

Surname <i>StemUp Model Solution</i>	Centre Number	Candidate Number
First name(s)		2



GCE A LEVEL

1410U30-1



S23-1410U30-1

MONDAY, 12 JUNE 2023 – MORNING

CHEMISTRY – A2 unit 3
Physical and Inorganic Chemistry

1 hour 45 minutes

Section A

Section B

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
1. to 7.	10	
8.	14	
9.	13	
10.	18	
11.	11	
12.	14	
Total	80	

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ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:

- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid. You may use a pencil for graphs and diagrams only.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions.

Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q9(a)**.

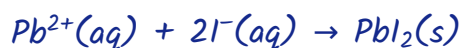


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SECTION A

Answer **all** questions.

1. Addition of aqueous lead nitrate to aqueous potassium iodide causes a precipitate to form. Write an ionic equation for the formation of the precipitate, including state symbols. [1]



2. Use the data shown to explain why silver chloride is insoluble in water. [2]

	Enthalpy / kJ mol^{-1}
Standard enthalpy of hydration for Ag^{+}	-464
Standard enthalpy of hydration for Cl^{-}	-364
Enthalpy of lattice formation of AgCl	-905

$$\Delta H_{\text{soln}} = (-464) + (-364) - (-905) = +77 \text{ kJ mol}^{-1}$$

The enthalpy of solution is positive (endothermic), so AgCl is insoluble in water.

3. A white crystalline solid gives a red colour in a flame test and addition of concentrated sulfuric acid to the solid gives purple fumes and a smell of rotten eggs. Name the ions present, giving your reasons. [2]

Lithium ion, Li^{+} : it gives a red flame test.

Iodide ion, I^{-} : purple fumes are iodine, I_2 , and the rotten egg smell is hydrogen sulfide, H_2S .

4. Aluminium chloride forms Al_2Cl_6 dimers using coordinate bonding. Explain why the coordinate bonds form. [2]

Al in AlCl_3 is electron deficient: only six outer electrons, not a full octet.

A lone pair on a Cl atom of another AlCl_3 molecule is donated into the empty orbital on Al .



5. Addition of ammonia solution to aqueous copper(II) sulfate causes a pale blue precipitate to form followed by a coloured solution when excess ammonia solution is added.

Give the colour of the solution formed.

[1]

Royal blue

6. The Haber process uses a heterogeneous catalyst.
State what is meant by the term 'heterogeneous' in this context.

[1]

The catalyst is in a different physical state from the reactants (solid iron catalyst, gaseous N_2 and H_2).

7. Hexagonal boron nitride is sometimes called white graphite. Give **one** difference between the physical properties of hexagonal boron nitride and graphite.

[1]

Graphite conducts electricity but hexagonal boron nitride does not conduct electricity.

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SECTION B

8. When performing redox titrations the concentration of one solution is found by reaction with another solution of known concentration. Some oxidising agents are classed as primary standards as their concentrations can be calculated precisely from the mass used. Other oxidising agents need to be standardised by reaction with solutions of known concentration before use.

- (a) Potassium dichromate, $K_2Cr_2O_7$, is a primary standard. Calculate the concentration of a solution of potassium dichromate made from 5.00 g of potassium dichromate in 250 cm³ of deionised water. [2]

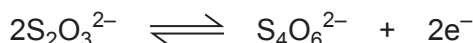
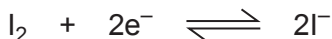
$$M_r(K_2Cr_2O_7) = 2(39.1) + 2(52.0) + 7(16.0) = 294.2$$

$$\text{moles} = 5.00 \div 294.2 = 0.0170 \text{ mol}$$

$$\text{concentration} = 0.0170 \div 0.250 = 0.0680 \text{ mol dm}^{-3}$$

$$\text{concentration} = \underline{0.0680} \text{ mol dm}^{-3}$$

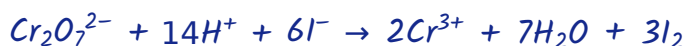
- (b) Sodium thiosulfate, $Na_2S_2O_3$, can be standardised using potassium dichromate. To do this, acidified potassium dichromate is used to oxidise iodide ions to iodine molecules and the sodium thiosulfate is then used to reduce the iodine formed.



- (i) Write the half-equation for acidified dichromate ions acting as an oxidising agent. [1]



- (ii) Write an equation for the oxidation of iodide ions to iodine molecules using acidified dichromate. [1]



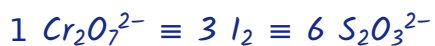
- (iii) Excess KI(aq) was added to 25.0 cm^3 of the aqueous potassium dichromate from part (a) with a small amount of dilute acid. This produced iodine. Aqueous sodium thiosulfate was added from a burette and 24.30 cm^3 of $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ was needed for complete reaction with the iodine.

I. The titration used an indicator. Name the indicator used. [1]

Starch

II. Calculate the concentration of the aqueous sodium thiosulfate. [3]

$$\text{moles } \text{Cr}_2\text{O}_7^{2-} = 0.0680 \times 25.0 \div 1000 = 1.70 \times 10^{-3} \text{ mol}$$



$$\text{moles } \text{S}_2\text{O}_3^{2-} = 6 \times 1.70 \times 10^{-3} = 0.0102 \text{ mol}$$

$$\text{concentration} = 0.0102 \div (24.30 \div 1000) = 0.420 \text{ mol dm}^{-3}$$

$$\text{concentration} = \underline{0.420} \text{ mol dm}^{-3}$$



- (c) Addition of aqueous sodium hydroxide to the solution of potassium dichromate causes a colour change.
State the colour change and explain why this is not a redox reaction. [2]

Orange to yellow.

Cr has oxidation state +6 in both $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ; it does not change, so there is no oxidation or reduction.

- (d) Heating solid potassium dichromate can cause it to decompose releasing oxygen gas.



$$\Delta H^\ominus = 348 \text{ kJ mol}^{-1} \quad \Delta S^\ominus = 385 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substance	Standard enthalpy change of formation, $\Delta_f H^\ominus / \text{kJ mol}^{-1}$
K_2CrO_4	-1382
Cr_2O_3	-1128

- (i) Calculate the standard enthalpy change of formation of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. [2]

$$\Delta H^\ominus = \Sigma \Delta_f H^\ominus(\text{products}) - \Sigma \Delta_f H^\ominus(\text{reactants})$$

$$348 = 4(-1382) + 2(-1128) + 3(0) - 4\Delta_f H^\ominus(\text{K}_2\text{Cr}_2\text{O}_7)$$

$$4\Delta_f H^\ominus = -5528 - 2256 - 348 = -8132, \text{ so } \Delta_f H^\ominus = -2033$$

$$\Delta_f H^\ominus = \dots\dots\dots -2033 \dots\dots\dots \text{ kJ mol}^{-1}$$

- (ii) Calculate the minimum temperature required for this reaction. [2]

$$\text{minimum } T \text{ when } \Delta G = 0, \text{ so } T = \Delta H \div \Delta S$$

$$T = 348\,000 \div 385 = 904 \text{ K}$$

$$\text{minimum temperature} = \dots\dots\dots 904 \dots\dots\dots \text{ K}$$



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9. (a) The elements of the p-block show a variety of oxidation states within the same group, whilst some elements of the d-block can show an even wider range of oxidation states.

- Some oxides of group 4 have an oxidation state of +4 such as CO_2 , SiO_2 and PbO_2 and others have an oxidation state of +2 such as CO and PbO . There is no stable oxide with the formula SiO .
- Some chlorides of group 5 have a +5 oxidation state such as PCl_5 and some have an oxidation state of +3 such as NCl_3 and PCl_3 . There is no stable chloride with the formula NCl_5 .
- Manganese forms a range of oxides including MnO , Mn_2O_3 and MnO_2 which have oxidation states of +2, +3 and +4 respectively.

Explain why these elements can form the oxidation states shown and why SiO and NCl_5 do not form. [6 QER]

Group 4: the +4 state is most stable at the top of the group (C, Si) but +2 becomes more stable down the group and is most stable for Pb. This is the inert pair effect: the outer s^2 pair is less likely to be used in bonding, and the effect increases down the group.

So PbO is more stable than PbO_2 (PbO_2 is an oxidising agent), while CO_2 is more stable than CO (CO is a reducing agent). SiO does not form because +2 cannot be stable this high up the group, where the inert pair effect is weak.

Group 5: P can show +5 in PCl_5 because, in period 3, it has available 3d orbitals, so it can expand its octet. N is in period 2 and has no available d orbitals, so it cannot expand its octet beyond 8 electrons and NCl_5 cannot form; N is limited to +3.

Manganese: a characteristic of transition metals is a variety of oxidation states. The 3d and 4s orbitals have similar energies, so successive ionisation energies are similar and Mn can lose different numbers of electrons to give +2, +3 and +4.



- (b) Tin(II) ions, Sn^{2+} (aq), can be used as reducing agents for a range of metal ions. In one study of the reduction of Pt^{4+} ions to Pt^{2+} ions in an acid solution, the reaction was found to be first order with respect to both Pt^{4+} and Sn^{2+} with a rate constant of $895 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 297 K.

- (i) Write a rate equation for this reaction. [1]



- (ii) A student suggests studying this reaction using sampling and quenching with samples taken every 30 seconds for 5 minutes. Explain why this would not be an appropriate sampling interval. [2]

The rate constant is large, so the reaction is very fast.

The reaction would be complete (almost all reactant used up) within the first 30 seconds, so later samples give no useful data.

- (c) (i) A second student decides to use colorimetry to study the rate of this reaction. Explain what the student should consider when choosing an appropriate wavelength of light for their colorimetry experiment. [1]

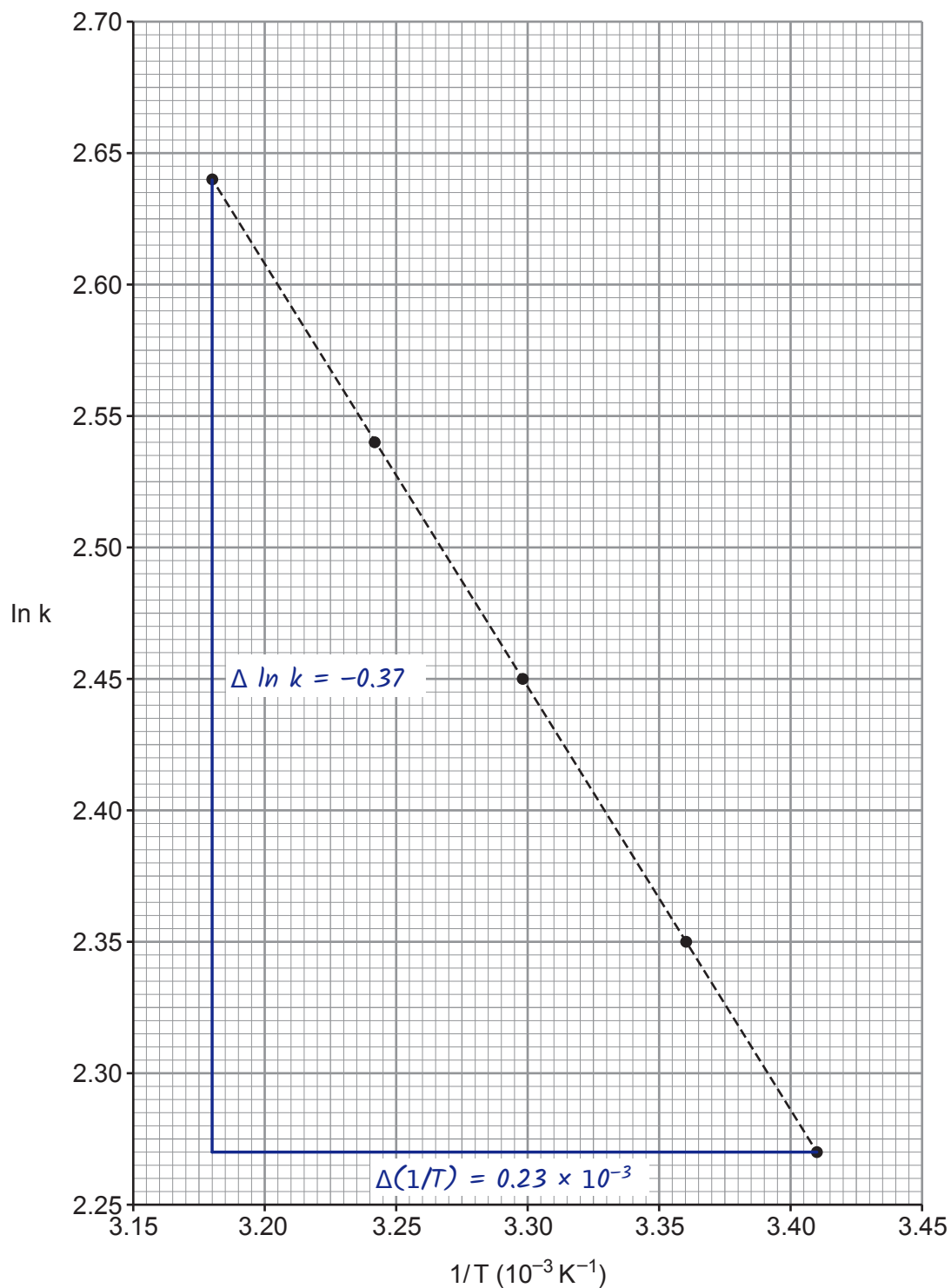
Choose a wavelength (frequency) that is absorbed by only one species, e.g. absorbed by one reactant but not by its product, so the absorbance changes as the reaction proceeds.



- (ii) The value of the rate constant was measured at five different temperatures to attempt to find the activation energy.

$$\ln k = \ln A - (E_a/RT)$$

A graph was plotted of ($\ln k$) against ($1/\text{Temperature}$) and this is shown below.



Find the activation energy of the reaction.

[3]

$$\text{gradient} = (2.27 - 2.64) \div (3.41 - 3.18) \times 10^{-3} = -1.61 \times 10^3 \text{ K}$$

$$\text{gradient} = -E_a/R, \text{ so } E_a = 1.61 \times 10^3 \times 8.31 = 13\,400 \text{ J mol}^{-1}$$

activation energy, E_a = ...13.4..... kJ mol⁻¹

13



10. Oxygen forms several molecular compounds of formula X_2O . These include compounds with fluorine and chlorine.

(a) Some thermodynamic data for F_2O and Cl_2O are given below.

Substance	Standard enthalpy change of formation, $\Delta_f H^\theta / \text{kJ mol}^{-1}$	Standard molar entropy, $S^\theta / \text{JK}^{-1} \text{mol}^{-1}$
F_2O	24.5	247
Cl_2O	80.3	266
O_2		205
F_2		203
Cl_2	0	

A student examines the data and states that there is sufficient information to find the minimum temperature for decomposition of F_2O to its elements but not for Cl_2O .

Is the student correct? Justify your answer.

[3]

Yes. The minimum temperature needs both ΔH and ΔS ($T = \Delta H / \Delta S$).

ΔH is known for both: it is the reverse of $\Delta_f H$ ($\Delta_f H$ of elements is zero).

ΔS can be found for F_2O but not Cl_2O , as $S^\theta(Cl_2)$ is not known (and is not zero).

- (b) F_2O is a strong oxidising agent and can oxidise Xe to XeF_4 whilst releasing oxygen gas.

(i) Write an equation for this process.

[1]



(ii) Show that the xenon is oxidised in the process.

[1]

Xe oxidation state increases from 0 (Xe) to +4 (XeF_4), so xenon is oxidised.



- (c) F_2O reacts slowly with water to produce HF, a weak acid.



A small amount of F_2O is added to 400 cm^3 of water at 15°C and it reacts completely. The reaction produces 82 cm^3 of oxygen gas at this temperature and 1 atm pressure.

- (i) Calculate the concentration of the HF solution formed. [2]

$$\begin{aligned} n(O_2) &= pV/RT = (1.01 \times 10^5 \times 82 \times 10^{-6}) \div (8.31 \times 288) \\ &= 3.46 \times 10^{-3} \text{ mol, so } n(HF) = 2 \times 3.46 \times 10^{-3} = 6.92 \times 10^{-3} \text{ mol} \\ [HF] &= 6.92 \times 10^{-3} \div 0.400 = 0.0173 \text{ mol dm}^{-3} \end{aligned}$$

concentration = 0.0173 mol dm⁻³

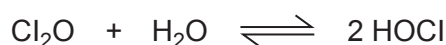
- (ii) Calculate the pH of the HF solution formed. [3]

$$\begin{aligned} K_a(HF) &= 6.6 \times 10^{-4} \text{ mol dm}^{-3} \\ K_a &= [H^+][F^-]/[HF] \text{ and } [H^+] = [F^-], \text{ so } [H^+]^2 = K_a \times [HF] \\ [H^+]^2 &= 6.6 \times 10^{-4} \times 0.0173 = 1.14 \times 10^{-5} \\ [H^+] &= 3.38 \times 10^{-3} \text{ mol dm}^{-3} \\ pH &= -\log(3.38 \times 10^{-3}) = 2.47 \end{aligned}$$

pH = 2.47



- (d) Cl_2O can react with water in a reversible reaction.



This reaction can occur in non-aqueous solvents and in a particular solvent the value of the equilibrium constant, K_c , at 273 K is 5.0 and it has no units.

- (i) Write an expression for the equilibrium constant K_c . [1]

$$K_c = \frac{[\text{HOCl}]^2}{[\text{Cl}_2\text{O}][\text{H}_2\text{O}]}$$

- (ii) A student studies the equilibrium at a higher temperature. She adds samples of 0.40 mol of H_2O and 0.14 mol of Cl_2O to the non-aqueous solvent giving a total volume of 1000 cm^3 .

At equilibrium the concentration of HOCl is 0.22 mol dm^{-3} .

- I. Find the value of the equilibrium constant K_c at this temperature. [3]

0.11 mol dm^{-3} of each reactant reacts to give 0.22 mol dm^{-3} HOCl

$[\text{H}_2\text{O}] = 0.40 - 0.11 = 0.29$ $[\text{Cl}_2\text{O}] = 0.14 - 0.11 = 0.03 \text{ mol dm}^{-3}$

$K_c = 0.22^2 \div (0.03 \times 0.29) = 0.0484 \div 0.0087 = 5.56$

$K_c = \dots\dots\dots 5.56$

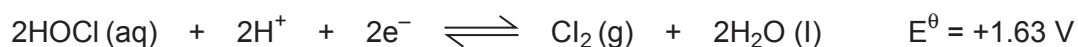
- II. State, giving a reason, whether this reaction is endothermic or exothermic. [2]

K_c is larger at the higher temperature ($5.56 > 5.0$), so equilibrium has shifted to the right.

So the forward reaction is endothermic.



III. HOCl can act as an oxidising agent.



Give the formulae of all the metal ions in the table that can be oxidised by HOCl (aq). Explain why you have chosen these ions. [2]

	Standard electrode potential, $E^\ominus/\text{V}$
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Tl}^{3+} + 2\text{e}^- \rightleftharpoons \text{Tl}^+$	+1.25
$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.69
$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$	+1.82

Tl⁺ and Fe²⁺

$E^\ominus$ for HOCl/Cl₂ (+1.63 V) is more positive than for Fe³⁺/Fe²⁺ (+0.77 V) and Tl³⁺/Tl⁺ (+1.25 V), so HOCl oxidises these ions (positive EMF); Pb²⁺ and Co²⁺ have more positive $E^\ominus$.



11. Carboxylic acids are classed as weak acids.

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

[1]

An acid that only partially dissociates in water to release H^+ ions (a reversible reaction).

(b) Substituted propanoic acids, $CH_3CHXCOOH$, have different acid strengths. The table below gives some information about three substituted propanoic acids.

Substituted propanoic acid, $CH_3CHXCOOH$	
$X = H$	The pH of a 0.50 mol dm^{-3} aqueous solution is 2.59
$X = Cl$	$K_a = 1.48 \times 10^{-3} \text{ mol dm}^{-3}$
$X = OH$	$pK_a = 3.86$

Place these acids in order of increasing acid strength. **You must show your working.**

[3]

$$X = H: [H^+] = 10^{-2.59} = 2.57 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_a = [H^+]^2/[HA] = (2.57 \times 10^{-3})^2 \div 0.50 = 1.32 \times 10^{-5}, pK_a = 4.88$$

$$X = Cl: pK_a = -\log(1.48 \times 10^{-3}) = 2.83$$

$$X = OH: K_a = 10^{-3.86} = 1.38 \times 10^{-4} \text{ mol dm}^{-3}, pK_a = 3.86$$

Larger K_a (smaller pK_a) means a stronger acid.

Weakest $X = H$ < $X = OH$ < $X = Cl$ Strongest



- (c) A buffer is produced by mixing 100 cm^3 of ethanoic acid ($K_a = 1.8 \times 10^{-5}\text{ mol dm}^{-3}$) of concentration 0.80 mol dm^{-3} with 50 cm^3 of aqueous sodium hydroxide of concentration 0.80 mol dm^{-3} at a temperature of 298 K .

- (i) Calculate the initial pH of the aqueous sodium hydroxide. [2]

$$[\text{OH}^-] = 0.80\text{ mol dm}^{-3}$$

$$[\text{H}^+] = K_w/[\text{OH}^-] = 1.00 \times 10^{-14} \div 0.80 = 1.25 \times 10^{-14}\text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.25 \times 10^{-14}) = 13.9$$

$$\text{pH} = \dots 13.9 \dots$$

- (ii) Calculate the pH of the buffer solution. [2]

$$n(\text{CH}_3\text{COOH}) = 0.100 \times 0.80 = 0.080\text{ mol}$$

$$n(\text{NaOH}) = 0.050 \times 0.80 = 0.040\text{ mol}$$

leaves $0.040\text{ mol CH}_3\text{COOH}$ and $0.040\text{ mol CH}_3\text{COO}^-$: $[\text{salt}] = [\text{acid}]$

$$\text{so pH} = \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = \dots 4.74 \dots$$

- (iii) Explain how buffers such as this work. [3]

$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ (the acid is only partially dissociated)

The salt is fully ionised, $\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$, so there are large reservoirs of CH_3COOH and CH_3COO^- .

Adding a small amount of H^+ : it reacts with CH_3COO^- , the equilibrium shifts to the left and removes the added H^+ , so the pH hardly changes.

Adding a small amount of OH^- : it removes H^+ (forming water), the equilibrium shifts to the right to produce more H^+ , so the pH hardly changes.



12. The formula of an unknown mineral is $\text{Mg}_a\text{X}_b(\text{CO}_3)_c(\text{OH})_d \cdot e\text{H}_2\text{O}$.

A student performs a series of experiments to calculate the values **a**, **b**, **c**, **d** and **e** and name element X.

Experiment Number	Experiment	Result
1	Heating a sample of 0.0200 mol of the mineral to dryness.	The sample loses 1.44 g of mass.
2	Addition of 0.0200 mol of the mineral to excess hydrochloric acid.	A volume of 490 cm ³ of carbon dioxide gas is released at 298 K and 1 atm pressure. The remaining solution has a green colour.
3	Addition of excess aqueous sodium hydroxide gradually to the solution produced in experiment 2.	A precipitate forms that shows a mixture of white and grey-green colours. Addition of excess sodium hydroxide leaves a white precipitate in a green solution.
4	Addition of a sample of 1.00×10^{-3} mol of the mineral to 25.0 cm ³ of HCl of concentration 1.00 mol dm ⁻³ . Titration of the remaining acid against standard aqueous sodium hydroxide of concentration 0.500 mol dm ⁻³ .	A volume of 14.00 cm ³ of the aqueous sodium hydroxide is required for complete reaction.

- (a) Find the value of **e**, the number of water molecules in each formula unit. [2]

$$\text{mass lost} = \text{mass of water} = 1.44 \text{ g}$$

$$n(\text{H}_2\text{O}) = 1.44 \div 18.02 = 0.0800 \text{ mol}$$

$$e = 0.0800 \div 0.0200 = 4$$

$$e = \dots\dots\dots 4$$

- (b) Find the value of **c**, the number of carbonate ions in each formula unit. [2]

$$n(\text{CO}_2) = 490 \div 24\,500 = 0.0200 \text{ mol (24.5 dm}^3 \text{ at 298 K)}$$

$$\text{one CO}_3^{2-} \text{ gives one CO}_2, \text{ so } c = 0.0200 \div 0.0200 = 1$$

$$c = \dots\dots\dots 1$$



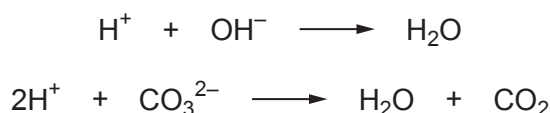
- (c) Explain the observations seen in experiment 3. Use these to name element X. [3]

The white precipitate is $\text{Mg}(\text{OH})_2$, formed from Mg^{2+} ions.

The grey-green precipitate is $\text{Cr}(\text{OH})_3$, from Cr^{3+} ions, so X is chromium, Cr.

$\text{Cr}(\text{OH})_3$ is amphoteric, so it dissolves in excess NaOH to give a green solution ($[\text{Cr}(\text{OH})_6]^{3-}$); white $\text{Mg}(\text{OH})_2$ does not dissolve.

- (d) In experiment 4 the acid reacts with all the hydroxide and carbonate ions.



Calculate the value of **d**, the number of hydroxide ions present in each formula unit. [4]

$$n(\text{HCl}) \text{ added} = 25.0 \div 1000 \times 1.00 = 0.0250 \text{ mol}$$

$$n(\text{NaOH}) = 14.00 \div 1000 \times 0.500 = 0.00700 \text{ mol} = n(\text{HCl}) \text{ remaining}$$

$$n(\text{HCl}) \text{ reacting with } \text{OH}^- \text{ and } \text{CO}_3^{2-} = 0.0250 - 0.00700 = 0.0180 \text{ mol}$$

$$n(\text{CO}_3^{2-}) = 1.00 \times 10^{-3} \text{ mol } (c = 1), \text{ which uses } 0.00200 \text{ mol HCl}$$

$$n(\text{HCl}) \text{ reacting with } \text{OH}^- = 0.0180 - 0.00200 = 0.0160 \text{ mol}$$

$$d = 0.0160 \div 1.00 \times 10^{-3} = 16$$

$$d = \underline{\quad 16 \quad}$$



- (e) The compound has 56 atoms in each formula unit.
Use your answers to (a), (b), (c) and (d), and the total number of atoms to find the formula of the mineral.

[3]



$$\text{charges: } 2a + 3b = 2 + 16 = 18$$

$$\text{atoms: } a + b + 4 + 32 + 12 = 56, \text{ so } a + b = 8$$

$$2a + 3(8 - a) = 18, \text{ so } b = 2 \text{ and } a = 6$$

Formula $\text{Mg}_6\text{Cr}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$

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