suggest an explanation for the difference in the  $pK_a$  values of phenol and nitrophenol.

.....  
.....  
.....  
.....

- (iii) Using the information in the table opposite, predict which of the following  $pK_a$  values is the most likely for the 4-nitrophenylammonium ion.

For  
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Use



Place a tick (✓) in the box beside the value you have chosen.

$pK_a$	
1.0	
4.5	
7.0	
10.0	

- (iv) Explain your answer to part (iii).

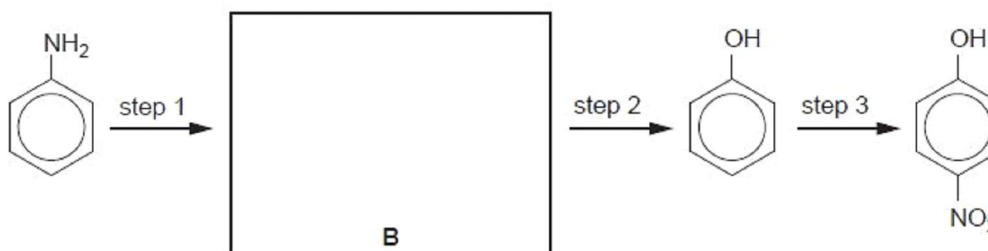
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.....

.....

[5]

- (c) Phenylamine can be converted to 4-nitrophenol by the following steps.



- (i) Suggest the identity of intermediate **B** by drawing its structure in the box above.
- (ii) Suggest reagents and conditions for the three steps in the above scheme.

	reagent(s)	conditions
step 1		
step 2		
step 3		

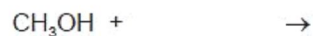
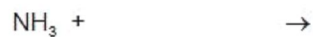
[5]

[Total: 14]

**Q17.**

- 3 (a) (i)** Using the symbol **HZ** to represent a Brønsted-Lowry acid, write equations which show the following substances acting as Brønsted-Lowry bases.

Ext



- (ii)** Using the symbol **B<sup>-</sup>** to represent a Brønsted-Lowry base, write equations which show the following substances acting as Brønsted-Lowry acids.



[4]

- (b)** State briefly what is meant by the following terms.

- (i)** reversible reaction

.....

- (ii)** dynamic equilibrium

.....

.....

[2]

- (c) (i)** Explain what is meant by a *buffer solution*.

.....

.....

.....

- (ii)** Explain how the working of a buffer solution relies on a reversible reaction involving a Brønsted-Lowry acid such as **HZ** and a Brønsted-Lowry base such as **Z<sup>-</sup>**.

.....

.....

.....

.....

[4]

(d) Propanoic acid,  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ , is a weak acid with  $K_a = 1.34 \times 10^{-5} \text{ mol dm}^{-3}$ .

F  
Exam  
U

(i) Calculate the pH of a  $0.500 \text{ mol dm}^{-3}$  solution of propanoic acid.

Buffer solution **F** was prepared by adding  $0.0300 \text{ mol}$  of sodium hydroxide to  $100 \text{ cm}^3$  of a  $0.500 \text{ mol dm}^{-3}$  solution of propanoic acid.

(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

.....

(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.

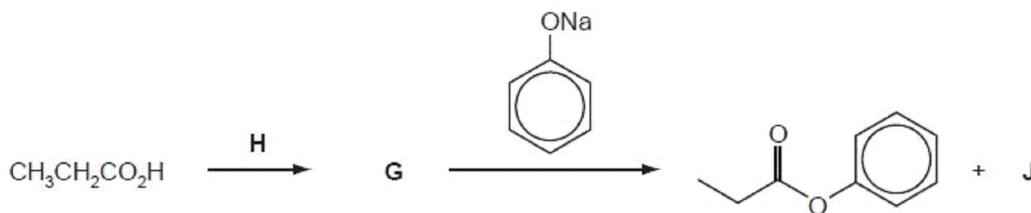
[propanoic acid] = .....  $\text{mol dm}^{-3}$

[sodium propanoate] = .....  $\text{mol dm}^{-3}$

(iv) Calculate the pH of buffer solution **F**.

pH = .....  
[6]

(e) Phenyl propanoate cannot be made directly from propanoic acid and phenol. Suggest the identities of the intermediate **G**, the reagent **H** and the by-product **J** in the following reaction scheme.



**G** is .....

**H** is .....

**J** is .....

[2]

[Total: 18]



**Q18.**

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**8** In a world with a rapidly increasing population, access to clean drinking water is critical. For many countries, groundwater sources, rather than stored rainwater or river-water, are vital. *Groundwater* is water that exists in the pore spaces and fractures in rock and sediment beneath the Earth's surface. The World Health Organisation (WHO) provides maximum recommended concentrations for different ions present in drinking water.

**(a)** The geological nature of the soil determines the chemical composition of the groundwater. The table shows some ions which may contaminate groundwater.

ion present	WHO maximum permitted concentration / mg dm <sup>-3</sup>
Ba <sup>2+</sup>	0.30
Cl <sup>-</sup>	250.00
NO <sub>3</sub> <sup>-</sup>	50.00
Pb <sup>2+</sup>	0.01
Na <sup>+</sup>	20.00
SO <sub>4</sub> <sup>2-</sup>	500.00

**(i)** Nitrate, NO<sub>3</sub><sup>-</sup>, ions are difficult to remove from groundwater. What is the reason for this?

.....

**(ii)** State which ions in the table above are likely to be removed from the water by treatment with powdered limestone, CaCO<sub>3</sub>, giving reasons for each of your answers.

.....  
.....  
.....

[4]

**(b)** Nitrates and phosphates can enter water courses such as rivers or streams as a result of human activity. Both of these ions are nutrients for algae.

**(i)** What is the origin of these nitrates?

.....

(ii) Suggest an origin for the phosphates found in water courses.

.....

(iii) What effect do nitrates and phosphates have on water courses?

.....

.....

[3]

(c) Acid rain can have a major impact on natural waters, particularly lakes. In recent years there has been a worldwide effort to reduce the amount of acid rain produced.

(i) Write equations to show the production of acid rain from sulfur dioxide,  $\text{SO}_2$ .

.....

.....

(ii) The use of fossil fuels is one major source of sulfur dioxide.  
Name another major industrial source.

.....

[2]

[Total: 9]

Q19.

Fahad H. Ahmad

- 2 (a) State **two** assumptions of the kinetic theory of gases, as applied to ideal gases.

Ex

.....  
.....  
[2]

- (b) (i) State the conditions of temperature and pressure under which real gases behave **least** like an ideal gas.

.....

- (ii) Explain why real gases do **not** behave ideally under these conditions.

.....

.....  
[2]

- (c) Gaseous aluminium chloride is dimeric at low temperatures, but the dimer dissociates on heating.

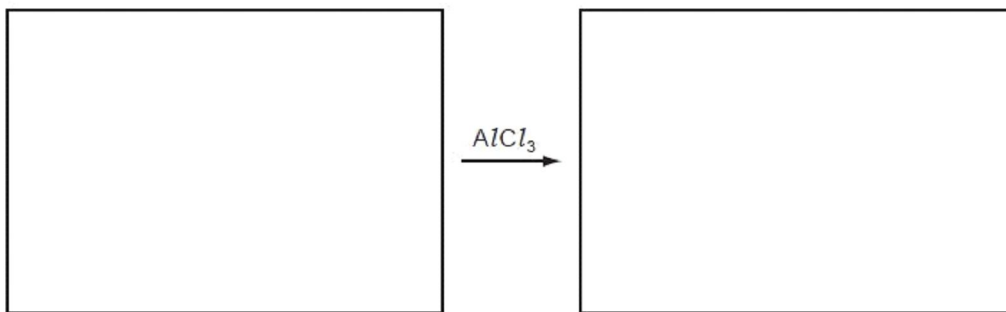


- (i) State whether this dissociation is endothermic or exothermic. Explain your answer.

.....

.....

- (ii) Choose **one** reaction in organic chemistry that is catalysed by  $AlCl_3$ , and write the structural formulae of the reactants and products in the boxes below.



[3]

[Total: 7]







**Q1.**

- 2 (a) (i)  $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$  [1] units:  $\text{mol}^2\text{dm}^{-6}$  [1] ecf
- (ii)  $[\text{Ba}^{2+}] = \sqrt{(1.3 \times 10^{-10})} = 1.14 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$  [1]
- (iii)  $\text{BaCO}_3$  can react with/dissolve in the acid/HCl in the stomach [1]  
(or unbalanced equation showing, e.g.  $\text{BaCO}_3 + \text{HCl} \rightarrow$ )
- 4**
- (b) (i)  $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$  [1] units:  $\text{mol}^3\text{dm}^{-9}$  [1] ecf
- (ii) calling  $[\text{Mg}^{2+}] = x$ , then  $K_{sp} = x(2x)^2 = 4x^3 \Rightarrow x = \sqrt[3]{(K_{sp}/4)}$  [1]  
 $\therefore [\text{Mg}^{2+}] = \sqrt[3]{(2 \times 10^{-11}/4)} = 1.7 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$  [1]
- allow ecf for use of  $\sqrt[3]{}$
- (iii) % left =  $100 \times (1.7 \times 10^{-4})/(0.054) = 0.32\%$   
 $\therefore$  % extracted = **99.7 (%)** [1]
- 5**
- (c) (i)  $\Delta H_r = \Delta H_f^\circ(\text{Mg}^{2+}) + 2\Delta H_f^\circ(\text{Cl}^-) - \Delta H_f^\circ(\text{MgCl}_2)$   
 $= -467 + 2(-167) - (-641)$   
 $= -160 \text{ (kJ mol}^{-1}\text{)}$  [1]
- (ii) highly exothermic enthalpy change of solution  
or  $\Delta H_{sol}$  is very negative [1]
- 2**
- (d) mention of hydration enthalpy and lattice enthalpy [1]  
hydration enthalpy decreases more than does lattice enthalpy  
or  
enthalpy change of solution or  $\Delta H_{sol}$  becomes  
less negative/more positive [1]
- 2**

**Total: 13, max 12**

**Q2.**

5 (a)  $K_a = \frac{[\text{RCO}_2^-][\text{H}^+]}{[\text{RCO}_2\text{H}]}$  [1]

Part (a): [1]

(b) (i) The more chlorine atoms in the molecule, the stronger the acid, [1]

due to the electron-withdrawing (inductive) effect of Cl... [1]

**either**...stabilising the anion, **or** spreading (-) charge more,  
**or**...weakening the O-H bond in the acid, **or**...increasing ionisation,  
**or**...facilitates  $\text{H}^+$  donation

**or**...causing the equilibrium  $\text{RCO}_2\text{H} = \text{RCO}_2^- + \text{H}^+$  to lie further to the right.

Mark is conditional on reference to the effect of presence of chlorine. [1]

(ii)  $[\text{H}^+] = \sqrt{0.1 \times 1.4 \times 10^{-3}} = 0.0118 \text{ (mol dm}^{-3}\text{)}$  allow 0.012 [1]

$\therefore \text{pH} = -\log_{10}(0.0118) = 1.93$  Allow 1.9 or 1.92 e.c.f. [1]

(iii)  $\text{p}K_a = -\log_{10}(5.5 \times 10^{-2}) = 1.26$  Allow 1.3 [1]

Part (b): [6]

**Q3.**

2 (a) (i)  $K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$  [1]

units are:  $\text{mol}^2\text{dm}^{-6}$  ecf [1]

(ii)  $[\text{CaSO}_4] = \sqrt{K_{sp}} = 5.5 \times 10^{-3} \text{ (5.477} \times 10^{-3}\text{)} \text{ (mol dm}^{-3}\text{)}$  ecf [1]

(iii)  $n(\text{CaSO}_4) \text{ in } 100 \text{ dm}^3 = 5.5 \times 10^{-3} \times 100 = 0.55 \text{ moles}$  ecf from (ii) [1]

$M_r(\text{CaSO}_4) = 136.1$

Thus  $\text{mass}(\text{CaSO}_4) = 0.55 \times 136.1 = 74.8 \text{ g}$  (0.55  $\times M_r$ ) [1]  
(if the accurate  $[\text{CaSO}_4]$  is held throughout the calculation, ans = 74.5g)

[5]

(b) (i) down the group: the  $\Delta H_{\text{dissolution}}$  becomes more endothermic;  
**both** lattice energy **and**  $\Delta H_{\text{hydration}}$  become less (exothermic);  
due to **ionic** radius (of  $\text{M}^{2+}$ ) increasing;  
but  $\Delta H_{\text{hydration}}$  changes more than lattice energy *any three points* [3]

(ii)  $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (9 \times 10^{-6})^2 = 8.1 \times 10^{-11}$  **NO** ecf [1]

[4]

(c) (i) LE is the energy change when **1 mole** of (ionic) solid [1]

is formed from its **gaseous ions** [1]

(ii)  $\text{LE}(\text{BaSO}_4) < \text{LE}(\text{MgSO}_4)$ , due to larger radius of  $\text{Ba}^{2+}$  both points [1]

[3]

[Total: 12]



## Q4.

- 2 (a) (i)  $\Delta H = 4 \times 278 - 244 - 2 \times 496$  [1]  
 $= -124 \text{ (kJ mol}^{-1}\text{)}$  [1]  
 (correct ans [2])
- (ii) shape is bent/V-shaped/non-linear (or diagram) [1]  
 due to (one) lone pair and/or (1) odd/unpaired electron (or shown on diag) [1]  
 (assume electrons are on chlorine unless explicitly stated otherwise, in which case award no mark)
- (iii)  $3\text{KClO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{KClO}_4 + \text{H}_2\text{O} + 2\text{ClO}_2$  [1] [5]
- (b) (i) coal-fired power stations; fuel in cars; car exhausts/gas emissions; other named use of a fossil fuel; contact process; cement manufacture; brick manufacture; roasting of sulphide ores; burning tyres (any 2) [1]  
 (NOT volcanoes etc; NOT burning of natural gas)  
 (no marks for only 1 correct source)
- (ii) causes acid rain [1]  
 which lower pH of lakes; leaches aluminium from soils; kills fish/plants/rainforests; dissolves/corrodes/damages buildings (any 1) [1]  
 (NOT asthma etc – since this is not environmental) [3]
- (c) (i)  $\text{CO}_2$ : simple + molecular/covalent or weak intermolecular forces  
 $\text{SiO}_2$ : giant/macro + molecular/covalent  
 $\text{SnO}_2$ : ionic/electrovalent (ignore "giant") (all 3 correct) [2]  
 (2 correct = [1], 1 correct = [0])
- (ii)  $\text{SnO}_2$  is stable,  $\text{PbO}_2$  is not or  $\text{SnO}_2$  is the more stable [1]  
 $\text{PbO}_2 \longrightarrow \text{PbO} + \frac{1}{2} \text{O}_2$  [1]
- (iii)  $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$  [1]  
 $K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{O}][\text{CO}_2]}$  or  $[\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$  ecf [1]
- (iv)  $\text{HCO}_3^- + \text{H}^+ \longrightarrow \text{H}_2\text{CO}_3$  or  $\text{H}_2\text{O} + \text{CO}_2$  (or equation with  $\text{H}_3\text{O}^+$ ) [1]  
 $\text{HCO}_3^- + \text{OH}^- \longrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$  (NB NOT  $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow$ ) [1]
- (words can substitute for one of the equations but not both. If two correct word descriptions are given, in the absence of at least one correct equation, award [1] mark only) [8]

[Total: 16 max 15]

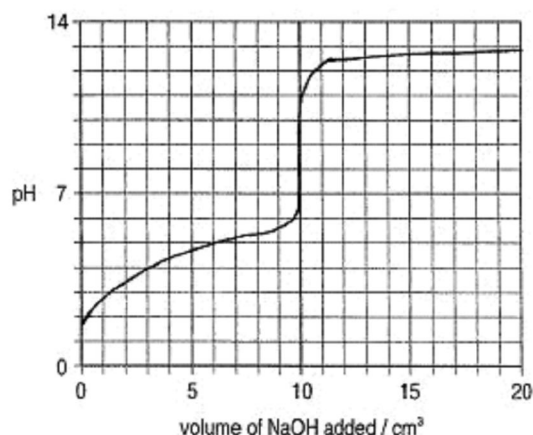
## Q5.

- 1 (a) acids are proton/ $H^+$  donors [1]  
 bases are proton/ $H^+$  acceptors [1] [2]

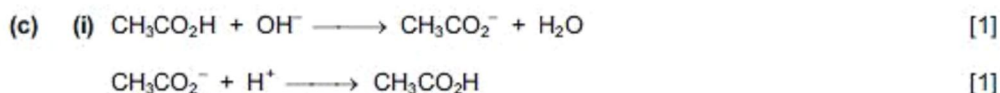
- (b) (i) more *Cl* atoms produce a **stronger acid** or the larger the  $K_a$  the **stronger the acid** [1]  
 (NOT just "the more *Cl* atoms, the larger the  $K_a$ " – must refer to acid strength) [1]  
 because the anion/ $RCO_2^-$  is more stable or the O-H bond is weaker/polarised [1]  
 due to the electronegativity/electron-withdrawing effect of *Cl* [1]

- (ii)  $[H^+] = \sqrt{K_a \cdot c} = 0.0114 \text{ (mol dm}^{-3}\text{)}$  [1]  
 pH = **1.94** (allow 1.9) ecf from  $[H^+]$  [1]  
 (correct answer = [2])

(iii)



- start at pH = 1.94 (ecf from (ii) and goes up > 2 pH units before steep portion) [1]  
 steep portion (over at least 3 pH units) at  $V = 10 \text{ cm}^3$  [1]  
 flattens off at pH 12–13 [1] [8]



- (ii)  $pK_a = -\log_{10}(1.7 \times 10^{-5}) = 4.77$  or  $[H^+] = 8.5 \times 10^{-6} \text{ (mol dm}^{-3}\text{)}$  [1]  
 $pH = pK_a + \log_{10}(0.2/0.1) = 5.07$  (allow 5.1) [1]  
 (correct answer = [2]) [4]

[Total: 14]

Q6.

- 2 (a) (i) One that can go in either direction. [1]
- (ii) both forward & reverse reactions are going on at the same time, but the concentrations of all species do not change (owtte) or rate of forward = rate of backward reaction [1]
- (b) (i)  $K_c = \frac{[H^+][OH^-]}{[H_2O]}$  [1]
- (ii)  $K_w = [H^+][OH^-]$  [1]  
 rearrangement of equation in (i) gives  $K_c[H_2O] = [H^+][OH^-]$  &  $K_w = K_c[H_2O]$  (owtte) or the  $[H_2O]$  is contained within  $K_w$  [1]
- (iii)  $K_w$  will be higher in hot water **because** reaction is endothermic [1]
- (c) (i)  $[OH^-] = 5 \times 10^{-2}$ ;  $[H^+] = (1 \times 10^{-14}) / 5 \times 10^{-2} = 2 \times 10^{-13}$  [1]  
 $pH = -\log_{10}[H^+] = 12.7$  (correct ans = [2]) ecf [1]
- (ii)  $[NH_4^+] = [OH^-] (= x)$  [1]  
 $x^2 = 1.8 \times 10^{-6} \times 0.05 \Rightarrow x (= [OH^-]) = 9.49 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$  (correct ans = [2]) [1]
- (iii)  $[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 9.49 \times 10^{-4} = 1.05 \times 10^{-11} \text{ (mol dm}^{-3}\text{)}$  ecf [1]
- (iv)  $pH = 11.0$  ecf [1]

[Total: 12 max 11]

## Q7.

- 1 (a)  $[H^+] = \sqrt{(0.05 \times 5.6 \times 10^{-4})} = 5.29 \times 10^{-3} \text{ mol dm}^{-3}$  [1]  
 $pH = -\log_{10}(5.29 \times 10^{-3}) = 2.3$  [1]  
 [2]
- (b) (i) (Brønsted-Lowry) acid-base/proton transfer/neutralisation/exothermic/reversible/equilibrium [1]
- (ii)
- $$\begin{array}{c} \text{H} \text{ : } \text{N} \text{ : } \text{H} \\ \text{..} \\ \text{..} \\ \text{H} \end{array}$$

[1]

$$\text{H} \text{ : } \text{F} \text{ :}$$

[1]

$$\left[ \begin{array}{c} \text{H} \text{ : } \text{N} \text{ : } \text{H} \\ \text{..} \\ \text{..} \\ \text{H} \end{array} \right]^{\oplus} \left[ \begin{array}{c} \text{F} \text{ :} \\ \text{..} \\ \text{..} \end{array} \right]^{\ominus}$$

[1]

3 x [1]
- (iii) (in  $NH_4F$ ):  
 covalent: between N & H [1]  
 dative: between N & H [1]  
 ionic: between  $NH_4^+$  &  $F^-$  or  $N^+$  &  $F^-$  or ammonium and fluoride (i.e. in words) or between (oppositely charge) ions [1]
- (iv) (**reverse** reaction, remember)  
 high temperature, because reverse reaction is endothermic [1]  
 low pressure, because reverse reaction causes an increase in no. of gaseous molecules or an increase in partial pressure/volume. [1]  
 [9]

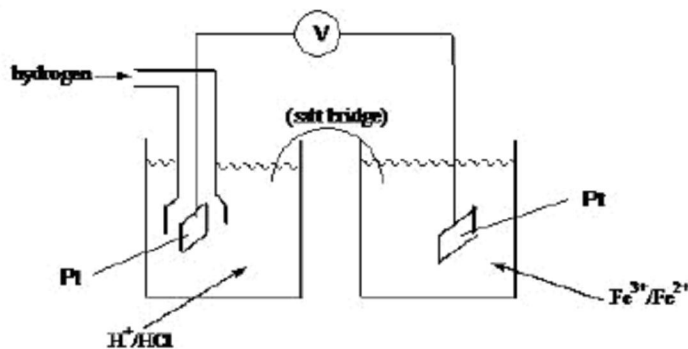
- (c) (i)  $4\text{NH}_3 + \text{CuS} + 2\text{O}_2 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  [1]
- (ii) deep/dark/royal blue or purple [NOT violet] [1]
- (iii) deep blue colour would change to light blue [NOT intensity of colour decreases] [1]  
 $\Rightarrow$  hexaquocopper(II) ion or  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Cu}(\text{H}_2\text{O})_n(\text{NH}_3)_{6-n}]^{2+}$ , where a = 4 or 6  
 or ligand exchange (of  $\text{NH}_3$ ) by  $\text{H}_2\text{O}$  [1]  
**[4]**
- (d) ligand exchange/substitution/displacement/replacement [IN WORDS] [1]  
 (use of named ligands are OK instead of 'ligand'. e.g. "water is displaced by chloride")
- formula of anion (see below for possibilities) [1]  
 balanced equation. e.g.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + n\text{Cl}^- \rightarrow [\text{Cu}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{2-n} + n\text{H}_2\text{O}$  [1]
- (Allow  $n=1$  up to  $n=6$ . Also allow  $[\text{CuCl}_n]^{2-n}$  as product. Examples from many possible are:  
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{Cl}^- \rightarrow [\text{Cu}(\text{H}_2\text{O})_4\text{Cl}_2] + 2\text{H}_2\text{O}$   
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$   
 equation could include  $\text{HCl}$  on the LHS, for example:  
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{HCl} \rightarrow \text{H}_2\text{CuCl}_4 + 2\text{H}^+ + 6\text{H}_2\text{O}$  or  $\rightarrow \text{CuCl}_4^{2-} + 4\text{H}^+ + 6\text{H}_2\text{O}$  **[3]**

**[Total: 18 max 17]**

**Q8.**

- 1 (a) The potential of an **electrode** compared to that of a standard hydrogen electrode (SHE)  
 or  
 the EMF of a **cell** composed of the test electrode and the SHE [1]
- all measurement concentrations of  $1 \text{ mol dm}^{-3}$  and  $298\text{K}$  /  $1 \text{ atm}$  pressure [1]  
**[2]**

(b)



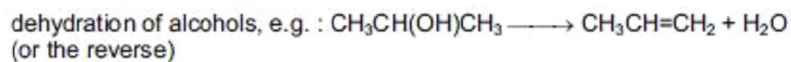
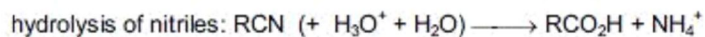
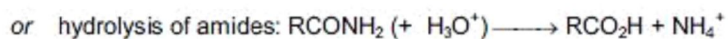
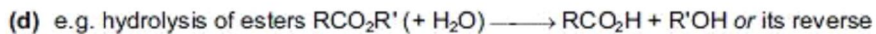
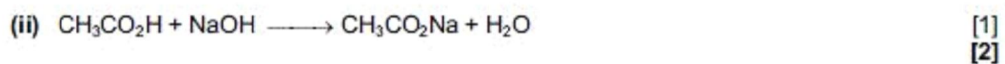
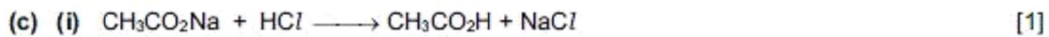
- $\text{H}_2$  and good delivery system [1]  
 $\text{Fe}^{2+}/\text{Fe}^{3+}$  solution labelled [1]  
 platinum electrodes (both) [1]  
 salt bridge and voltmeter [1]  
 $\text{H}^+$  or  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  [1]  
 (acid is not sufficient)  
**[5]**

- (c) (i)  $E^{\ominus} = 0.77 - 0.54 = 0.23$  (V) [1]
- (ii) Since  $E^{\ominus}$  is positive/  $E^{\ominus} > 0$
- So more products / the equilibrium will be over to the right / forward reaction is favoured  
ecf from (c)(i) [1]
- (iii)  $K_c = [\text{Fe}^{2+}]^2[\text{I}_2]/[\text{Fe}^{3+}]^2[\text{I}^-]^2$  [1]
- units are  $\text{mol}^{-1} \text{dm}^3$  ecf on expression [1]
- (iv) ( $[\text{Fe}^{2+}]$  must always be twice  $[\text{I}_2]$ , so  $[\text{Fe}^{2+}] = 0.02$  ( $\text{mol dm}^{-3}$ ) [1]
- ( $[\text{I}^-]$  must always be equal to  $[\text{Fe}^{3+}]$ , so  $[\text{I}^-] = 2 \times 10^{-4}$  ( $\text{mol dm}^{-3}$ ) [1]
- (v)  $K_c = \{(0.02)^2 \times 0.01\} / \{(2 \times 10^{-4})^2 \times (2 \times 10^{-4})^2\}$  correct expression [1]  
(allow ecf from incorrect expression in (c)(iii))  
(allow ecf from (c)(iv))  
 $= (4 \times 10^{-6}) / (1.6 \times 10^{-15}) = 2.5 \times 10^9$  ( $\text{mol}^{-1} \text{dm}^3$ ) [1]

[Total: 15]

## Q9.

- (b) there are two ways of calculating the ratio:  
 $\text{p}K_a = -\log_{10}(K_a) = -\log_{10}(1.79 \times 10^{-5}) = 4.747$  (4.75) or  $[\text{H}^+] = 10^{-5.5} = 3.16 \times 10^{-6}$  [1]
- $\log_{10}([\text{B}] / [\text{A}]) = \text{pH} - \text{p}K_a = 0.753$  (0.75) or  $[\text{salt}] / [\text{acid}] = K_a / [\text{H}^+]$  [1]
- $\therefore [\text{B}] / [\text{A}] = 10^{0.753} = 5.66$   
 or  $= 1.79 \times 10^{-5} / 3.16 \times 10^{-6} = 5.66$   
 (or  $[\text{A}] / [\text{B}] = 0.177$ ) [1]
- (correct ratio = [3] marks)
- since  $\text{B} + \text{A} = 100$ ,  $\therefore (100 - \text{A}) / \text{A} = 5.66 \Rightarrow$   $\frac{\text{vol of acid} = 15 \text{ cm}^3}{\text{vol of salt} = 85 \text{ cm}^3}$  [1]



[3]

Q10.

Fahad H. Ahmad

- 2 (a) (i)  $K_a = [\text{HCO}_2^-][\text{H}^+]/\text{HCO}_2\text{H}$  (1)
- (ii)  $\sqrt{K_a[\text{HCO}_2\text{H}]} = \sqrt{1.77 \times 10^{-4} \times 0.05} = 2.97 \times 10^{-3}$  (1)  
(3.0 x 10<sup>-3</sup>)
- (iii)  $100 \times 2.97 \times 10^{-3} / 0.05 = 5.94\%$  (6%) (1)
- (iv)  $\text{pH} = -\log_{10}(2.97 \times 10^{-3}) = 2.5(2)$  (1) [4]
- (b)  $\text{pH} = -\log_{10}(0.05) = 1.30$  (1) [1]

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- (c) (i)  $2\text{HCO}_2\text{H} + \text{Mg} \rightarrow (\text{HCO}_2)_2\text{Mg} + \text{H}_2$  (1)  
(or  $2\text{H}^+ + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{H}_2$ )
- (ii) moles of  $\text{H}^+$  =  $0.05 \times 20/1000 = 1 \times 10^{-3}$  (1)  
moles of  $\text{H}_2 = 1 \times 10^{-3}/2 = 0.5 \times 10^{-3}$
- volume of  $\text{H}_2 = 0.5 \times 10^{-3} \times 24,000 = 12 \text{ cm}^3$  (1)  
(or  $0.5 \times 10^{-3} \times 22400 = 12 \text{ cm}^3$ )
- (iii) (rate  $\propto [\text{H}^+]$ ) lower  $[\text{H}^+]$  in methanoic acid or  $\text{HCO}_2\text{H}$  dissociates slowly/partially (1)
- (iv) the equilibrium ( $\text{HCO}_2\text{H} \rightleftharpoons \text{HCO}_2^- + \text{H}^+$ ) continually shifts to the right as  $\text{H}^+$  is used up (1) [5]
- Total: 10**

Q11.

- 1 (a) (i) strong, because final pH is about 14 [1]
- (ii)  $(\text{pH} = 0.70) \Rightarrow [\text{H}^+] = 10^{-0.7} = 0.20 \text{ (mol dm}^{-3}\text{)}$  [1]  
 $\therefore [\text{H}_2\text{SO}_4] = (0.10 \text{ mol dm}^{-3})$  ecf [1]
- (iii) (end point is at  $34.0 \text{ cm}^3 (\pm 0.5 \text{ cm}^3)$ , so)  
 amount of  $\text{H}^+$  used =  $0.2 \times 25/1000 = 0.0050 \text{ mol}$  ecf from (ii) [1]  
 moles of guanidine = moles of  $\text{H}^+$  =  $0.0050 \text{ mol}$   
 [guanidine] =  $0.005 \times 1000/34.0 = 0.147 \text{ (mol dm}^{-3}\text{)}$  [1]  
 allow range:  $0.145 - 0.149$  ecf in 0.005 or 34.0
- (iv)  $M_r = 8.68/0.147 = 59$  (allow range 58 – 60) ecf from (iii) [1] 6
- (b) (i)  $\longrightarrow 7 \text{ CaSO}_4 + 3 \text{ Ca(H}_2\text{PO}_4)_2 + 2 \text{ HF}$  [1]
- (ii)  $M_r$  values:  $\text{Ca(H}_2\text{PO}_4)_2 = 234.1$ ,  $\text{H}_2\text{SO}_4 = 98.0$  [1]  
 $234.1 \times 3 = 702.3$   $98 \times 7 = 686$  both [1]  
 ecf from ratios in equation, and from  $M_r$  values  
 $\therefore$  mass of  $\text{H}_2\text{SO}_4$  needed =  $1.0 \times 686/702.3 = 0.98 \text{ kg}$  [1]  
 (correct answer = [3] marks. accurate value is: 0.977 kg.  
 Allow ecf from incorrect  $M_r$  or incorrect multipliers) 4
- (c) (i) A solution that **resists** changes in pH [NOT: results in **no** pH change] [1]  
 when **small amounts** of  $\text{H}^+$  or  $\text{OH}^-$  are added [1]
- (ii)  $\text{pH} = -\log_{10}(6.3 \times 10^{-8}) + \log_{10}(0.1/0.2) = 6.9$  [1]  
 or  $[\text{H}^+] = (6.3 \times 10^{-8}) \times 0.2/0.1 = 1.26 \times 10^{-7}$   
 $\therefore \text{pH} = -\log_{10}(1.26 \times 10^{-7}) = 6.9$  3

**Total 13**

**Q12.**



- 2 (a) (i) [one chiral centre only] (1)
- (ii)  $C_{13}H_{18}O_2$  (1)
- (iii)  $M_r = 206$  ecf (1)
- mass =  $0.15 \times (100/1000) \times 206 = 3.1$  g ecf (1)  
(correct ans = (2) marks)
- (iv)  $n(\text{NaOH}) = 0.1 \times 12/100 = 1.2 \times 10^{-3}$  moles (1)
- $n(\text{A}) = 0.6 \times 10^{-3}$ , so  $M_r = 0.1/(0.6 \times 10^{-3}) = 167$  (allow 166-170) (1)  
(correct ans = (2) marks)
- This fits with  $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$  (which has  $M_r = 166$ ) (1) [7]
- (b) (i)  $(K_a =) [\text{H}^+][\text{A}^-]/[\text{HA}]$  (1)
- (ii)  $[\text{H}^+] = \sqrt{K_a \cdot c} = \sqrt{6.3 \times 10^{-6} \times 0.15} = 9.72 \times 10^{-4}$  (1)
- pH = 3.0 (1)  
(correct ans = (2) marks) [3]
- (c) (i) one that **resists/control/maintains** changes in pH (**NOT no** change in pH) (1)
- when **small amounts** of acid/ $\text{H}^+$  (or base/ $\text{OH}^-$ ) are added. (1)
- (ii)  $\text{HPO}_4^{2-} + \text{H}^+ \longrightarrow \text{H}_2\text{PO}_4^-$  (1)  
 $\text{H}_2\text{PO}_4^- + \text{OH}^- \longrightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$  (1)
- (iii) pH =  $\text{p}K_a + \log([\text{base}]/[\text{acid}])$   
=  $7.2 + \log(.002/.005) = 6.8$  (2)  
(correct ans = (2) marks: deduct (1) for each error,  
e.g. if ratio is upside down, hence pH = 7.6, answer is worth (1)) [6]
- [Total: 16 max 15]

### Q13.

- 1 (a) (i)  $K_a = [\text{H}^+][\text{RCO}_2^-]/[\text{RCO}_2\text{H}]$  [1]
- (ii)  $\text{p}K_a = -\log_{10}K_a$  or  $-\log K_a$  or  $\log [\text{H}^+]^2/[\text{RCO}_2\text{H}]$  NOT ln; [1]  
[2]
- (b) (i) acid strength increases from no. 1 to no. 3 or down the table or as Cls increase [1]  
due to the electron-withdrawing effect/electronegativity of chlorine (atoms) [1]  
stabilising the anion or weakening the O-H bond NOT  $\text{H}^+$  more available [1]
- (ii) chlorine atom is further away (from O-H) in no. 4, so has less influence [1]
- (iii) either: pH =  $\frac{1}{2}(\text{p}K_a - \log_{10}[\text{acid}])$  or  $K_a = 10^{-\text{p}K_a} = 1.259 \times 10^{-3}$  [1]  
=  $\frac{1}{2}(4.9 + 2)$   $[\text{H}^+] = \sqrt{(K_a \cdot c)} = 3.55 \times 10^{-4}$  [1]  
= 3.4 (allow 3.5) pH = 3.4 ecf [1]  
([1] for correct expression & values; [1] for correct working) [6]

Q14.

- 2 (a) ethylamine > NH<sub>3</sub>, but phenylamine < NH<sub>3</sub> [1]

in ethylamine, the alkyl group donates electrons to the N, making lone pair more available [1]

in phenylamine, the lone pair is delocalised over the ring, so is less available [1]

[3]

(b)

halide	observation when AgNO <sub>3</sub> (aq) is added	observation when dilute NH <sub>3</sub> (aq) is added	observation when concentrated NH <sub>3</sub> (aq) is added
chloride	<b>white ppt</b>	<b>dissolves</b>	<b>dissolves</b>
bromide	<b>cream ppt</b>	<b>no reaction / slightly dissolves</b>	<b>dissolves</b>
iodide	<b>(pale) yellow ppt</b>	<b>no reaction</b>	<b>no reaction</b>

[1]

[1]

[1]

[3]

- (c) (i)  $[Ag^+(aq)] = \sqrt{K_{sp}} = \sqrt{(5 \times 10^{-13})} = 7.1 (7.07) \times 10^{-7} \text{ mol dm}^{-3}$  [1]

- (ii) AgBr will be **less soluble** in KBr, due to common ion effect or equilibrium is shifted to the left / or by Le Chatelier's principle [1]

[2]

- (d) (i)  $K_c = \frac{[Ag(RNH_2)_2^+]}{[Ag^+][RNH_2]^2}$  [1]  
units are mol<sup>-2</sup> dm<sup>6</sup> [1]

- (ii) assume that most of the Ag<sup>+</sup>(aq) has gone to the complex, then

$$\begin{aligned} [Ag^+(aq)] &= 7.1 \times 10^{-7} \\ [Ag(NH_3)_2^+] &= 0.1 \end{aligned}$$

$$\text{and } [NH_3] = \sqrt{\frac{[Ag(NH_3)_2^+]}{K_c[Ag^+]}} = \sqrt{\frac{0.1}{(1.7 \times 10^7 \times 7.1 \times 10^{-7})}} = 0.091 \text{ mol dm}^{-3} \quad [1]$$

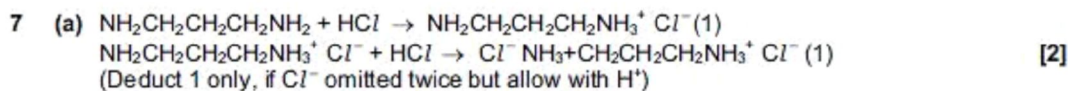
[1]

- (iii) When R = C<sub>2</sub>H<sub>5</sub>, K<sub>c</sub> is likely to be greater, since the ethyl group will cause the lone pair on N to be more available / nucleophilic / increases basicity [1]

[5]

[Total: 13]

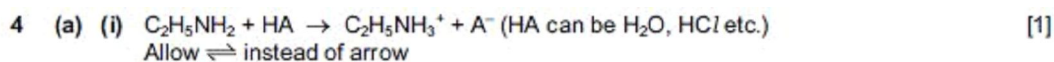
Q15.



(b) starts at 11.3 and finished as 1.6 (1)  
 steep portions at 10  $\text{cm}^3$  and 20  $\text{cm}^3$  volume added (1) [2]

[Total: 4]

## Q16.



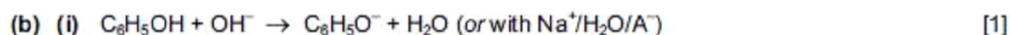
(ii)

most basic		least basic
<b>ethylamine</b>	<b>ammonia</b>	<b>phenylamine</b>

[1]

(iii) ethylamine >  $\text{NH}_3$  due to electron-donating ethyl/alkyl group [1]  
 phenylamine <  $\text{NH}_3$  due to delocalisation of lone pair over ring [1]

[4]



(ii) pKa of nitrophenol is smaller/ $K_a$  is larger because it's a stronger acid/dissociates more than phenol [1]  
 stronger because the anionic charge is spread out moreover the  $\text{NO}_2$  group or  $\text{NO}_2$  is electron-withdrawing [1]

(iii) pKa = 1.0 [1]

(iv) Nitro group increases acidity / electron-withdrawing groups increase acidity [1]  
 [5]



(ii)

reaction	reagent(s)	conditions
Step 1	<b><math>\text{NaNO}_2 + \text{HCl}</math> or <math>\text{HNO}_2</math></b> [1]	<b><math>\text{T} &lt; 10^\circ\text{C}</math></b> [1]
Step 2	<b><math>\text{H}_2\text{O} / \text{aq}</math></b>	<b>heat/boil/<math>\text{T} &gt; 10^\circ</math></b> (both) [1]
Step 3	<b><math>\text{HNO}_3</math> NB <math>\text{HNO}_3(\text{aq})</math> OK for both</b>	<b>dilute</b> (both) [1]

[4]

[5]

## Q17.

- 3 (a) (i)  $\text{NH}_3 + \text{HZ} \longrightarrow \text{NH}_4^+ + \text{Z}^-$  [1]  
 $\text{CH}_3\text{OH} + \text{HZ} \longrightarrow \text{CH}_3\text{OH}_2^+ + \text{Z}^-$  [1]
- (ii)  $\text{NH}_3 + \text{B}^- \longrightarrow \text{NH}_2^- + \text{BH}$  [1]  
 $\text{CH}_3\text{OH} + \text{B}^- \longrightarrow \text{CH}_3\text{O}^- + \text{BH}$  [1]
- [4]
- (b) (i) a reaction that can go in either direction [1]
- (ii) **rate** of forward = **rate** of backward reaction  
 or forward/back reactions occurring but concentrations of all species do not change [1]
- [2]
- (c) (i) a solution that resists changes in pH [1]  
 when small quantities of acid or base/alkali are added [1]
- (ii) in the equilibrium system  $\text{HZ} + \text{H}_2\text{O} = \text{Z}^- + \text{H}_3\text{O}^+$  [1]  
 addition of acid: reaction moves to the left  
 or  $\text{H}^+$  combines with  $\text{Z}^-$  **and** forms  $\text{HZ}$  [1]
- addition of base: the reaction moves to the right  
 or  $\text{H}^+$  combines with  $\text{OH}^-$  **and** more  $\text{Z}^-$  formed [1]
- [5 max 4]
- (d) (i)  $[\text{H}^+] = \sqrt{0.5 \times 1.34 \times 10^{-5}} = 2.59 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$  [1]  
 pH = **2.59/2.6** (min 1 d.p) ecf [1]
- (ii)  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{Na} + \text{H}_2\text{O}$  [1]
- (iii)  $n(\text{acid})$  in  $100 \text{ cm}^3 = 0.5 \times 100/1000 = 0.05 \text{ mol}$   
 $n(\text{acid})$  remaining =  $0.05 - 0.03 = 0.02 \text{ mol}$   
 $[\text{acid remaining}] = \mathbf{0.2} \text{ (mol dm}^{-3}\text{)}$  [1]
- likewise,  $n(\text{salt}) = 0.03 \text{ mol}$   
 $[\text{salt}] = \mathbf{0.3} \text{ (mol dm}^{-3}\text{)}$  [1]
- (iv)  $\text{pH} = 4.87 + \log(0.3/0.2) = \mathbf{5.04-5.05}$  ecf [1]
- [6]
- (e) **G** is  $\text{CH}_3\text{CH}_2\text{COCl}$   
**H** is  $\text{SOCl}_2$  or  $\text{PCl}_5$   
**J** is  $\text{NaCl}$  [2]  
 (or corresponding Br compounds for **G**, **H** and **J**;  $\text{CH}_3\text{CH}_2\text{COBr}$ ,  $\text{SOBr}_2$ ,  $\text{NaBr}$ )
- [Total: 18]

Q18.

- 8 (a) (i) (nitrates are) soluble [1]
- (ii)  $\text{Ba}^{(2+)}$  and  $\text{Pb}^{(2+)}$  [1]
- $\text{SO}_4^{(2-)}$  [1]
- $\text{BaCO}_3/\text{PbCO}_3/\text{CaSO}_4$  are insoluble [1]
- [4]
- (b) (i) fertilisers/animal manure [1]
- (ii) washing powder/detergents/fertilisers/animal manure [1]
- (ii) growth/production of algae/weeds/plants  
or eutrophication [1]
- [3]
- (c) (i) *any one of:*
- $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$  and  $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$
- or  $\text{SO}_2 + \text{NO}_2 \longrightarrow \text{SO}_3 + \text{NO}$  and  $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$
- or  $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$  [1]
- (ii) roasting sulfide ores/extraction of metals from sulfide ores [1]
- [2]
- [Total: 9]

Q19.

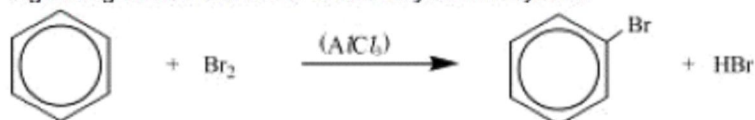
- 2 (a) *any two from:* molecules have negligible volume  
 negligible intermolecular forces *or* particles are not attracted to each other  
*or* to the walls of the container  
 random motion  
 no loss of **kinetic** energy during collisions *or* elastic collisions (NOT  
 elastic molecules) 2 × [1]  
[2]

- (b) (i) low temperature **and** high pressure both required [1]  
 (ii) (at low T) forces between particles are more important, [1]  
 (at high P) volume of molecules are significant [1]

[3 max 2]

- (c) (i) endothermic; because the equilibrium moves to the right on heating *or* with  
 increasing temperature *or* because bonds are broken during the reaction [1]

- (ii) e.g. halogenation *or* Friedel-Crafts alkylation / acylation



reactants [1]  
 products [1]

other possibilities: Cl<sub>2</sub>, I<sub>2</sub>, R-Cl, RCOCl etc.

[3]

[Total: 7]

