4 Separate samples of 0.01 mol of magnesium nitrate and 0.01 mol of strontium nitrate are heated until completely decomposed to the metal oxide, nitrogen dioxide and oxygen.

(a) State which of these two Group 2 nitrates requires the **higher** temperature before it begins to decompose. Explain your answer.

.....

.....

.....

..... [2]

(b) After decomposition is complete the 0.01 mol sample of magnesium oxide is taken and increasing amounts of water are added to it, with stirring, until no solid remains.

This procedure is repeated with the 0.01 mol sample of strontium oxide.

Identify the sample to which most water must be added to cause all the solid to dissolve. Explain your answer by reference to the solubilities of the products formed when water is added to the oxides. You should refer to relevant energy terms in your answer.

.....

.....

.....

.....

..... [3]

(c) The nitrogen dioxide given off by the decomposition of 0.0100 mol of strontium nitrate is dissolved in water. The oxidising agent $H_2O_2(aq)$ is then added to give 150.0 cm^3 of a solution in which nitric acid, HNO_3, is the only nitrogen-containing product.

(i) Calculate the concentration, in mol dm^{-3}, of HNO_3 in the 150.0 cm^3 of solution.

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

(ii) The HNO_3 present in 25.0 cm^3 of this solution is neutralised using 0.125 mol dm^{-3} NaOH(aq).

Calculate the minimum volume, in cm^3, of NaOH(aq) needed. Give your answer to three significant figures.

volume = ... cm^3 [1]

[Total: 7]

3 Ammonium chloride, $NH_4Cl(s)$, dissolves in water to form an acidic solution. This is due to the dissociation of the ammonium ions.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

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

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

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

(ii) Calculate the value of pK_a of the ammonium ion.

pK_a = ... [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]

9 Butylamine, $CH_3CH_2CH_2CH_2NH_2$, can be synthesised from different organic compounds by using suitable reagents. Each reaction involves one step.

(a) Complete the table to describe three different syntheses.

- One of the three syntheses should involve a nucleophilic substitution reaction.
- The starting organic compound for each synthesis should contain a different functional group.
- A different reagent should be used for each synthesis.

starting organic compound	reagent and conditions

[6]

(b) Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

..... > ..... > .....

most basic least basic

.....

.....

.....

.....

.....

..... [4]

[Total: 10]

4 **(a)** Calcium carbonate decomposes on heating.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

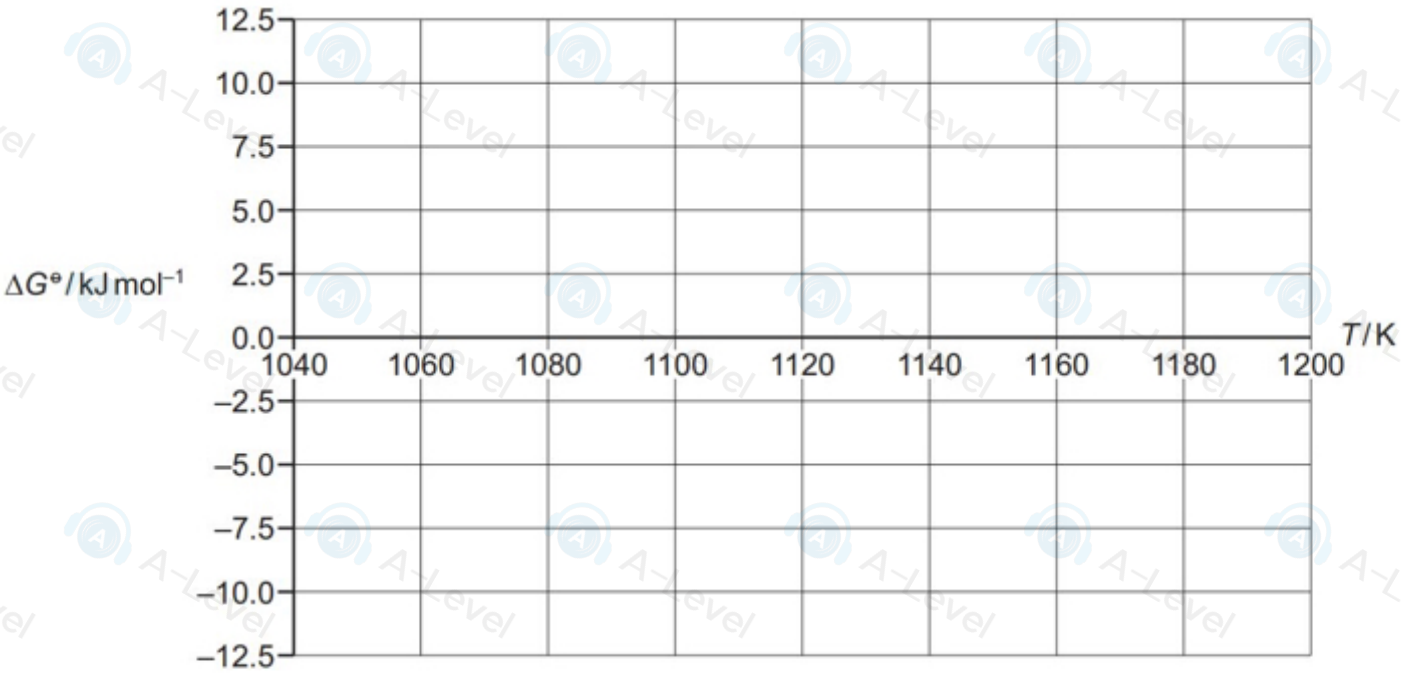
Table 4.1 shows the values of the Gibbs free energy change, $\Delta G^\ominus$, for this reaction at various temperatures.

Table 4.1

T/K	$\Delta G^\ominus$/kJ mol^{-1}
1050	9.9
1085	4.3
1120	–1.3
1148	–5.8
1176	–10.3

Assume the standard enthalpy change, $\Delta H^\ominus$, and the standard entropy change, $\Delta S^\ominus$, for this reaction remain constant over this temperature range.

(i) Use the data in Table 4.1 to plot a graph of $\Delta G^\ominus$ against T on the grid.



[2]

(ii) Calculate the gradient of your graph. Determine the $\Delta S^\ominus$ in J K^{-1} mol^{-1} for this reaction. Show all working.

$\Delta S^\ominus$ = ... J K^{-1} mol^{-1} [2]

(c) The buffer system in seawater contains a mixture of HCO_3^- and H_2CO_3.

equilibrium **5** $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

(i) Define a buffer solution.

.....

.....

..... [2]

(ii) Construct **two** equations to show how equilibrium **5** acts as a buffer solution.

.....

..... [2]

(iii) The $[HCO_3^-]/[H_2CO_3]$ ratio in a sample of seawater is 14.1.

Calculate the pH of this sample.
[pK_a: H_2CO_3, 6.35]

pH = ... [3]

[Total: 14]

2 Benzoic acid, C_6H_5COOH, is a weak acid. The K_a of benzoic acid is 6.31×10^{-5} mol dm^{-3} at 298 K.

A 1.00 dm^3 buffer solution is made at 298 K containing 1.00 g of C_6H_5COOH and a slightly greater mass of sodium benzoate, $C_6H_5COO^-Na^+$.

This buffer solution has a pH of 4.15.

(a) Define buffer solution.

.....

..... [1]

(b) Write equations to show how this solution acts as a buffer solution when the named substances are added to it:

(i) dilute aqueous sodium hydroxide

..... [1]

(ii) dilute aqueous nitric acid.

..... [1]

(c) Calculate the H^+ concentration and the C_6H_5COOH concentration in the buffer solution described. Use the expression for the K_a of C_6H_5COOH to calculate the concentration of $C_6H_5COO^-Na^+$ in the buffer solution.

Show your working and give each answer to a minimum of **three** significant figures.

$[H^+]$ = ... mol dm^{-3}

$[C_6H_5COOH]$ = ... mol dm^{-3}

$[C_6H_5COO^-Na^+]$ = ... mol dm^{-3}

[3]

(d) A 10.0 cm^3 sample of the buffer solution is mixed with 10.0 cm^3 of 1.00 mol dm^{-3} KOH. Both solutions are at 298 K. A reaction is allowed to occur without stirring.

Two observations are recorded:

- the temperature, after the reaction is complete, is fractionally above 298 K
- the pH, after the reaction, is greater than 13.

Explain these two observations.

.....

.....

..... [2]

(e) Magnesium benzoate, $Mg(C_6H_5COO)_2$, has a solubility in water of less than 1.00 g dm^{-3} at 298 K.

$$K_{sp} = [Mg^{2+}][C_6H_5COO^-]^2 = 1.76 \times 10^{-7} \text{ at } 298\,K$$

(i) Calculate the solubility of $Mg(C_6H_5COO)_2$ in water at 298 K. Give your answer in g dm^{-3}.

Show your working.

[M_r: $Mg(C_6H_5COO)_2$, 266.3]

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

(ii) An excess of $Mg(C_6H_5COO)_2$ is added to a sample of 0.50 mol dm^{-3} $MgSO_4$ at 298 K.

State whether the equilibrium concentration of $Mg(C_6H_5COO)_2$ is higher than, the same as, or lower than your answer to **(i)**. Explain your answer.

The concentration is ..... the concentration in **(i)**.

explanation .....

.....

[1]

[Total: 11]

3 **(a)** Complete Table 3.1 by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

Table 3.1

energy change	always positive	always negative	can be either negative or positive
bond energy			
enthalpy change of atomisation			
enthalpy change of formation			

[1]

(b) Define standard enthalpy change of atomisation.

.....

.....

..... [2]

(c) Table 3.2 shows some energy changes.

Table 3.2

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of silver	+285
first ionisation energy of silver	+731
second ionisation energy of silver	+2074
bond energy of O=O	+496
bond energy of O–O	+150
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
first ionisation energy of oxygen	+1314
standard enthalpy change of formation of silver oxide, $Ag_2O(s)$	–31

(d) Suggest the trend in the magnitude of the lattice energies of the silver compounds Ag_2S, Ag_2O and Ag_2Se.

Explain your answer.

....
least exothermic most exothermic

.....

.....

.....

[2]

(e) Silver sulfite, $Ag_2SO_3(s)$, is sparingly soluble in water.

(i) Give an expression for the solubility product, K_{sp}, of Ag_2SO_3.

K_{sp} =

[1]

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2SO_3 at 298 K.

[K_{sp}: Ag_2SO_3, 1.50×10^{-14} mol^3 dm^{-9} at 298 K]

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

(f) The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $AgNO_3(s)$ in water is +22.6 kJ mol^{-1}.

Suggest how the feasibility of dissolving $AgNO_3(s)$ in water changes with temperature.

Explain your answer.

8 **(a)** Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic acid and phenol. Explain your reasoning.

..... > ..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

.....

.....

[4]

(b) An excess of ethanedioic acid, HOOCCOOH(aq), is reacted with warm acidified $KMnO_4$(aq).

State the type of reaction undergone by ethanedioic acid.
Describe what you would observe.
Write an equation for this reaction.

Your equation can use [O] or [H] as necessary.

type of reaction .....

observations .....

equation .....

[2]

Draw the structures of the two monomers that form this polyester.

[2]

(d) Serine can polymerise to form two different types of condensation polymer; a polyester and a polypeptide.

serine

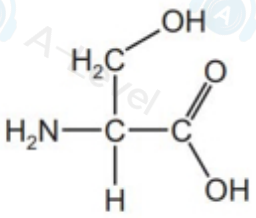


Fig. 8.2

Draw the structure of the polypeptide showing **two** repeat units. The peptide linkage should be shown displayed.

[2]

(e) Explain why condensation polymers normally biodegrade more readily than addition polymers.

.....

..... [1]

[Total: 11]

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

- pH = ...

.....

- K_a for a weak acid, HA = ...

.....

[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.

.....

.....

..... [2]

7/20

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

$$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + H^+(aq) + Cl^-(aq)$$

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 $K_a = 2.9 \times 10^{-8}$ mol dm^{-3}.]

pH = ... [3]

[Total: 7]