

A2 Chemistry

Topical Questions of Equilibria

pH and pOH

K_a and pK_a

K_c and K_w

pH of Buffer solution

Titration Curves

K_{sp} and K_{pc}

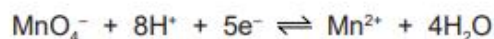
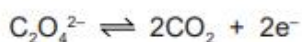
By Faizan Saleem

Question No 1

- (ii) An impure sample of BaC_2O_4 , of mass 0.500 g, is added to 50.0 cm^3 of $0.0200 \text{ mol dm}^{-3}$ acidified MnO_4^- (aq), an excess. A redox reaction takes place and all the BaC_2O_4 reacts.

The resulting solution, containing unreacted acidified MnO_4^- , is titrated with $0.0500 \text{ mol dm}^{-3}$ Fe^{2+} (aq).

The end-point is reached when 30.40 cm^3 of $0.0500 \text{ mol dm}^{-3}$ Fe^{2+} (aq) has been added.



Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.

[M_r : BaC_2O_4 , 225.3]

percentage by mass of BaC_2O_4 = ... [4]

- I) Barium hydroxide, $\text{Ba}(\text{OH})_2$, is completely dissociated in aqueous solution.

Calculate the pH of $0.120 \text{ mol dm}^{-3}$ $\text{Ba}(\text{OH})_2$ (aq) at 298 K.

pH = ... [2]

2(c)(ii)	M1: [a] initial moles $\text{MnO}_4^- = 0.0200 \times 0.050 = 1.00 \times 10^{-3}$ [b] moles $\text{Fe}^{2+} = 0.050 \times 0.0304 = 1.52 \times 10^{-3}$ M2: [a] moles MnO_4^- unreacted $= 1.52 \times 10^{-3} / 5 = 3.04 \times 10^{-4}$ [b] moles MnO_4^- reacted $= 1.00 \times 10^{-3} - 3.04 \times 10^{-4} = 6.96 \times 10^{-4}$ M3: moles $\text{C}_2\text{O}_4^{2-}$ reacted $= 6.96 \times 10^{-4} \times 5/2 = 1.74 \times 10^{-3}$ M4: mass of $\text{BaC}_2\text{O}_4 = 225.3 \times 1.74 \times 10^{-3} = 0.392 \text{ g}$ % Purity of $\text{BaC}_2\text{O}_4 = 100 \times 0.392/0.50 = 78.4$	4
2(d)	M1: $[\text{OH}^-] = 2 \times 0.12 = 0.24 \text{ (mol dm}^{-3}\text{)}$ $[\text{H}^+] = 1 \times 10^{-14}/0.24 = 4.17 \times 10^{-14} / \text{pOH} = -\log(0.24) \text{ OR } 0.62$ M2: $\text{pH} = -\log[\text{H}^+] = 13.4 \text{ OR } \text{pH} = 14 - 0.6 = 13.4$	2

Question No 2

(g) The ionic product, K_w , for D_2O has a value of $1.35 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K.

(i) Write the expression for the K_w of D_2O .

$$K_w =$$

[1]

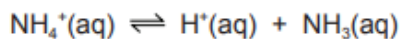
(ii) Calculate the pH of pure, neutral D_2O at 298 K.
Assume $[\text{D}^*]$ is equivalent to $[\text{H}^*]$ for pH calculations.

pH = ... [2]

(g)(i)	$K_w = [\text{D}^*][\text{DO}^*]$	1
(g)(ii)	M1 $[\text{D}^*] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8}$ M2 $\text{pH} = -\log [\text{D}^*] = 7.4(3) \quad \text{min 2sf}$	2

Question No 3

Ammonium chloride, $\text{NH}_4\text{Cl}(\text{s})$, dissolves in water to form an acidic solution. This is due to the dissociation of the ammonium ions.



(a) The ammonium ion is a weak acid. The pH of a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride is 4.89 under standard conditions.

(i) Calculate the $[\text{H}^+]$ in a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride.

$[\text{H}^+] = \dots\dots\dots \text{mol dm}^{-3}$ [1]

(ii) Calculate the value of $\text{p}K_{\text{a}}$ of the ammonium ion.

$\text{p}K_{\text{a}} = \dots\dots\dots$ [2]

(b) A buffer solution can be made by mixing ammonium chloride with ammonia solution.

(i) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong acid is added.

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

(ii) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong base is added.

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

(c) (i) Use the value of K_w to calculate $[H^*]$ in pure water under standard conditions.

Show your working.

$$[H^*] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(ii) The pH of pure water at 50 °C is 6.64.

Calculate the numerical value of K_w at 50 °C.

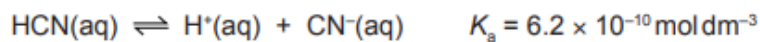
$$K_w = \dots\dots\dots [2]$$

[Total: 8]

(a)(i)	1.3×10^{-5}	1
(a)(ii)	M1: K_a expression used correctly and $K_a = 5.5(3) \times 10^{-10}$ M2: $pK_a = 9.26$ Award 2 marks for correct answer	2
(b)(i)	$NH_3 + H^+ \rightarrow NH_4^+$	1
(b)(ii)	$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ or $H^+ + OH^- \rightarrow H_2O$ and reference to expression in Q shifting R	1
(c)(i)	quotes $K_w = 1 \times 10^{-14}$ or 1×10^{-1} $[H^*][OH^-]$ $[H^*] = 1 \times 10^{-7}$	1
(c)(ii)	M1: $[H^*] = 2.3 \times 10^{-7}$ (calculator value 2.290867×10^{-7}) and $K_w = [2.3 \times 10^{-7}]^2$ M2: $K_w = 5.2 \times 10^{-14}$ calculator 5.248074×10^{-14} Award 2 marks for correct answer	2

Question No 4

(a) Hydrogen cyanide, HCN, is a weak acid in aqueous solution.



(i) Calculate the pH of 0.10 mol dm⁻³ HCN(aq).

pH = ... [2]

(ii) Draw a 'dot-and-cross' diagram to represent the bonding in the hydrogen cyanide molecule. Show the outer shell electrons only.

[1]

(iii) State the hybridisation of the carbon and nitrogen atoms in hydrogen cyanide, and give the H–C–N bond angle.

hybridisation of C

hybridisation of N

H–C–N bond angle

[2]

(a)(i)	$[\text{H}^+] = \sqrt{(K_a \cdot c)} = \sqrt{(6.2 \times 10^{-10} \times 0.1)}$ $[\text{H}^+] = 7.9 \times 10^{-6}$ $\text{pH} = -\log[\text{H}^+] = 5.1(0)$	2
(a)(ii)		1
(a)(iii)	C: sp and N: sp angle 180°	2

Question No 5

(c) When sodium oxide reacts with water an alkaline solution is obtained.

- (i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

.....

 [2]

- (ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm³ of water.

pH = ... [3]

(c)(i)	the reaction produces sodium hydroxide / hydroxide ions / OH ⁻ ions	1
	the hydroxide ions can receive / accept H ⁺ ions / protons	1
(c)(ii)	Calculation of Na ₂ O moles 3.10 g / 62 OR 0.05	1
	Calculation of [OH ⁻] 0.05 × (2 / 0.400) = 0.25 mol dm ⁻³	1
	Calculation of pH -log 0.25 = 0.60 14 - 0.60 = 13.40	1

Question No 6

(b) SiCl_4 reacts with water to produce an acidic solution.

(i) Write an equation for this reaction.

..... [1]

(ii) Describe **two** visual observations when silicon tetrachloride is added drop by drop to a small amount of water.

1

2

[2]

(iii) A sample of 0.8505 g of SiCl_4 is added to 800 cm^3 of water. All of the soluble acidic product is dissolved in the water.

Calculate the pH of the solution obtained.

pH = ... [3]

1(b)(i)	$\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$ or $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{HCl}$	1
1(b)(ii)	white solid	1
	steamy fumes / white fumes / misty fumes	1
1(b)(iii)	moles of $\text{SiCl}_4 = 0.8505 / 170.1 = 0.005$	1
	conc of $\text{H}^+ (0.005) \times 4 / 0.8 = 0.025$	1
	$\text{pH} = -\log(0.025) = 1.6$	1

$$n' \quad 'n \leq 4 f? \quad | \quad 3.16 \times 10^{-3} \text{ mol} = 10 \text{ mm}^3$$

Ka,pka and Buffer Solution

Question No 7

- (b) (i) Isocyanic acid is a weak acid.



Calculate the pH of a 0.10 mol dm^{-3} solution of isocyanic acid.

pH = ... [2]

- (ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid. Sodium cyanate is prepared commercially by reacting urea, $(\text{NH}_2)_2\text{CO}$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

..... [1]

- (c) Barium hydroxide, $\text{Ba}(\text{OH})_2$, is completely ionised in aqueous solutions. During the addition of 30.0 cm^3 of 0.100 mol dm^{-3} $\text{Ba}(\text{OH})_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid, the pH was measured.

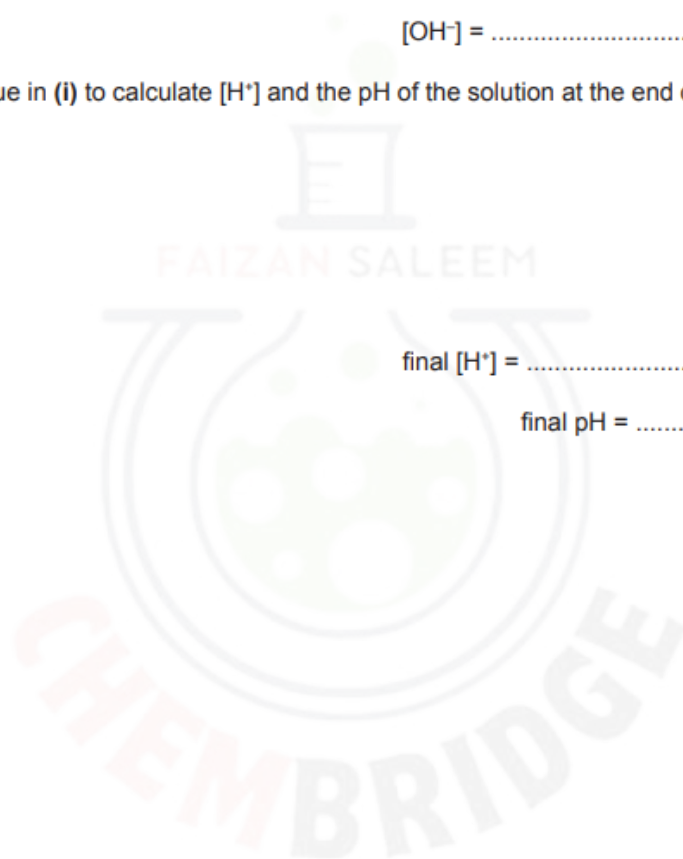
(i) Calculate the $[\text{OH}^-]$ at the end of the addition.

$[\text{OH}^-] = \dots\dots\dots \text{mol dm}^{-3}$ [2]

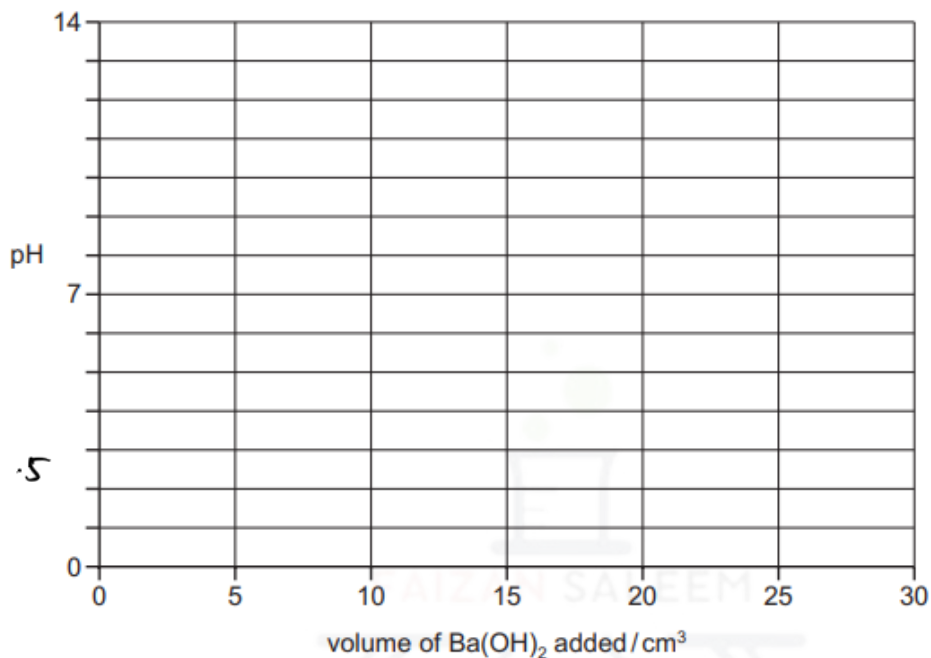
(ii) Use your value in (i) to calculate $[\text{H}^+]$ and the pH of the solution at the end of the addition.

final $[\text{H}^+] = \dots\dots\dots \text{mol dm}^{-3}$

final pH = $\dots\dots\dots$
[2]



- (iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm³ of 0.100 mol dm⁻³ Ba(OH)₂ to 20.0 cm³ of 0.100 mol dm⁻³ isocyanic acid.



[3]

(b)(i)	$[H^+] = \sqrt{([HNC\bar{O}]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})}$ or 3.46×10^{-3}	1
	$pH = \log [H^+] = 2.5$ (2.46)	1
b)(ii)	$Na_2CO_3 + 2(NH_2)_2CO \longrightarrow 2NaNCO + CO_2 + 2NH_3 + H_2O$	1
(c)(i)	(n(OH ⁻) at start = $(2 \times 0.1 \times 30) / 1000 = 6 \times 10^{-3}$ mol) (n(OH ⁻) reacted = $(0.1 \times 20) / 1000 = 2 \times 10^{-3}$ mol) n(OH ⁻) remaining = $(6-2) \times 10^{-3} = 4 \times 10^{-3}$ mol, (in 50 cm ³)	1
	so $[OH^-]_{end} = (4 \times 10^{-3} \times 1000) / 50 = 0.08 \text{ mol dm}^{-3}$	1

Question	Answer	Marks
(c)(ii)	$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13} \text{ mol dm}^{-3}$	1
	so $pH = -\log(1.25 \times 10^{-13}) = 12.9$	1
(c)(iii)	curve starts at 2.46 / 2.5	1
	vertical portion (end point) at vol added = 10.0 cm ³	1
	finishes at pH = 12.9	1

Question No 8

The table lists some organic acids and their pK_a values.

acid	formula	pK_a
ethanoic acid	CH_3CO_2H	4.76
chloroethanoic acid	$ClCH_2CO_2H$	2.86
aminoethanoic acid (glycine)	$H_2NCH_2CO_2H$	9.87

- (a) (i) State the relationship between pK_a and the strength of an acid.

..... [1]

- (ii) State the mathematical relationship between pK_a and the acidity constant K_a .

..... [1]

- (iii) Give reasons for why the pK_a value for chloroethanoic acid is **smaller** than that for ethanoic acid.

.....

.....

..... [2]

- (b) (i) Use the zwitterionic structure for aminoethanoic acid (glycine) in aqueous solution to write an equation for its dissociation giving $H^+(aq)$ ions.

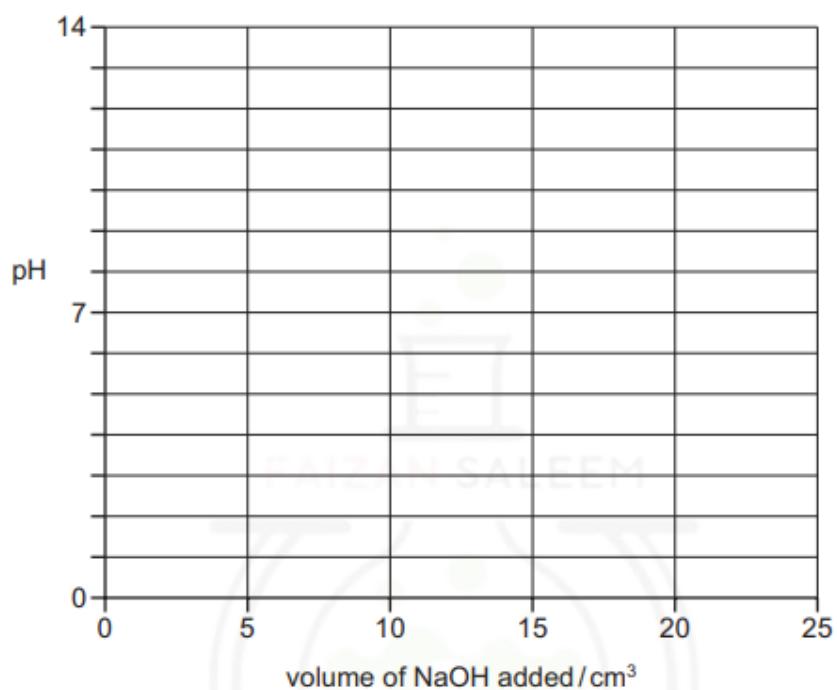
..... [1]

- (ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of aminoethanoic acid.

pH = ... [2]

A 10.0 cm^3 sample of 0.100 mol dm^{-3} aminoethanoic acid (glycine) was titrated with 0.100 mol dm^{-3} NaOH. After 20.0 cm^3 of NaOH, an excess, had been added, the pH was found to be 12.5.

(iii) Using the following axes, sketch a graph showing how the pH changes during this titration.



[3]

[Total: 10]

6(a)(i)	the lower / smaller the pK_a , the stronger the acid	1
3(a)(ii)	$pK_a = -\log(K_a)$ or $pK_a = -\lg(K_a)$ or $K_a = 10^{-pK_a}$	1
3(a)(iii)	(stronger than ethanoic acid because) <i>Cl</i> is electron-withdrawing	1
	and so stabilises the RCO_2^- anion / conjugate base or weakens O-H bond (so H^+ is more easily released)	1
6(b)(i)	$NH_3^+CH_2CO_2^- \longrightarrow NH_2CH_2CO_2^- + H^+$ OR $NH_3^+CH_2CO_2^- + H_2O \longrightarrow NH_2CH_2CO_2^- + H_3O^+$	1
3(b)(ii)	$K_a = 10^{-9.87} = 1.35 \times 10^{-10}$ $[H^+] = \sqrt{(K_a \cdot c)} = 3.67 \times 10^{-6}$	1
	pH = 5.4 (5.43–5.44) min 2sf	1

Question	Answer	Marks
3(b)(iii)	curve starts at 5.4 and continuous	1
	vertical portion (end point) at vol added = 10.0 cm^3	1
	finishes at pH = 12.5 at 20 cm^3 (and does not increase in pH)	1
	Total:	10

Question No 9

Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak acid*.

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

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	$\text{CH}_3\text{CO}_2\text{H}$	4.8
2	$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	4.9
3	$\text{CH}_3\text{CHClCO}_2\text{H}$	2.8
4	$\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a .

..... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

.....
.....

- acid 2 and acid 3,

.....
.....

- acid 3 and acid 4.

.....
.....

[3]

(d) A monobasic acid, **D**, has $K_a = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of **D**.

pH = ... [2]

(a) (i)	(an acid that is) partially / incompletely ionised / dissociated	1
(b) (i)	$\text{p}K_a = -\log K_a$ or $K_a = 10^{-\text{p}K_a}$	1

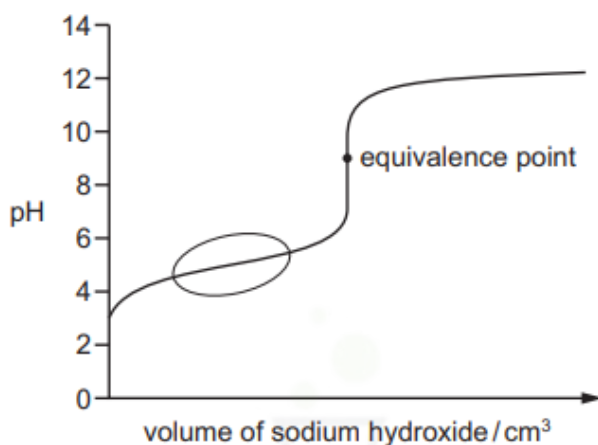
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Page 3	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – May/June 2016	9701	42

Question	Answer	Marks
(ii)	ethanoic acid (1) is more acidic than propanoic acid (2) due to smaller electron-donating (R/alkyl) group/less electron-donating (R/alkyl) group(s) 2-chloropropanoic acid (3) is more acidic than propanoic acid (2) due to electron-withdrawing / electronegative (Cl/chlorine) atom 2-chloropropanoic acid (3) is more acidic than 3-chloropropanoic acid (4) since the Cl/chlorine / electronegative atom is closer to the CO_2^- / acid	3

Question No 10

(a) The sketch graph for the titration of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, with sodium hydroxide is shown.



- (i) In the region circled on the graph, identify the **two** organic species that are present in the solution. Explain why the pH of the mixture only changes slowly and gradually in this region when sodium hydroxide is being added.

two species present
.....
.....
.....
..... [3]

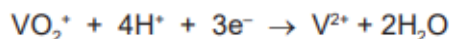
- (ii) The equivalence point in this acid-base titration is where the two solutions have been mixed in exactly equal molar proportion.

Suggest why the pH is greater than 7 at the equivalence point in this titration.

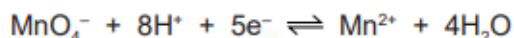
.....
.....
.....
..... [1]

- (b) An impure sample of ammonium vanadate(V), NH_4VO_3 , with mass 0.150 g, is dissolved in an excess of dilute acid.

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.



When the resulting solution is titrated, 20.10 cm^3 of $0.0250 \text{ mol dm}^{-3}$ acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.



Calculate the percentage by mass of NH_4VO_3 in the 0.150 g impure sample of NH_4VO_3 .

Give your answer to **three** significant figures.

[M_r : NH_4VO_3 , 116.9]

percentage by mass of NH_4VO_3 = ... % [3]

[Total: 7]

Question	Answer	Marks
8(a)(i)	M1: $\text{CH}_3\text{CO}_2\text{H}$ and CH_3CO_2^- M2: due to buffering action / acting as a buffer solution M3: $\text{CH}_3\text{CO}_2\text{H}$ reacts with $\text{NaOH} / \text{OH}^-$ (forming CH_3CO_2^- and water) OR OH^- reacts with H^+ <u>and</u> equilibrium $\text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}^+$ shifts to the right	3
8(a)(ii)	identifying CH_3CO_2^- is present (with water) at the equivalence point OR CH_3CO_2^- react with water forming OH^- OR titrating a weak acid with a strong base	1

Question	Answer	Marks
8(b)	M1: moles $\text{MnO}_4^- = 0.025 \times 0.0201 = 5.025 \times 10^{-4}$ moles $\text{V}^{2+} = 5.025 \times 10^{-4} \times 5 / 3 = 8.375 \times 10^{-4}$ M2: moles $\text{VO}_3^- = 8.375 \times 10^{-4}$ mass of $\text{NH}_4\text{VO}_3 = 116.9 \times 8.375 \times 10^{-4} = 0.0979 \text{ g}$ M3: % Purity of $\text{NH}_4\text{VO}_3 = 100 \times 0.0979 / 0.15 = 65.3$ must be 3 sf	3

Question No 11

Solution **Y** is hydrochloric acid, HCl(aq) . Solution **Z** is aqueous 4-chlorobutanoic acid, $\text{Cl(CH}_2)_3\text{CO}_2\text{H(aq)}$. The $\text{p}K_a$ of $\text{Cl(CH}_2)_3\text{CO}_2\text{H(aq)}$ is 4.52. The pH of both solutions is 4.00.

(a) (i) Write an expression for the K_a of $\text{Cl(CH}_2)_3\text{CO}_2\text{H(aq)}$.

$$K_a =$$

[1]

(ii) Write a mathematical expression to describe the relationship between K_a and $\text{p}K_a$.

..... [1]

(iii) Calculate $[\text{H}^+]$ in solutions **Y** and **Z**.

$$[\text{H}^+] = \text{..... mol dm}^{-3} \quad [1]$$

(iv) Calculate the ratio $\frac{[\text{HCl}] \text{ dissolved in solution Y}}{[\text{Cl(CH}_2)_3\text{CO}_2\text{H}] \text{ dissolved in solution Z}}$.

$$\frac{[\text{HCl}] \text{ dissolved in solution Y}}{[\text{Cl(CH}_2)_3\text{CO}_2\text{H}] \text{ dissolved in solution Z}} = \text{.....} \quad [2]$$

- (b) A buffer solution of pH 5.00 is produced by adding sodium propanoate to 5.00 g of propanoic acid in 100 cm³ of distilled water.

Calculate the mass of sodium propanoate that must be used to produce this buffer solution. The K_a of propanoic acid is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$.

[M_r : propanoic acid, 74.0; sodium propanoate, 96.0]

mass of sodium propanoate = ... g [3]

- (c) Some dilute sulfuric acid is mixed with a small sample of the buffer solution described in (b). The final pH of the mixture is close to 1.

Explain this observation.

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

[Total: 10]

1(a)(i)	$K_a = \frac{[H^+][Cl(CH_2)_3CO_2^-]}{[Cl(CH_2)_3CO_2H]}$ [1]	1
(a)(ii)	$pK_a = -\log K_a$ OR $K_a = 10^{-pK_a}$ [1]	1
1(a)(iii)	$[H^+] = 10^{-4.0} = 1 \times 10^{-4}$ [1]	1

ES 2021

Page 5 of 16

/41

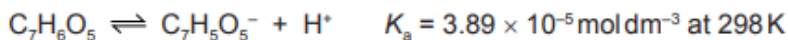
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Question	Answer	Marks
1(a)(iv)	$[HC\equiv] = 1 \times 10^{-4}$ ecf 2(a)(iii) $K_a = 10^{-4.52} = 3.02 \times 10^{-5}$ $[Cl(CH_2)_3CO_2H] = (1 \times 10^{-4})^2 / 3.02 \times 10^{-5} = 3.3 \times 10^{-4}$ ecf $\frac{[HCl]}{[Cl(CH_2)_3CO_2H]} = \frac{1 \times 10^{-4}}{3.3 \times 10^{-4}} = 0.302$ min 2sf ecf	2
2(b)	M1 $[H^+] = 10^{-5}$ OR 1×10^{-5} $K_a = [H^+][A^-] / [HA]$ OR $pH = pK_a + \log [A^-] / [HA]$ ✓ [1] M2 moles of $A^- = (1.35 \times 10^{-5})(5/74) / (1 \times 10^{-5})$ moles of $A^- = 0.0912$ [1] ecf M3 mass of sodium propanoate = $0.0912 \times 96 = 8.76$ [1] min 2sf ecf	3
2(c)	all of the (sodium) propanoate (ion) has been protonated / converted to (propanoic) acid / neutralised [1] H^+ is in excess / H^+ is 0.1 mol dm^{-3} (from the H_2SO_4) [1]	2

Question No 12

- (b) A buffer solution was prepared by dissolving 2.04 g of gallic acid in 250 cm³ of a solution containing 0.0600 mol dm⁻³ of gallate ions, C₇H₅O₅⁻.



- (i) Define the term *buffer solution*.

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

- (ii) Calculate the pH of this buffer solution.

pH = ... [3]

- (iii) Write **two** equations to show how a solution containing gallic acid, C₇H₆O₅, and gallate ions, C₇H₅O₅⁻, acts as a buffer.

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

i(b)(i)	M1 a solution which resists changes in pH / controls pH / keeps pH within a small range M2 when small amounts of H ⁺ or OH ⁻ are added	2
i(b)(ii)	M1 no. of mol of gallic acid = 2.04 ÷ 170.0 OR 0.012(0) mol M2 [H ⁺] = K _a [HA] / [A ⁻] = 3.89 × 10 ⁻⁵ × 0.012 / 0.250 ÷ 0.0600 = 3.89 × 10 ⁻⁵ × (0.048 ÷ 0.0600) = 3.112 × 10 ⁻⁵ M3 pH = -log ₁₀ (3.112 × 10 ⁻⁵) = 4.5(1) min 2sf	3
(b)(iii)	M1 C ₇ H ₆ O ₅ + OH ⁻ → C ₇ H ₅ O ₅ ⁻ + H ₂ O OR H ⁺ + OH ⁻ → H ₂ O AND C ₇ H ₆ O ₅ → C ₇ H ₅ O ₅ ⁻ + H ⁺ M2 C ₇ H ₅ O ₅ ⁻ + H ⁺ → C ₇ H ₆ O ₅	2

Question No 13

- (b) (i) The numerical values of K_a for methanoic acid, HCO₂H, and pyruvic acid, CH₃COCO₂H, are given.

acid	K _a
HCO ₂ H	1.78 × 10 ⁻⁴
CH ₃ COCO ₂ H	4.07 × 10 ⁻³

An equilibrium mixture containing the two acid-base pairs is formed.



Use the K_a values to calculate the equilibrium constant, K_{eq}, for this equilibrium.

$$K_{\text{eq}} = \dots\dots\dots [1]$$

- (ii) Use your value of K_{eq} to predict the position of this equilibrium. Indicate this by placing a tick (✓) in the appropriate box in the table. Explain your answer.

equilibrium lies to the left	equilibrium lies in the middle	equilibrium lies to the right
☐	☐	☐

.....

 [1]

- (iii) Ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$, has two dissociation constants, K_{a1} and K_{a2} , whose $\text{p}K_a$ values are 1.23 and 4.19.

Suggest equations to show the two dissociations that give rise to these $\text{p}K_a$ values.

$\text{p}K_{a1}$ 1.23

$\text{p}K_{a2}$ 4.19 [2]

- (iv) State the mathematical relationship between $\text{p}K_a$ and the acid dissociation constant K_a .

..... [1]

(b)(i)	$K_{eq} = 4.07 \times 10^{-3} / 1.78 \times 10^{-4} = 22.9$	1
(b)(ii)	3 rd box ticked [to the right] AND as the K_{eq} is greater than one ecf on K_{eq}	1
(b)(iii)	$\text{p}K_a$ 1.23 $\text{HO}_2\text{CCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{HO}_2\text{CCO}_2^- + \text{H}_3\text{O}^+$ OR $\text{HO}_2\text{CCO}_2\text{H} \rightleftharpoons \text{HO}_2\text{CCO}_2^- + \text{H}^+$ $\text{p}K_a$ 4.19 $\text{HO}_2\text{CCO}_2^- + \text{H}_2\text{O} \rightleftharpoons ^-\text{O}_2\text{CCO}_2^- + \text{H}_3\text{O}^+$ OR $\text{HO}_2\text{CCO}_2^- \rightleftharpoons ^-\text{O}_2\text{CCO}_2^- + \text{H}^+$	2
(b)(iv)	$\text{p}K_a = -\log K_a$	1

Question No 14

- (d) Calcium iodate(V), $\text{Ca}(\text{IO}_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of $\text{Ca}(\text{IO}_3)_2$, and state its units.

$$K_{sp} =$$

units = ... [2]

- (ii) Calculate the numerical value for K_{sp} $\text{Ca}(\text{IO}_3)_2$ at 298 K.

$$K_{sp} = \dots\dots\dots [1]$$

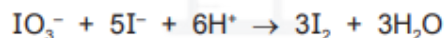
- (iii) When a few cm³ of concentrated Ca(NO₃)₂(aq) is added to a saturated solution of Ca(IO₃)₂ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

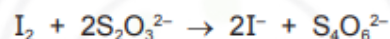
.....
.....
..... [2]

- (e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), NaIO₃.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm³ in a volumetric flask with distilled water.
- 50.0 cm³ of this solution is pipetted into an excess of aqueous acidified potassium iodide.



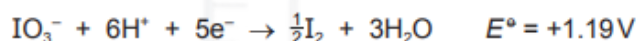
- The iodine produced requires 12.40 cm³ of 0.00200 mol dm⁻³ aqueous sodium thiosulfate solution for complete reaction.



Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of NaIO₃ = ... g [3]

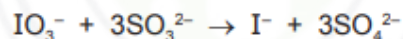
- (f) The half-equation for the reduction of iodate(V) ions is shown.



Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

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

- (g) Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.



The initial rate of reaction was found to be first order with respect to IO₃⁻, first order with respect to SO₃²⁻ and first order with respect to H⁺.

- (i) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm⁻³ s⁻¹

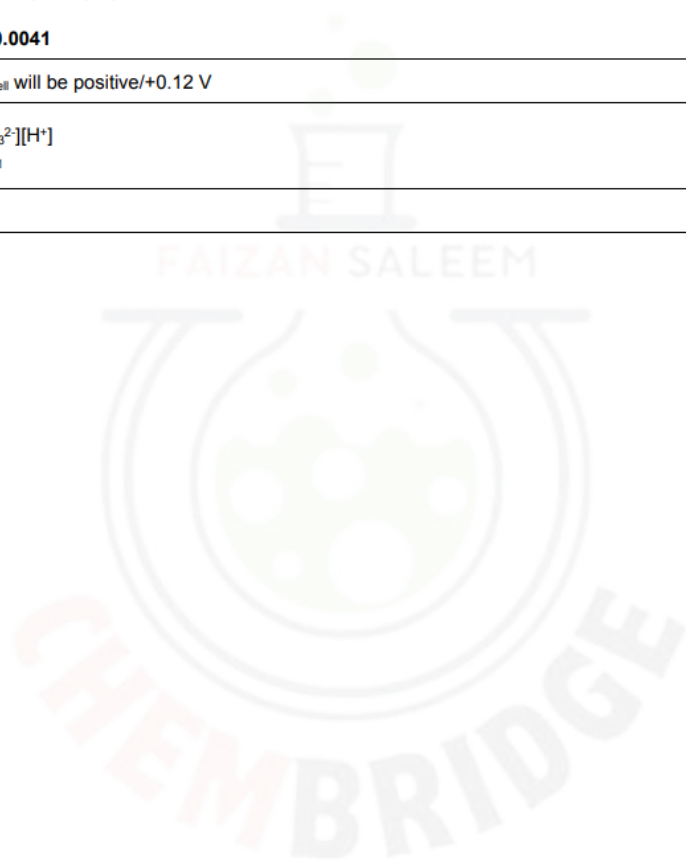
units of *k* = ... [2]

- (ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of *x*.

x = ... [1]

2(d)(i)	M1 $K_{sp} = [\text{Ca}^{2+}][\text{IO}_3^-]^2$ M2 units = $\text{mol}^3 \text{dm}^{-9}$	2
2(d)(ii)	$K_{sp} = 4 \times (5.6 \times 10^{-3})^3$ $K_{sp} = 7.03 \times 10^{-7}$ 2sf min	1
(d)(iii)	M1 $\text{Ca}(\text{IO}_3)_2$ AND as solubility of $\text{Ca}(\text{IO}_3)_2$ decreases M2 due to common ion effect	2
2(e)	M1 moles $\text{S}_2\text{O}_3^{2-} = 0.002 \times 12.4/1000$ $= 2.48 \times 10^{-5}$ moles of $\text{I}_2 = 1.24 \times 10^{-5}$ M2 moles of $\text{IO}_3^- = 4.13 \times 10^{-6}$ in 50 cm^3 moles of $\text{IO}_3^- = 2.07 \times 10^{-5}$ in 250 cm^3 mass of $\text{NaIO}_3 = 2.07 \times 10^{-5} \times 197.9$ M3 mass of $\text{NaIO}_3 = 0.0041$	3
2(f)	It is feasible as the E_{cell} will be positive/+0.12 V	1
2(g)(i)	M1 Rate = $k[\text{IO}_3^-][\text{SO}_3^{2-}][\text{H}^+]$ M2 units = $\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$	2
2(g)(ii)	0.10	1



Question No 15



- (a) Write an expression for the K_a of the weak acid HA in terms of the concentrations of the species involved.

$$K_a =$$

[1]

- (b) The hydroxylammonium ion, $HONH_3^+$, is a weak acid. A $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ solution of hydroxylammonium ions has a pH of 4.41.

- (i) Calculate the K_a of $HONH_3^+$.



$$K_a = \frac{3.9 \times 10^{-5} \times 3.9 \times 10^{-5}}{1.00 \times 10^{-3}}$$

$$K_a = \dots\dots\dots [2]$$

- (ii) Calculate the pK_a of $HONH_3^+$.

$$pK_a = \dots\dots\dots [1]$$

- (c) The solubility product of manganese(II) hydroxide, $Mn(OH)_2$, in water is $1.1 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ at 298 K.

Calculate the solubility of $Mn(OH)_2$ in water at 298 K.

$$\text{solubility} = \dots\dots\dots \text{mol dm}^{-3} [2]$$

[Total: 6]

2(a)	$[H^+][A^-] / [HA]$ [1]	1
2(b)(i)	$[H^+] = 3.9 \times 10^{-5}$ [1] $K_a = 1.5 \times 10^{-6}$ [1]	2
2(b)(ii)	5.82 [1]	1
2(c)	$4 \times 3 = 1.1 \times 10^{-11}$ [1] $x = 1.4 \times 10^{-4}$ [1]	2

Question No 16

(a) (i) Use mathematical expressions to define the following terms.

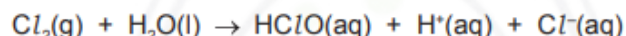
- $\text{pH} = \dots\dots\dots$
 $\dots\dots\dots$
 - K_a for a weak acid, $\text{HA} = \dots\dots\dots$
 $\dots\dots\dots$
- [2]

(ii) Write equations to show how a buffer solution consisting of a mixture of HA(aq) and NaA(aq) controls pH when an acid or an alkali is added.

$\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$

[2]

(b) When chlorine dissolves in water the following reaction occurs.



When solutions of chlorine are used for water purification, the pH of the solution of chlorine is kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 of a solution containing 0.170 mol of HClO and 0.170 mol of HCl .

A buffer solution is then prepared by adding 0.200 mol of NaOH(s) to this solution. The NaOH reacts initially with the HCl .

Calculate the pH of the buffer solution.

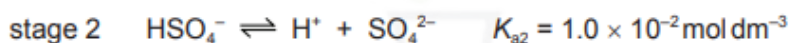
[HClO is a weak acid with $K_a = 2.9 \times 10^{-8} \text{ mol dm}^{-3}$.]

$\text{pH} = \dots\dots\dots$ [3]

3(a)(i)	M1 $\text{pH} = -\log[\text{H}^+]$ M2 $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$	2
3(a)(ii)	M1 $\text{A}^- + \text{H}^+ \rightarrow \text{HA}$ OR $\text{NaA} + \text{H}^+ \rightarrow \text{HA} + \text{Na}^+$ M2 $\text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^-$	2
3(b)	remaining $n(\text{HClO}) = 0.17 - 0.03 = 0.14 \text{ mol (dm}^{-3}\text{)}$ $[\text{H}^+] = 1.35 \times 10^{-7} \text{ mol dm}^{-3}$ OR calculate pK_a (7.54) from K_a $\text{pH} = -\log(1.35 \times 10^{-7}) = 6.87/6.9$ OR $\text{pH} = 7.54 + \log(0.03/0.14) = 6.87$	3

Question No 17

(d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.



K_{a2} is the acid dissociation constant for stage 2.

(i) Write the expression for the acid dissociation constant K_{a2} .

$$K_{a2} =$$

[1]

(ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2} .

..... [1]

(e) Benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, is a weak acid. A solution of $0.0250 \text{ mol dm}^{-3}$ benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

$$K_a = \dots\dots\dots \text{mol dm}^{-3}$$

[2]

(d)(i)	$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	1
(d)(ii)	K_a of H_2SO_4 is larger than K_{a2}	1

Question	Answer	Marks
7(e)	M1: $[H^+] = 10^{-2.90} = 1.26 \times 10^{-3}$ M2: $K_a = [1.26 \times 10^{-3}]^2 / 0.025 = 6.3 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$	2



Question No 18

Silver sulfide, Ag_2S , is very insoluble in water.

- (a) (i) Write an expression for the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$.

$$K_{\text{sp}} =$$

[1]

- (ii) The solubility of $\text{Ag}_2\text{S}(\text{s})$ in water at 298 K is $1.16 \times 10^{-17} \text{ mol dm}^{-3}$.

Calculate the numerical value of the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$ at 298 K.

$$K_{\text{sp}} = \dots\dots\dots [2]$$

- (iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $\text{Ag}_2\text{S}(\text{s})$ under standard conditions.

$$\text{volume} = \dots\dots\dots \text{ dm}^3 [2]$$

(b) Bromic(I) acid, HOBr(aq) , is a weak acid. Its K_a is $2.0 \times 10^{-9} \text{ mol dm}^{-3}$.

(i) Calculate the pH of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH , are added to 20.0 cm^3 of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

moles of Acid = 0.003 mol in 25 cm^3 of 0.20 mol dm^{-3} .

$25 \text{ cm}^3 = 0.025 \text{ dm}^3$

$1000 \text{ cm}^3 = 1 \text{ dm}^3$

$X = \frac{1000 \times 0.003}{25}$

moles of Salt = 0.001 mol in 25 cm^3 of 0.20 mol dm^{-3}

$25 \text{ cm}^3 = 0.025 \text{ dm}^3$

$1000 \text{ cm}^3 = 1 \text{ dm}^3$



0.001

$$K_a = \frac{[\text{BrO}^-][\text{H}^+]}{[\text{HBrO}]}$$

$$2.0 \times 10^{-9} = \frac{(0.001)[\text{H}^+]}{(0.003)}$$

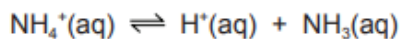
$$2.0 \times 10^{-9} \times 0.003$$

5(a)(i)	$K_{sp} = [Ag^+]^2[S^{2-}]$	1
5(a)(ii)	$[S^{2-}] = 1.16 \times 10^{-17}$ $[Ag^+] = 2.32 \times 10^{-17}$ $K_{sp} = 6.2(4) \times 10^{-51}$ minimum 2 sig. fig. correct answer scores 2 marks Award 1 mark for two points, award 2 marks for three points	2
5(a)(iii)	M1: moles $Ag_2S = 1 / 247.9 = 0.00403$ moles [1] 2sf min M2: $1.16 \times 10^{-17} = 0.0040 / V$ so $V = 3.5 \times 10^{14} (dm^3)$ [1] 2sf min ecf on M1 correct answer scores 2 marks	2
5(b)(i)	M1: $[H^+] = \sqrt{2.0 \times 10^{-9} \times 0.20}$ $[H^+] = 2.0 \times 10^{-5} (1.9976 \times 10^{-5})$ M2: pH = 4.7 (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	2

Question	Answer	Marks
5(b)(ii)	M1: Both equilibria correctly stated moles KOH = $0.005 \times 0.2 = 1 \times 10^{-3}$ moles HOBr(initial) = $0.020 \times 0.2 = 4 \times 10^{-3}$ moles HOBr(eqm) = $4 \times 10^{-3} - 1 \times 10^{-3} = 3 \times 10^{-3}$ moles BrO₂(eqm) = 1×10^{-3} M2: ratio $[OBr^-]/[HOBr] = 1/3$ $[H^+] = 3 \times 2.0 \times 10^{-9} = 6 \times 10^{-9}$ pH = 8.2(2) correct answer scores 2 marks	2

Question No 19

Ammonium chloride, $\text{NH}_4\text{Cl}(\text{s})$, dissolves in water to form an acidic solution. This is due to the dissociation of the ammonium ions.



(a) The ammonium ion is a weak acid. The pH of a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride is 4.89 under standard conditions.

(i) Calculate the $[\text{H}^+]$ in a $0.300 \text{ mol dm}^{-3}$ solution of ammonium chloride.

$[\text{H}^+] = \dots\dots\dots \text{ mol dm}^{-3}$ [1]

(ii) Calculate the value of $\text{p}K_{\text{a}}$ of the ammonium ion.

$\text{p}K_{\text{a}} = \dots\dots\dots$ [2]

(b) A buffer solution can be made by mixing ammonium chloride with ammonia solution.

(i) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong acid is added.

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

(ii) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong base is added.

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

(c) (i) Use the value of K_w to calculate $[H^*]$ in pure water under standard conditions.

Show your working.

$$[H^*] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(ii) The pH of pure water at 50 °C is 6.64.

Calculate the numerical value of K_w at 50 °C.

$$K_w = \dots\dots\dots [2]$$

[Total: 8]

(a)(i)	1.3×10^{-5}	1
(a)(ii)	M1: K_a expression used correctly and $K_a = 5.5(3) \times 10^{-10}$ M2: $pK_a = 9.26$ Award 2 marks for correct answer	2
(b)(i)	$NH_3 + H^+ \rightarrow NH_4^+$	1
(b)(ii)	$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ or $H^+ + OH^- \rightarrow H_2O$ and reference to expression in Q shifting R	1
(c)(i)	quotes $K_w = 1 \times 10^{-14}$ or 1×10^{-1} $[H^*][OH^-]$ $[H^*] = 1 \times 10^{-7}$	1
(c)(ii)	M1: $[H^*] = 2.3 \times 10^{-7}$ (calculator value 2.290867×10^{-7}) and $K_w = [2.3 \times 10^{-7}]^2$ M2: $K_w = 5.2 \times 10^{-14}$ calculator 5.248074×10^{-14} Award 2 marks for correct answer	2

Question No 20

(d) A solution of valine in water acts as a buffer solution.

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

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

(ii) Write **two** equations to explain how valine can act as a buffer. Use the formula $\text{H}_2\text{NCH(R)CO}_2\text{H}$ for valine in your equations.

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

(d)(i)	resists change in pH / pH kept within a small range	1
	when small amount of acid or alkali / base is added	1
(d)(ii)	$\text{H}_2\text{NCH(R)CO}_2\text{H} + \text{H}^+ \rightarrow \text{H}_3\text{N}^+\text{CH(R)CO}_2\text{H}$	1
	$\text{H}_2\text{NCH(R)CO}_2\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{NCH(R)CO}_2^- + \text{H}_2\text{O}$	1

Question No 21

- (b) (i)** Write the expression for K_w , the ionic product of water.

$$K_w =$$

[1]

- (ii)** The numerical value of K_w increases with increasing temperature.

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[H^+]:[OH^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH			
ratio $[H^+]:[OH^-]$			

[2]

- (c)** An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

concentration = ... mol dm^{-3} [2]

- (d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

Write **two** equations to describe how hydrogencarbonate ions, HCO_3^- , and carbonic acid, H_2CO_3 , control the pH of blood.

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

- (e) The K_a for ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

- (i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.



[2]

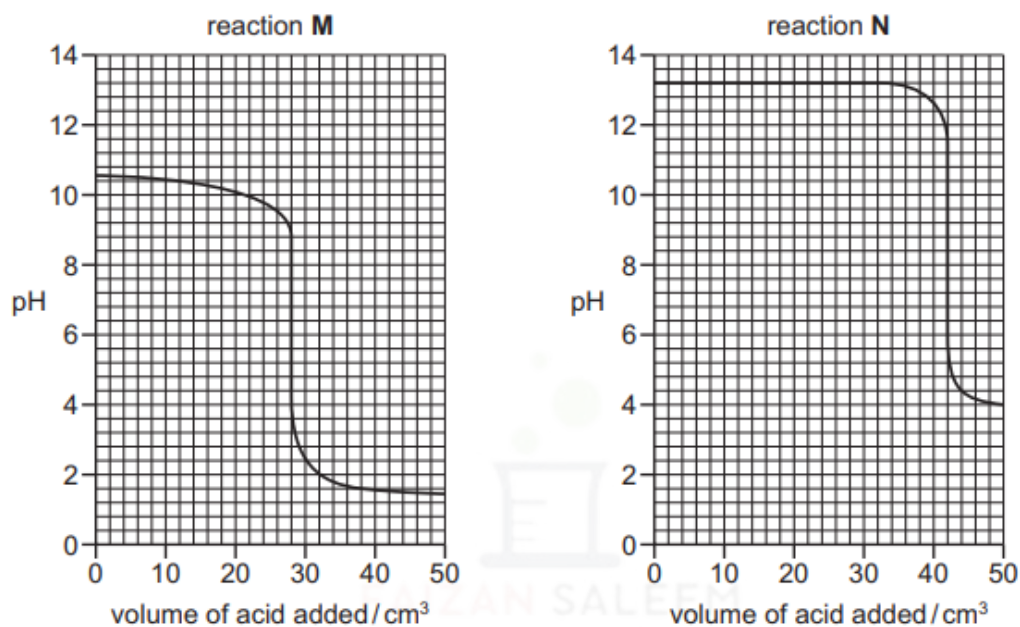
- (ii) A buffer solution was prepared by adding 30.0 cm^3 of 0.25 mol dm^{-3} ethanoic acid, an excess, to 20.0 cm^3 of 0.15 mol dm^{-3} sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. Give your answer to **one** decimal place.

pH = ... [4]



(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.



- (i) Use the titration curve for reaction **M** to deduce the volume of acid added at the end-point for this titration.

volume of acid added at the end-point = ... cm³ [1]

- (ii) The table shows some acid-base indicators.

name of indicator	pH range of colour change
malachite green	0.2–1.8
bromocresol green	3.8–5.4
bromothymol blue	6.0–7.6
thymolphthalein	9.3–10.6

Name a suitable indicator for each of the acid-base titrations **M** and **N**. Explain your answers.

reaction **M** reaction **N**

explanation

[2]

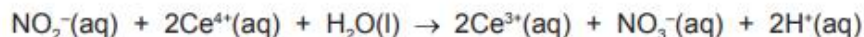
[Total: 19]

(b)(ii)	[1] or each correct tick	2												
	<table><tr><td>effect of increasing temperature</td><td>decreases</td><td>stay the same</td><td>increase</td></tr><tr><td>pH</td><td>✓</td><td></td><td></td></tr><tr><td>ratio of [H⁺]:[OH⁻]</td><td></td><td>✓</td><td></td></tr></table>	effect of increasing temperature	decreases	stay the same	increase	pH	✓			ratio of [H ⁺]:[OH ⁻]		✓		
effect of increasing temperature	decreases	stay the same	increase											
pH	✓													
ratio of [H ⁺]:[OH ⁻]		✓												
4(c)	$[H^+] = 10^{-13.25} = 5.62 \times 10^{-14}$ [1] $[OH^-] = K_w/[H^+] = 1.0 \times 10^{-14}/5.62 \times 10^{-14}$ $[OH^-] = 0.18$ (0.178) (mol dm ⁻³) [1] ecf correct answer scores [2]	2												
4(d)	$HCO_3^- + H^+ \rightarrow H_2CO_3$ OR $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ [1] $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ [1]	2												
(e)(i)	CH₃COOH + H ₂ O $\rightleftharpoons$ CH ₃ COO ⁻ + H ₃ O ⁺ [1] acid + base $\rightleftharpoons$ base + acid [1]	2												
(e)(ii)	M1 moles NaOH = 0.15 × 20/1000 = 0.0030 AND initial moles CH ₃ COOH = 0.25 × 30/1000 OR 0.0075 [1] M2 equilibrium moles CH ₃ COOH = 0.0045 AND equilibrium moles CH ₃ COONa = 0.0030 [1] M3 [CH ₃ COOH] = 0.0045/0.05 = 0.090 AND [CH ₃ COONa] = 0.003/0.05 = 0.060 [H ⁺] = K _a × [CH ₃ COOH]/[CH ₃ COONa] = 2.625 × 10⁻⁵ [1] M4 pH = -log[H ⁺] = 4.6 [1] correct answer scores [4]	4												
4(f)(i)	end point = 28 cm ³	1												
4(f)(ii)	M1 reaction M bromothymol (blue) / bromocresol (green) AND reaction N bromothymol (blue) / thymolphthalein [1] M2 (both indicators have) a pH range / colour change within / in end-point / vertical region / sharp fall of the graph [1]	2												

Question No 22

(b) Sodium nitrite, NaNO_2 , is a decomposition product from heating sodium nitrate, NaNO_3 .

A student analysed a sample of sodium nitrite by titration with aqueous cerium(IV) ions, $\text{Ce}^{4+}(\text{aq})$. The equation for the titration reaction is shown.



- 0.138 g of impure sodium nitrite was dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution required 21.80 cm^3 of $0.0400\text{ mol dm}^{-3}$ $\text{Ce}^{4+}(\text{aq})$ to reach the end-point.

You should assume the impurity does not react with $\text{Ce}^{4+}(\text{aq})$.

Calculate the percentage purity of the sample of sodium nitrite.

..... % [3]

(c) Acidified manganate(VII) ions, MnO_4^- , can also be used to analyse solutions containing nitrite ions, NO_2^- , by titration. In acidic solution, NO_2^- ions exist as HNO_2 .

(i) Use the *Data Booklet* to construct an ionic equation for this reaction.

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

(ii) Use E° values to calculate the E°_{cell} for this reaction.

$E^\circ_{\text{cell}} = \text{..... V}$ [1]

(d) Nitrous acid, HNO_2 , is a weak acid with a K_a of $6.9 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K.

(i) Explain the difference between a strong acid and a weak acid.

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

(ii) Write the expression for the acid dissociation constant, K_a , for HNO_2 .

$K_a =$ [1]

(iii) Calculate the pH of $0.15 \text{ mol dm}^{-3} \text{ HNO}_2$.

pH = ... [2]

(iv) Calculate the percentage of HNO_2 molecules that are ionised in $0.15 \text{ mol dm}^{-3} \text{ HNO}_2$.

% ionisation = ... [1]

(e) Solutions containing a mixture of HNO_2 and NaNO_2 are buffer solutions.

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

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

(ii) Write **two** equations to show how a solution containing a mixture of HNO_2 and NaNO_2 acts as a buffer.

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

5(b)	- moles of $\text{Ce}^{4+} = 0.0400 \times 21.8 / 1000 = 8.72 \times 10^{-4}$ (moles of Ce^{4+}) - moles of $\text{NO}_2^- = 8.72 \times 10^{-4} / 2 = 4.36 \times 10^{-4}$ in 25 cm^3 (use of 2:1 ratio correctly) - moles of $\text{NO}_2^- = 4.36 \times 10^{-4} \times 4 = 1.74(4) \times 10^{-3}$ in 100 cm^3 (use of 4:1 ratio correctly) - mass $\text{NaNO}_2 = 1.74(4) \times 10^{-3} \times (23.0 + 14.0 + 32.0) = 0.120 \text{ g}$ (use of M_r correctly) % purity = $0.120 / 0.138 = 86.96\%$ (use of 0.0138 correctly) two points = [1] four points = [2] all five points = [3]	3
(c)(i)	$5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$ OR $5\text{HNO}_2 + 2\text{MnO}_4^- + \text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$ all species correct [1] balanced [1]	2
(c)(ii)	$E^\circ_{\text{cell}} = 1.52 - 0.94 = \mathbf{0.58 \text{ (V)}}$	1
(d)(i)	weak acid is partly ionised and strong acid is completely ionised	1
(d)(ii)	$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$	1
(d)(iii)	$K_a = [\text{H}^+]^2 / [\text{HNO}_2]$ $[\text{H}^+] = \sqrt{0.00069 \times 0.15} = 1.02 \times 10^{-2} \text{ [1]}$ $\text{pH} = -\log[\text{H}^+] = \mathbf{2.0 \text{ (1.99)}}$ [1] minimum 2 significant figures	2
(d)(iv)	% ionisation = $100 \times 1.02 \times 10^{-2} / 0.15 = \mathbf{6.7-6.8 \text{ \%}}$	1

ICLES 2018

Page 8 of 13

01/42

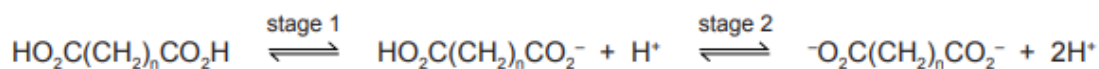
Cambridge International AS/A Level – Mark Scheme
PUBLISHED

October/November 2018

Question	Answer	Marks
(e)(i)	M1 A solution that resists changes in pH [1] M2 when small amounts of acid or alkali are added to it [1]	2
(e)(ii)	M1 $\text{HNO}_2 + \text{OH}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$ [1] M2 $\text{NO}_2^- + \text{H}^+ \rightarrow \text{HNO}_2$ [1]	2

Question No 23

Dicarboxylic acids dissociate in stages.



(a) The $\text{p}K_{\text{a}}$ values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$	$\text{p}K_{\text{a}}(1)$ for stage 1	$\text{p}K_{\text{a}}(2)$ for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the $\text{p}K_{\text{a}}$ of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, is 4.76.

(i) State the mathematical relationship between $\text{p}K_{\text{a}}$ and the acid dissociation constant K_{a} .

..... [1]

(ii) With reference to the table above, suggest why the $\text{p}K_{\text{a}}(1)$ values

- are all smaller than the $\text{p}K_{\text{a}}$ of ethanoic acid,

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

- become larger as n increases.

..... [3]

(iii) Suggest why all the $\text{p}K_{\text{a}}(2)$ values in the table above are larger than the $\text{p}K_{\text{a}}$ of ethanoic acid.

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

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

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

.....
 [2]

(ii) Write two equations to show how monosodium butanedioate, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na}$, acts as a buffer.

.....
 [2]

[Total: 9]

(a) (i)	$\text{p}K_{\text{a}} = -\log K_{\text{a}}$	[1]
(ii)	diacids are more acidic than $\text{CH}_3\text{CO}_2\text{H}$	[1]
	$\text{HO}_2\text{C}-$ group is electron-withdrawing, stabilising the monoanion	
	OR $\text{HO}_2\text{C}-$ group is electron-withdrawing, weakening the O–H bond	[1]
	OR monoanion is stabilised by H–bonding	[1]
	as n increases, the electron-withdrawing group is further away from the ionising CO_2H group OR the (intervening) alkyl groups destabilise the anion	[1]
(iii)	removing H^+ from an anion is not electrostatically favourable	[1]
(b) (i)	a solution which <i>resists</i> changes in pH when <i>small</i> amounts of H^+ or OH^- are added	[1]
		[1]

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Page 5	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – May/June 2016	9701	41

Question	Answer	Marks
(ii)	$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na} + \text{H}^+ \rightarrow \text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} + \text{Na}^+$	[1]
	$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na} + \text{NaOH} \rightarrow \text{NaO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na} + \text{H}_2\text{O}$	[1]
		[Total: 9]

Question No 23

Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak acid*.

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

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	$\text{CH}_3\text{CO}_2\text{H}$	4.8
2	$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	4.9
3	$\text{CH}_3\text{CHClCO}_2\text{H}$	2.8
4	$\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a .

..... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

.....
.....

- acid 2 and acid 3,

.....
.....

- acid 3 and acid 4.

.....
.....

[3]

(d) A monobasic acid, **D**, has $K_a = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of **D**.

pH = ... [2]

(a) (i)	(an acid that is) partially / incompletely ionised / dissociated	1
(b) (i)	$\text{p}K_a = -\log K_a$ or $K_a = 10^{-\text{p}K_a}$	1

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Page 3	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – May/June 2016	9701	42

Question	Answer	Marks
(ii)	ethanoic acid (1) is more acidic than propanoic acid (2) due to smaller electron-donating (R/alkyl) group/less electron-donating (R/alkyl) group(s) 2-chloropropanoic acid (3) is more acidic than propanoic acid (2) due to electron-withdrawing / electronegative (Cl/chlorine) atom 2-chloropropanoic acid (3) is more acidic than 3-chloropropanoic acid (4) since the Cl/chlorine / electronegative atom is closer to the CO_2^- / acid	3
(i)	$K_a = 1.23 \times 10^{-5}$ $[\text{H}^+] = \sqrt{(K_a \cdot c)} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{pH} = 3.0$ (2.96) ecf from $[\text{H}^+]$	2

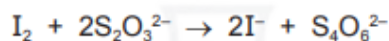
Question No 23

100 cm³
50 Sugar in 100 cm³

(a) Sodium chlorate(I), NaClO, is the active ingredient in commercial bleach. The concentration of chlorate(I) ions was determined by titration.

- 10.0 cm³ of a bleach solution was diluted to 250 cm³ in a volumetric flask using distilled water.
- Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm³ portion of this solution to liberate iodine.
- The resulting solution required 20.80 cm³ of 0.100 mol dm⁻³ aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.



Calculate the concentration, in mol dm⁻³, of ClO⁻ ions in the bleach solution.

concentration of ClO⁻ = ... mol dm⁻³ [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

..... [1]

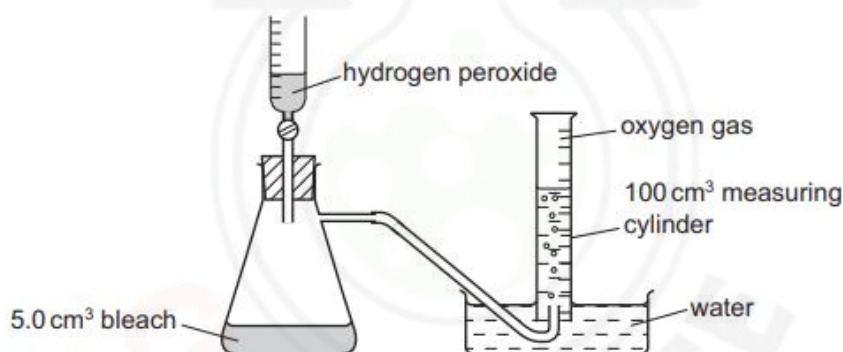
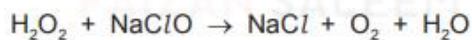
(ii) State the expected colour change you would observe at the end-point in this titration.

from to [1]

(iii) State when in the procedure you would add the indicator.

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

(c) The concentration of chlorate(I) ions can also be determined by adding an excess of hydrogen peroxide to the sample of bleach and measuring the volume of oxygen gas produced.



When an excess of aqueous hydrogen peroxide was added to 5.0 cm³ of a different bleach solution, 82 cm³ of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO⁻ ions in this bleach solution.

concentration of ClO⁻ = ... mol dm⁻³ [2]

- (d) Trichlorocyanuric acid, $C_3Cl_3N_3O_3$, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, $HCIO$.



- (i) Write the expression for K_c for this equilibrium.

$$K_c =$$

[1]

- (ii) In outdoor swimming pools, the $HCIO$ is decomposed by sunlight. The decomposition of $HCIO$ is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of $HCIO$ on the equilibrium in (d). State the effect on K_c .

.....
.....

effect on K_c

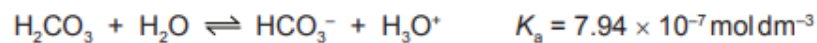
[2]

- (iii) The decomposition of HClO is a redox reaction.

Suggest an equation for this reaction.

..... [1]

- (e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3 , and hydrogencarbonate ions, HCO_3^- . Healthy blood has a pH of 7.40.



- (i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

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

- (ii) A patient's blood has a $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

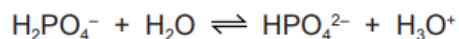
pH = ... [2]

[Total: 16]

7(a)	moles of thiosulfate = $0.1 \times 20.8 / 1000 = 2.08 \times 10^{-3}$ moles of ClO^- in 25 cm^3 portion = $2.08 \times 10^{-3} / 2 = 1.04 \times 10^{-3}$ (moles of ClO^- in $250 \text{ cm}^3 = 1.04 \times 10^{-2}$) concentration of $\text{ClO}^- = 1.04 \times 10^{-2} / (10 / 1000) = 1.04 \text{ (mol dm}^{-3}\text{)}$	1 1 1	3
(b)(i)	starch	1	1
(b)(ii)	blue OR black to colourless	1	1
(b)(iii)	towards / close to the end-point of the titration / when the solution goes yellow	1	1
7(c)	moles of $\text{O}_2 = 82 / 24\,000 = 3.42 \times 10^{-3} = \text{moles } \text{ClO}^- \text{ ions}$ concentration of $\text{ClO}^- = 3.42 \times 10^{-3} / (5 / 1000) = 0.68 / 0.683 / 0.684 \text{ (mol dm}^{-3}\text{)}$	1 1	2
(d)(i)	$K_c = \frac{[\text{C}_3\text{H}_3\text{N}_3\text{O}_3][\text{HClO}_3]^3}{[\text{C}_3\text{Cl}_3\text{N}_3\text{O}_3][\text{H}_2\text{O}]^3}$	1	1
(d)(ii)	(position of eqm) moves to the right / forward reaction predominates / more HClO made (as $[\text{HClO}]$ decreases) no effect on K_c	1 1	2
(d)(iii)	$2\text{HClO} \rightarrow 2\text{HCl} + \text{O}_2$ OR $2\text{HClO} \rightarrow \text{H}_2 + \text{Cl}_2 + \text{O}_2$	1	1
(e)(i)	addition of acid: $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ OR $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2$ addition of base: $\text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ OR $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ and position of eqm moves to the right OR $\text{OH}^- + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$	1 1	2
(e)(ii)	$K_a = ([\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3])$ $[\text{H}^+] = (7.94 \times 10^{-7}) \times 1 / 9.5 = 8.36 \times 10^{-8}$ $\text{pH} = -\log[\text{H}^+] = 7.08$	1 1	2
Total:			16

Question No 24

The phosphate buffer system operates in biological cells. The buffer contains dihydrogen phosphate, H_2PO_4^- , which acts as a weak acid.



(a) Write an expression for the K_a of H_2PO_4^- .

$$K_a =$$

[1]

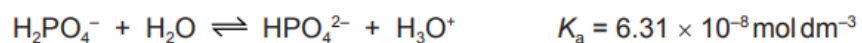
(b) (i) Explain what is meant by the term *buffer solution*.

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

(ii) Write **two** equations to show how a solution containing a mixture of H_2PO_4^- and HPO_4^{2-} acts as a buffer.

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

(c) The pH in many living cells is 7.40.



Calculate the value of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ needed to give a pH of 7.40 in the cells.

$$[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = \dots\dots\dots [3]$$

(d) (i) The H_2PO_4^- ion can also act as a base.

Write an equation to show H_2PO_4^- acting as a base.

..... [1]

(ii) The HPO_4^{2-} ion can also act as an acid.

Write an equation to show HPO_4^{2-} acting as an acid.

..... [1]

[Total: 10]

i(a)	$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$	1	1
b)(i)	a solution that resists changes in pH when small amounts of acid and base/alkali are added	1 1	2
b)(ii)	addition of acid: $\text{H}^+ + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{PO}_4^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ addition of base: $\text{HO}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$ OR $\text{OH}^- + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{O} + \text{PO}_4^{3-}$	1 1	2
i(c)	$[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8}$ $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = K_a/[\text{H}^+]$ $([\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]) = 6.31 \times 10^{-8}/3.98 \times 10^{-8} = 1.58-1.6$	1 1 1	3
d)(i)	$\text{HCl} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{Cl}^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ OR $\text{H}_2\text{O} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{OH}^-$	1	1

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Page 9	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer	Marks
d)(ii)	$\text{NaOH} + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O} + \text{Na}^+$ OR $\text{OH}^- + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$ OR $\text{H}_2\text{O} + \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}_3\text{O}^+$	1 1

Ksp

Question No 25

(e) $\text{Pb}(\text{IO}_3)_2$ is only sparingly soluble in water at 25°C .

The solubility product, K_{sp} , of $\text{Pb}(\text{IO}_3)_2$ is $3.69 \times 10^{-13} \text{ mol}^3 \text{ dm}^{-9}$ at 25°C .

(i) Write an expression for the solubility product of $\text{Pb}(\text{IO}_3)_2$.

$$K_{\text{sp}} =$$

[1]

(ii) Calculate the solubility, in mol dm^{-3} , of $\text{Pb}(\text{IO}_3)_2$ at 25°C .

solubility = ... mol dm^{-3} [2]

e)(i)	$K_{\text{sp}} = [\text{Pb}^{2+}][\text{IO}_3^-]^2$
e)(ii)	M1: $3.69 \times 10^{-13} = x(2x)^2$ OR $x = \sqrt[3]{(3.69 \times 10^{-13} \div 4)}$ M2: $= 4.5(2) \times 10^{-5} (\text{mol dm}^{-3})$ min 2sf ecf

Question No 25

(b) Calcium hydroxide is slightly soluble in water.

- (i)** Write an equation to show the dissociation of calcium hydroxide, $\text{Ca(OH)}_2(\text{s})$, in aqueous solution. Include state symbols.

..... $\rightleftharpoons$ [1]

- (ii)** Calculate the solubility, in mol dm^{-3} , of Ca(OH)_2 .
 $[K_{\text{sp}}: \text{Ca(OH)}_2, 5.02 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}]$

solubility = ... mol dm^{-3} [2]

- (iii)** Suggest how the solubility of Ca(OH)_2 in aqueous NaOH compares to its solubility in water.

Explain your reasoning.

.....

 [1]

1(b)(i)	$\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	1
1(b)(ii)	M1: $K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$ OR $K_{\text{sp}} = 4x^3$ M2: $x = \sqrt[3]{5.02 \times 10^{-6} / 4} = 0.0108 / 0.011 / 1.08 \times 10^{-2} / 1.1 \times 10^{-2} (\text{mol dm}^{-3})$ min 2 sf	2
1(b)(iii)	less soluble / decreases due to the common ion effect OR decreases as equilibrium in (b)(i) has shifted to the left OR decreases as $[\text{OH}^{-}]$ increases causing $[\text{Ca}^{2+}][\text{OH}^{-}]^2$ to exceed its K_{sp}	1

Question No 26

- (c) An aqueous solution of lead(II) nitrate is mixed with an aqueous solution of sodium iodide. A yellow precipitate of lead(II) iodide is formed and is filtered out, leaving solution **X**.

The concentration of Pb^{2+} in solution **X** is $5.68 \times 10^{-3} \text{ mol dm}^{-3}$.

The concentration of I^- in solution **X** is $4.20 \times 10^{-4} \text{ mol dm}^{-3}$.

- (i) Use these data to calculate a value for the solubility product, K_{sp} , of lead(II) iodide.

State the units of K_{sp} .

$K_{\text{sp}} = \dots\dots\dots$

units = $\dots\dots\dots$

[2]

- (ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

$\dots\dots\dots$

$\dots\dots\dots$

$\dots\dots\dots$ [2]

[Total: 10]

2(a)	M1 reference to equilibrium not being established / not at equilibrium [1] M2 concentration in water too high or conc in octan-1-ol too low owtte [1]	2
2(b)(i)	1.1 / 1.13 / 1.127 / 1.1272 [1]	1
2(b)(ii)	M1 $6.760 = (0.762 - x) / x$ [1] M2 $7.76x = 0.762$ $x = 0.0982$ g (correct value scores 2) [1] M3 $0.0982 / 74 = 0.0013 / 0.00133$ mol [1]	3
2(c)(i)	1.0×10^{-9} [1] $\text{mol}^3 \text{dm}^{-9}$ [1]	2
2(c)(ii)	yellow precipitate / yellow solid / yellow crystals [1] common ion effect / K_{sp} has been exceeded [1]	2

Question No 27

- (d) Calcium iodate(V), $\text{Ca}(\text{IO}_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of $\text{Ca}(\text{IO}_3)_2$, and state its units.

$$K_{sp} =$$

units = ... [2]

- (ii) Calculate the numerical value for K_{sp} $\text{Ca}(\text{IO}_3)_2$ at 298 K.

$$K_{sp} = \dots\dots\dots [1]$$

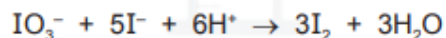
- (iii) When a few cm³ of concentrated Ca(NO₃)₂(aq) is added to a saturated solution of Ca(IO₃)₂ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

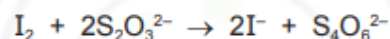
.....
.....
..... [2]

- (e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), NaIO₃.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm³ in a volumetric flask with distilled water.
- 50.0 cm³ of this solution is pipetted into an excess of aqueous acidified potassium iodide.



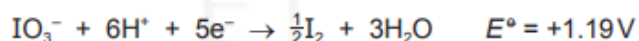
- The iodine produced requires 12.40 cm³ of 0.00200 mol dm⁻³ aqueous sodium thiosulfate solution for complete reaction.



Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of $\text{NaIO}_3 = \dots\dots\dots$ g [3]

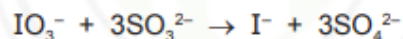
- (f) The half-equation for the reduction of iodate(V) ions is shown.



Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

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

- (g) Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.



The initial rate of reaction was found to be first order with respect to IO_3^- , first order with respect to SO_3^{2-} and first order with respect to H^+ .

- (i) Write the rate equation for this reaction, stating the units of the rate constant, k .

rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$

units of $k = \dots\dots\dots$ [2]

- (ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x .

$x = \dots\dots\dots$ [1]

2(d)(i)	M1 $K_{sp} = [\text{Ca}^{2+}][\text{IO}_3^-]^2$ M2 units = $\text{mol}^3 \text{dm}^{-9}$	2
2(d)(ii)	$K_{sp} = 4 \times (5.6 \times 10^{-3})^3$ $K_{sp} = 7.03 \times 10^{-7}$ 2sf min	1
(d)(iii)	M1 $\text{Ca}(\text{IO}_3)_2$ AND as solubility of $\text{Ca}(\text{IO}_3)_2$ decreases M2 due to common ion effect	2
2(e)	M1 moles $\text{S}_2\text{O}_3^{2-} = 0.002 \times 12.4/1000$ $= 2.48 \times 10^{-5}$ moles of $\text{I}_2 = 1.24 \times 10^{-5}$ M2 moles of $\text{IO}_3^- = 4.13 \times 10^{-6}$ in 50 cm^3 moles of $\text{IO}_3^- = 2.07 \times 10^{-5}$ in 250 cm^3 mass of $\text{NaIO}_3 = 2.07 \times 10^{-5} \times 197.9$ M3 mass of $\text{NaIO}_3 = 0.0041$	3
2(f)	It is feasible as the E_{cell} will be positive/+0.12 V	1
2(g)(i)	M1 Rate = $k[\text{IO}_3^-][\text{SO}_3^{2-}][\text{H}^+]$ M2 units = $\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$	2
2(g)(ii)	0.10	1

Question No 28

- (a) The following table lists the solubilities of the hydroxides and carbonates of some of the Group 2 elements, **M**, at 25°C .

element M	solubility / mol dm^{-3}	
	$\text{M}(\text{OH})_2$	MCO_3
Mg	2.0×10^{-4}	1.5×10^{-3}
Ca	1.5×10^{-2}	1.3×10^{-4}
Sr	3.4×10^{-2}	7.4×10^{-5}
Ba	1.5×10^{-1}	9.1×10^{-5}

(b) (i) Calculate the value of the solubility product, K_{sp} , of magnesium hydroxide at 25 °C.

$K_{sp} =$ [2]

(ii) State what would be observed if a few drops of a saturated solution of barium hydroxide are added to a saturated solution of barium carbonate. Explain your answer.

observation

explanation

[2]

(b)(i)	$K_{sp} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2$ OR $K_{sp} = (2.0 \times 10^{-4})(4.0 \times 10^{-4})^2$ $= 3.2 \times 10^{-11}$	2
(b)(ii)	M1 (white) ppt. / solid (of BaCO_3) will appear M2 due to the common ion effect OR the $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ equilibrium shifts to the left	2

Silver sulfide, Ag_2S , is very insoluble in water.

- (a) (i) Write an expression for the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$.

$$K_{\text{sp}} =$$

[1]

- (ii) The solubility of $\text{Ag}_2\text{S}(\text{s})$ in water at 298 K is $1.16 \times 10^{-17} \text{ mol dm}^{-3}$.

Calculate the numerical value of the solubility product, K_{sp} , of $\text{Ag}_2\text{S}(\text{s})$ at 298 K.

$$K_{\text{sp}} = \dots\dots\dots [2]$$

- (iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $\text{Ag}_2\text{S}(\text{s})$ under standard conditions.

$$\text{volume} = \dots\dots\dots \text{ dm}^3 [2]$$

(b) Bromic(I) acid, HOBr(aq) , is a weak acid. Its K_a is $2.0 \times 10^{-9} \text{ mol dm}^{-3}$.

(i) Calculate the pH of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH , are added to 20.0 cm^3 of $0.20 \text{ mol dm}^{-3} \text{ HOBr(aq)}$.

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

5(a)(i)	$K_{sp} = [Ag^+]^2[S^{2-}]$	1
5(a)(ii)	$[S^{2-}] = 1.16 \times 10^{-17}$ $[Ag^+] = 2.32 \times 10^{-17}$ $K_{sp} = 6.2(4) \times 10^{-51}$ minimum 2 sig. fig. correct answer scores 2 marks Award 1 mark for two points, award 2 marks for three points	2
5(a)(iii)	M1: moles $Ag_2S = 1 / 247.9 = 0.00403$ moles [1] 2sf min M2: $1.16 \times 10^{-17} = 0.0040 / V$ so $V = 3.5 \times 10^{14} (dm^3)$ [1] 2sf min ecf on M1 correct answer scores 2 marks	2
5(b)(i)	M1: $[H^+] = \sqrt{2.0 \times 10^{-9} \times 0.20}$ $[H^+] = 2.0 \times 10^{-5} (1.9976 \times 10^{-5})$ M2: pH = 4.7 (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	2

Question	Answer	Marks
5(b)(ii)	M1: Both equilibria correctly stated moles KOH = $0.005 \times 0.2 = 1 \times 10^{-3}$ moles HOBr(initial) = $0.020 \times 0.2 = 4 \times 10^{-3}$ moles HOBr(eqm) = $4 \times 10^{-3} - 1 \times 10^{-3} = 3 \times 10^{-3}$ moles BrO⁻(eqm) = 1×10^{-3} M2: ratio $[OBr^-]/[HOBr] = 1/3$ $[H^+] = 3 \times 2.0 \times 10^{-9} = 6 \times 10^{-9}$ pH = 8.2(2) correct answer scores 2 marks	2

Question No 29

(b) The solubility of $\text{Sr}(\text{OH})_2$ is $3.37 \times 10^{-2} \text{ mol dm}^{-3}$ at 0°C .

(i) Write an expression for the solubility product of $\text{Sr}(\text{OH})_2$.

$$K_{\text{sp}} =$$

[1]

(ii) Calculate the value of K_{sp} at 0°C . Include units in your answer.

$$K_{\text{sp}} = \dots\dots\dots \text{units} = \dots\dots\dots$$

[2]

(b)(i)	$K_{\text{sp}} = [\text{Sr}^{2+}][\text{OH}^-]^2$	1
(b)(ii)	$K_{\text{sp}} = (3.37 \times 10^{-2}) \times (6.74 \times 10^{-2})^2 = 1.5 \times 10^{-4}$ units: $\text{mol}^3 \text{dm}^{-9}$	2

Question No 30

(c) The solubility of calcium ethanedioate, CaC_2O_4 , is $6.65 \times 10^{-3} \text{ g dm}^{-3}$ at 298 K.

(i) Write an expression for the solubility product, K_{sp} , of CaC_2O_4 . Include its units.

$$K_{\text{sp}} =$$

units = $\dots\dots\dots$

[2]

(ii) Calculate the numerical value of K_{sp} CaC_2O_4 at 298 K. Give your answer in **standard form** to **two** significant figures.

$$K_{\text{sp}} \text{ CaC}_2\text{O}_4 = \dots\dots\dots$$
 [2]

(c)(i)	$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$ [1] units $\text{mol}^2 \text{dm}^{-6}$ [1]	2
(c)(ii)	$[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] = 6.65 \times 10^{-3}/128.1 = 5.19 \times 10^{-5} \text{ mol dm}^{-3}$ [1] $K_{sp} = (5.19 \times 10^{-5})^2 = 2.7 \times 10^{-9} \text{ mol}^2 \text{dm}^{-6}$ [1]	2

Question No 31

(d) The numerical value of the solubility product, K_{sp} , of CaF_2 is 3.45×10^{-11} at 298 K.

(i) Write an expression for the solubility product of CaF_2 . Include its units.

$$K_{sp} =$$

units = ...
[2]

(ii) Calculate the solubility of CaF_2 at 298 K.

solubility = ... mol dm^{-3} [1]

(d)(i)	$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$ [1] units = $\text{mol}^3 \text{dm}^{-9}$ [1]	2
(d)(ii)	$K_{sp} = 4x^3 = 3.45 \times 10^{-11}$ $x = 2.05 \times 10^{-4} (\text{mol dm}^{-3})$	1

Question No 32

- (a) The table lists values of solubility products, K_{sp} , of some Group 2 carbonates.

	solubility product in water at 298 K, $K_{sp} / \text{mol}^2 \text{dm}^{-6}$
MgCO_3	1.0×10^{-5}
CaCO_3	5.0×10^{-9}
SrCO_3	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

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

- (b) (i) Write an equation to show the equilibrium for the solubility product for MgCO_3 .
Include state symbols.

$\rightleftharpoons$ [1]

- (ii) With reference to your equation in (i), suggest what is observed when a few cm^3 of concentrated $\text{Na}_2\text{CO}_3(\text{aq})$ are added to a saturated solution of MgCO_3 . Explain your answer.

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

- (c) Use the data in the table to calculate the solubility of MgCO_3 in water at 298 K, in g dm^{-3} .

solubility of $\text{MgCO}_3 = \dots\dots\dots \text{g dm}^{-3}$ [2]

(d) (i) Magnesium nitrate decomposes at a **lower** temperature than barium nitrate.

Explain why.

.....

 [2]

(ii) A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

..... [1]

(iii) When water was added to the white solid produced in (d)(ii), an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

.....
 [2]

[Total: 11]

Question	Answer	Marks
2(a)	it/solubility decreases down the group and K_{sp} decreases	1
(b)(i)	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	1
(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	1
	as $[CO_3^{2-}]$ increases shifting equilibrium to the LHS (precipitating out $MgCO_3$)	1
2(c)	$\text{solubility} = \sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3} \text{ mol dm}^{-3}$	1
	$\text{solubility} = 3.2 \times 10^{-3} \times 84.3 = 0.27 \text{ g dm}^{-3}$	1
(d)(i)	Mg^{2+} ion is smaller than Ba^{2+} ion or ionic radii increase down group or a	1
	(Mg^{2+}) distorts / polarises / the anion / nitrate group / nitrate ion / $NO_3^{(1)-}$ / NO_3 ion more easily (than Ba^{2+}) or a	1
(d)(ii)	$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2}O_2$	1
(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	1
	$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$	1

Question No 33

- (a) When water is added to magnesium nitride, Mg_3N_2 , the products are a white suspension of $\text{Mg}(\text{OH})_2$ and an alkaline gas.

(i) Write an equation for this reaction.

..... [1]

- (ii) A 2.52 g sample of Mg_3N_2 is added to an excess of water.

Calculate the mass of $\text{Mg}(\text{OH})_2$ formed.

mass of $\text{Mg}(\text{OH})_2$ = ... g [2]

- (b) State and explain how the solubility of the Group 2 hydroxides varies down the group.

.....
.....
.....
.....
..... [4]

- (c) Magnesium hydroxide is sparingly soluble in water. The concentration of its saturated solution at 298 K is $1.7 \times 10^{-4} \text{ mol dm}^{-3}$.

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

$$K_{\text{sp}} =$$

[1]

- (ii) Calculate the value of K_{sp} for $\text{Mg}(\text{OH})_2$ at 298 K and state its units.

$K_{\text{sp}} =$ units [2]

- (d) The temperature at which the Group 2 hydroxides and carbonates start to decompose increases down the group.

Suggest an explanation for this trend in the decomposition temperature of the Group 2 hydroxides.

.....

.....

..... [2]

[Total: 12]

1(a)(i)	$\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$	1
(a)(ii)	moles of $\text{Mg}_3\text{N}_2 = 2.52 / 100.9 = 0.025$ (0.0249)	1
	(moles of $\text{Mg}(\text{OH})_2 = 0.075$ (0.0749)) mass of $\text{Mg}(\text{OH})_2 = (0.075 \times 58.3) = 4.37 \text{ g}$ or 4.4 g	1
2(b)	solubility increases (down the group)	1
	ΔH_{latt} and ΔH_{hyd} both decrease / less exothermic / more endothermic	1
	but ΔH_{latt} decreases more (than ΔH_{hyd} decreases)	1
	ΔH_{sol} becomes more negative / more exothermic / less endothermic	1
1(c)(i)	$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$	1
(c)(ii)	$K_{\text{sp}} = (1.7 \times 10^{-4}) \times (2 \times 1.7 \times 10^{-4})^2 = 2.0 \times 10^{-11}$ (1.97×10^{-11})	1
	$\text{mol}^3 \text{ dm}^{-9}$	1
2(d)	cations become bigger / ionic radius increases	1
	polarisation/distortion of anion / hydroxide ion decreases	1

Question No 34

Ethoxyethane, $C_2H_5OC_2H_5$, can dissolve both in water and in octan-1-ol. The expression and numerical value for the partition coefficient of ethoxyethane between water and octan-1-ol are given. Water and octan-1-ol are immiscible.

$$K_{pc} = \frac{\text{concentration of } C_2H_5OC_2H_5 \text{ in octan-1-ol}}{\text{concentration of } C_2H_5OC_2H_5 \text{ in water}} = 6.760 \text{ at } 20^\circ C$$

- (a) In an experiment, octan-1-ol at $20^\circ C$ is added to a solution of ethoxyethane in water at $20^\circ C$. The mixture is analysed immediately and a value of K_{pc} is calculated.

The calculation is performed correctly; the value calculated is 5.625.

Explain why the value calculated is **less** than 6.760.

Equilibrium is not being established and concentration of ethoxyethane is high in water as compared to octan-1-ol. [2]

- (b) A second experiment is performed and the value of K_{pc} is found to be 6.760. The concentration of ethoxyethane in the octan-1-ol layer is 7.62 g dm^{-3} .

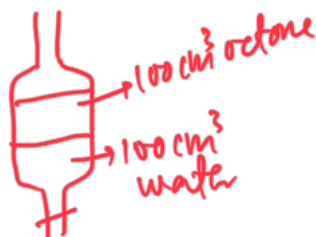
- (i) Calculate the concentration, in g dm^{-3} , of ethoxyethane in the aqueous layer.

$$K_{pc} = \frac{\text{Conc of ethoxyethane in octane}}{\text{Conc of ethoxyethane in water}}$$

$$6.76 = \frac{7.62}{x} \Rightarrow x = \frac{7.62}{6.76} = 1.127 \text{ g dm}^{-3} [1]$$

- (ii) 100 cm^3 of the octan-1-ol layer is taken and shaken with 100 cm^3 of water.

Calculate the maximum amount, in mol, of ethoxyethane that can be extracted into the water.



$$100 \text{ cm}^3 = 7.62 \text{ g}$$

$$100 \text{ cm}^3 = x$$

$$x = 0.762 \text{ g}$$

$$K_{pc} = \frac{\text{Conc in octane}}{\text{Conc in water}}$$

$$6.760 = \frac{0.762 - n}{100} \times \frac{100}{n}$$

$$6.760 = \frac{0.762}{n}$$

$$n = 0.0982 \text{ g} [3]$$

- (c) An aqueous solution of lead(II) nitrate is mixed with an aqueous solution of sodium iodide. A yellow precipitate of lead(II) iodide is formed and is filtered out, leaving solution **X**.

The concentration of Pb^{2+} in solution **X** is $5.68 \times 10^{-3} \text{ mol dm}^{-3}$.

The concentration of I^- in solution **X** is $4.20 \times 10^{-4} \text{ mol dm}^{-3}$.

- (i) Use these data to calculate a value for the solubility product, K_{sp} , of lead(II) iodide.

State the units of K_{sp} .

$K_{\text{sp}} = \dots\dots\dots$

units = $\dots\dots\dots$

[2]

- (ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

.....

 [2]

[Total: 10]

2(a)	M1 reference to equilibrium not being established / not at equilibrium [1] M2 concentration in water too high or conc in octan-1-ol too low owtte [1]	2
2(b)(i)	1.1 / 1.13 / 1.127 / 1.1272 [1]	1
2(b)(ii)	M1 $6.760 = (0.762 - x) / x$ [1] M2 $7.76x = 0.762$ $x = 0.0982 \text{ g}$ (correct value scores 2) [1] M3 $0.0982 / 74 = 0.0013 / 0.00133 \text{ mol}$ [1]	3
2(c)(i)	1.0×10^{-9} [1] $\text{mol}^3 \text{ dm}^{-9}$ [1]	2
2(c)(ii)	yellow precipitate / yellow solid / yellow crystals [1] common ion effect / K_{sp} has been exceeded [1]	2

Kpc

Question No 34

- (a) (i) Give the mathematical expression for each of the terms pH and K_w .

pH = ...

K_w = ... [2]

- (ii) Calculate the pH of 0.027 mol dm⁻³ NaOH(aq).

pH = ... [1]

- (b) The K_a value of chloric(I) acid, HClO, is 3.72×10^{-8} mol dm⁻³.

Calculate the pH of 0.010 mol dm⁻³ HClO(aq).

pH = ... [1]

- (c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00 g of ethanamide is added to 50.0 cm³ of water and this is then shaken with 50.0 cm³ of octan-1-ol, it is found that the water layer contains 0.935 g of ethanamide at equilibrium.

- (i) Calculate the partition coefficient, K_{pc} , for ethanamide in water and octan-1-ol.

K_{pc} = ... [1]

- (ii) The 50.0 cm³ of water containing 0.935 g of ethanamide is then shaken with 100.0 cm³ of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm³ of octan-1-ol at equilibrium.

mass of ethanamide = ... g
[2]

4(a)(i)	$(\text{pH} =) -\log[\text{H}^+] \text{ OR } -\lg[\text{H}^+] [1]$ $(K_w =) [\text{H}^+][\text{OH}^-] [1]$
4(a)(ii)	$[\text{H}^+] = 1 \times 10^{-14} / 0.027 = 3.7037 \times 10^{-13}$ $\text{pH} = -\log(3.7037 \times 10^{-13}) = \mathbf{12.4} [1] \text{ min 3sf}$
4(b)	$[\text{H}^+] = \sqrt{3.72 \times 10^{-8} \times 0.010} = 1.9287 \times 10^{-5}$ $\text{pH} = -\log(1.9287 \times 10^{-5}) = \mathbf{4.7} [1] \text{ min 2sf}$
4(c)(i)	$K_{\text{pc}} = (0.935 / 50) / (0.065 / 50)$ $K_{\text{pc}} = \mathbf{14.4} (14.38) [1] \text{ min 3sf}$
4(c)(ii)	M1: $14.4 = ((0.935 - x) / 50) / (x / 100) [1] \text{ ecf from 4(c)(i)}$ M2: $x = \mathbf{0.114} \text{ g} [1] \text{ min 2sf ecf from M1}$



Question No 35

- (a) Write an expression for the K_a of the weak acid HA in terms of the concentrations of the species involved.

$$K_a =$$

[1]

- (b) The hydroxylammonium ion, HONH_3^+ , is a weak acid. A $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ solution of hydroxylammonium ions has a pH of 4.41.

- (i) Calculate the K_a of HONH_3^+ .

$$K_a = \dots\dots\dots [2]$$

- (ii) Calculate the $\text{p}K_a$ of HONH_3^+ .

$$\text{p}K_a = \dots\dots\dots [1]$$

- (c) The solubility product of manganese(II) hydroxide, $\text{Mn}(\text{OH})_2$, in water is $1.1 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ at 298 K.

Calculate the solubility of $\text{Mn}(\text{OH})_2$ in water at 298 K.

$$\text{solubility} = \dots\dots\dots \text{mol dm}^{-3} [2]$$

[Total: 6]

2(a)	$[\text{H}^+][\text{A}^-] / [\text{HA}]$ [1]	1
2(b)(i)	$[\text{H}^+] = 3.9 \times 10^{-5}$ [1] $K_a = 1.5 \times 10^{-6}$ [1]	2
2(b)(ii)	5.82 [1]	1
2(c)	$4 \times 3 = 1.1 \times 10^{-11}$ [1] $x = 1.4 \times 10^{-4}$ [1]	2



Question No 36

- (a) (i) State what is meant by the term *partition coefficient*.

.....

.....

..... [1]

Ammonia is soluble in both water and organic solvents.
An aqueous solution of ammonia is shaken with the immiscible organic solvent trichloromethane.
The mixture is left to reach equilibrium.

Samples are taken from each layer and titrated with dilute hydrochloric acid.

- A 25.0 cm³ sample from the trichloromethane layer requires 13.0 cm³ of 0.100 mol dm⁻³ HCl to reach the end-point.
- A 10.0 cm³ sample from the aqueous layer requires 12.5 cm³ of 0.100 mol dm⁻³ HCl to reach the end-point.

- (ii) Calculate the partition coefficient, $K_{\text{partition}}$, of ammonia between trichloromethane and water.

$$K_{\text{partition}} = \dots\dots\dots [2]$$

- (iii) Butylamine, C₄H₉NH₂, is also soluble in both water and organic solvents.

Suggest how the value of $K_{\text{partition}}$ of butylamine between trichloromethane and water would compare to the value of $K_{\text{partition}}$ calculated in (ii). Explain your answer.

.....

.....

..... [2]

(a)(i)	(ratio of the) concentrations of a solute in two solvents / liquids at <u>equilibrium</u>	1
(a)(ii)	$[\text{NH}_3]_{\text{aq}} = 0.1 \times 12.5 / 10 = 0.125 \text{ mol dm}^{-3}$ $[\text{NH}_3]_{\text{CHCl}_3} = 0.1 \times 13 / 25 = 0.052 \text{ mol dm}^{-3}$ $\text{ratio} = K_{\text{partition}} = 0.052 / 0.125 = 0.416$	2
(a)(iii)	$K_{\text{partition}}$ will be larger for butylamine than for ammonia butylamine contains a hydrophobic / non-polar (C ₄) group	2

Question No 37

(d) (i) Explain what is meant by the term *partition coefficient*, $K_{\text{partition}}$.

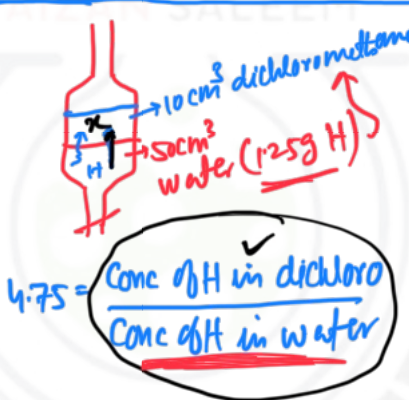
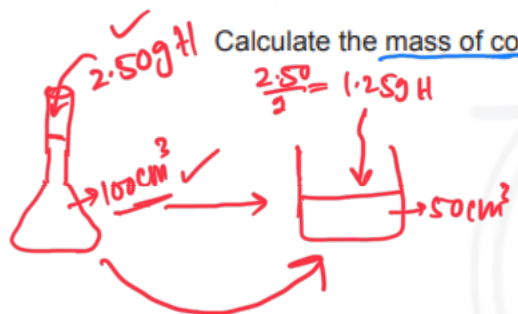
it is the ratio of the concentration of solute in two immiscible solvents at equilibrium

K_{pc}

(ii) The partition coefficient of organic compound H between dichloromethane and water is 4.75.

- 2.50 g of compound H was dissolved in water and made up to 100 cm³ in a volumetric flask
- 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane.

Calculate the mass of compound H that was extracted into the dichloromethane.



$$4.75 = \frac{\text{mass of H in dichloro}}{\text{Vol of dichloro}} \div \frac{\text{mass of H in water}}{\text{Vol of water}}$$

$$4.75 = \frac{\text{mass of H in dichloro}}{\text{Vol of dichloro}} \times \frac{\text{Vol of water}}{\text{mass of H in water}}$$

$$4.75 = \frac{x}{10} \times \frac{50}{1.25 - x}$$

mass of compound H extracted = ... g [2]

(d)(i)	M1 ratio of the concentrations of solute in two (immiscible) solvents [1] M2 at equilibrium [1]	2
(d)(ii)	$K_{\text{partition}} = (x/10)/(1.25-x/50)$ [1] $4.75(1.25-x) = 5x$ $x = 5.9375/9.75 = 0.61 \text{ g}$ [1] correct answer scores [2]	2

$$4.75 = \frac{50x}{10(1.25-x)}$$

$$4.75 = \frac{50x}{12.5 - 10x}$$

$$4.75(12.5 - 10x) = 50x$$

$$59.375 - 47.5x = 50x$$

$$59.375 = 50x + 47.5x$$

$$59.375 = 97.5x$$

$$x = 0.61$$

Question No 38

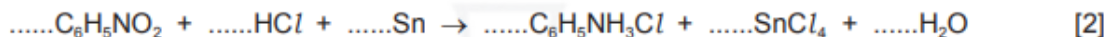
Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in acid solution in a two step process.

- (a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.



- (ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to (i) useful.



- (b) When 5.0g of nitrobenzene was reduced in this reaction, 4.2g of phenylammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

- (c) Following the reaction in (b), an excess of $\text{NaOH}(\text{aq})$ was added to liberate phenylamine from phenylammonium chloride.

- (i) Calculate the mass of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, produced when 4.20g of phenylammonium chloride reacts with an excess of $\text{NaOH}(\text{aq})$.

mass of phenylamine = ... g [1]

The final volume of the alkaline solution of phenylamine in (i) was 25.0 cm³. The phenylamine was extracted by addition of 50 cm³ of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

- (ii) Use the data to calculate the partition coefficient, $K_{\text{partition}}$, of phenylamine between dichloromethane and water.

$$K_{\text{partition}} = \dots\dots\dots [2]$$

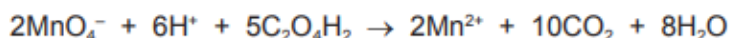
(a) (i)	$\text{C}_6\text{H}_5\text{NO}_2 + 6\text{e}^- + 6\text{H}^+ \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$	[1]
(ii)	$2\text{C}_6\text{H}_5\text{NO}_2 + 14\text{HCl} + 3\text{Sn} \rightarrow 2\text{C}_6\text{H}_5\text{NH}_3\text{Cl} + 3\text{SnCl}_4 + 4\text{H}_2\text{O}$	[2]
(b)	(M_r values: $\text{C}_6\text{H}_5\text{NO}_2 = 123$ $\text{C}_6\text{H}_5\text{NH}_3\text{Cl} = 129.5$) theoretical yield = $5.0 \times 129.5/123 = 5.26$ g percentage yield = $100 \times 4.2/5.26 = 79.8\%$ (80%)	[1] [1]
(c) (i)	$\text{C}_6\text{H}_5\text{NH}_2 = 93$ yield of phenylamine = $4.2 \times 93/129.5 = 3.016$ g	[1]
(ii)	mass left in water = $3.016 - 2.68 = 0.336$ g $K_{\text{part}} = (2.68/50)/(0.336/25) = 3.99$	[1] [1]

Question No 39

- (a) Ethanedioic acid, $\text{C}_2\text{O}_4\text{H}_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm³ with water.
- A 25.0 cm³ portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with 0.0200 mol dm⁻³ KMnO_4 .

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.



In the titration, 15.20 cm³ of KMnO_4 was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

percentage of ethanedioic acid = ... % [3]

(a)	$n(\text{MnO}_4^-) = 0.02 \times 15.2 / 1000 = 3.04 \times 10^{-4} \text{ mol}$ $n(\text{C}_2\text{O}_4\text{H}_2) = 3.04 \times 10^{-4} \times 5/2 = 7.6 \times 10^{-4} \text{ (in } 25 \text{ cm}^3) = 3.04 \times 10^{-3} \text{ mol in } 100 \text{ cm}^3$ $M_r = 24 + 64 + 2 = 90$ $\text{mass of C}_2\text{O}_4\text{H}_2 = 3.04 \times 10^{-3} \times 90$ $= 0.2736 \text{ g (0.274)}$ $\text{percentage} = 0.2736 \times 100/40 = 0.68\%$	 [1] [1] [1]
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