1) from the resource booklet.

Calculate the pH of the ethanoic acid before any NaOH is added, and justify any approximation you make.

[2 marks]

(b) Calculate the pH of the mixture after 15.0 mL of the NaOH solution has been added. Name the type of solution formed and explain why its pH changes only slightly when a small amount of strong base is added.

[3 marks]

(c) Calculate the pH at the equivalence point. A student suggests methyl orange (colour change over pH 3.1 to 4.4) as the indicator. Show by calculation why this would be unsuitable, and name a suitable indicator from Table 3 with a reason.

[3 marks]

TEST PAPERS HUB - NOT FOR RESALE OR REDISTRIBUTION

THE WORKED ANSWERS TO THOSE 3 QUESTIONS

Question 1 (8 marks) [Thermochemistry, entropy and Gibbs energy]

(a) Lime (calcium oxide) is made by heating limestone in a kiln: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Use the thermodynamic data in the table below (also Table 2 of the resource booklet); treat $\Delta H°$ and $S°$ as constant with temperature. Calculate $\Delta rH°$ (kJ mol^{-1}) and $\Delta rS°$ (J K^{-1} mol^{-1}) for the decomposition. Explain why $\Delta rS°$ has the sign you found.

(a) Answer: $\Delta rH° = +178$ kJ mol^{-1}; $\Delta rS° = +162$ J K^{-1} mol^{-1}

- Entry step: worth marks in the 1-4 range of the 8-point question score.
- $\Delta rH° = [\Delta fH°(CaO) + \Delta fH°(CO_2)] - \Delta fH°(CaCO_3) = (-635) + (-394) - (-1207) = +178$ kJ mol^{-1}. [1 mark]
- $\Delta rS° = 40 + 214 - 92 = +162$ J K^{-1} mol^{-1}. It is positive because the reaction produces a gas from a solid: the particles of $CO_2(g)$ are free to move and can be arranged in many more ways than in a solid lattice, so the number of accessible microstates (the dispersal of energy) increases. [1 mark]

> **KEY TAKEAWAY**
> Products minus reactants for both $\Delta H°$ and $S°$; a reaction that makes a gas from solids has a large positive entropy change.

(b) Calculate the minimum temperature, in K and in °C, at which the decomposition is thermodynamically spontaneous under standard conditions. Explain why the reaction is spontaneous above this temperature and not below it.

(b) Answer: $T \approx 1099$ K (826 °C)

- Scholarship band (5-6): the part needs your own method and accurate reasoning.
- Spontaneous when $\Delta G° = \Delta H° - T\Delta S° < 0$. At the changeover $\Delta G° = 0$, so $T = \Delta H° \div \Delta S° = 178\,000$ J mol^{-1} ÷ 162 J K^{-1} mol^{-1} = 1099 K. [1 mark]
- In °C: 1099 − 273 = 826 °C. [1 mark]
- $\Delta H°$ is positive (unfavourable) and $\Delta S°$ is positive. At low T the term $T\Delta S°$ is too small to outweigh $\Delta H°$, so $\Delta G° > 0$; as T rises $T\Delta S°$ grows until it exceeds $\Delta H°$ and $\Delta G°$ becomes negative, so the reaction is spontaneous above 1099 K. [1 mark]

> **KEY TAKEAWAY**
> $\Delta G° = \Delta H° - T\Delta S° = 0$ gives the changeover temperature; a positive $\Delta S°$ makes a reaction favourable at HIGH temperature only if $\Delta H°$ is also positive.

(c) A sample of limestone is heated at 1000 K in a sealed, evacuated vessel until the pressure stops changing. Calculate the equilibrium constant K at 1000 K for the decomposition and hence the equilibrium pressure of $CO_2(g)$ in bar. ($K = p(CO_2) \div p°$, with $p° = 1$ bar.) In an open kiln the CO_2 is carried away, so its partial pressure stays near 4.0×10^{-4} bar, the value in air. Calculate the lowest temperature at which limestone can decompose when $p(CO_2)$ is held at this value, and explain why it is far below your answer to part (b).

(c) Answer: $K = 0.146$; $p(CO_2) = 0.146$ bar; $T \approx 784$ K (511 °C)

- Outstanding band (7-8): the part needs insight and a complete, well-supported argument.

TEST PAPERS HUB · NOT FOR RESALE · NO REDISTRIBUTION

• ΔG° at 1000 K = 178 000 − 1000 × 162 = +16000 J mol^{-1}. K = e^(−ΔG°/RT) = e^(−16000 ÷ (8.314 × 1000)) = 0.1460, so p(CO_2) = 0.146 bar. [1 mark]

• Reaction is just possible when $\Delta G = 0$ with Q = 4.0 × 10^{-4}: $\Delta H^\circ - T\Delta S^\circ + RT \ln(4.0 \times 10^{-4}) = 0$, so T = $\Delta H^\circ \div [\Delta S^\circ - R \ln(4.0 \times 10^{-4})]$ = 178 000 ÷ (162 + 65.05) = 784 K (511 °C). [1 mark]

• Part (b) assumes standard conditions (1 bar CO_2). In an open kiln the product gas is removed, so Q is tiny and $\Delta G = \Delta G^\circ + RT \ln Q$ is much more negative than ΔG°; by Le Chatelier's principle removing CO_2 shifts the equilibrium to the right. The decomposition therefore starts at about 784 K, far below 1099 K, and is driven further by continuous removal of CO_2. [1 mark]

KEY TAKEAWAY

ΔG° tells you about standard conditions (1 bar); the real driving force is $\Delta G = \Delta G^\circ + RT \ln Q$, so removing a gaseous product lowers the temperature needed.

LOS: Thermochemistry, entropy and Gibbs energy (93102)

Question 2 (8 marks) [Aqueous equilibria and titration]

(a) A 25.0 mL sample of 0.100 mol L^{-1} ethanoic acid, CH_3COOH, is titrated with 0.100 mol L^{-1} sodium hydroxide, NaOH, at 25 °C. Use Ka = 1.74 × 10^{-5} (Table 3) and Kw = 1.00 × 10^{-14} (Table 1) from the resource booklet. Calculate the pH of the ethanoic acid before any NaOH is added, and justify any approximation you make.

(a) Answer: pH = 2.88

• Entry step: worth marks in the 1-4 range of the 8-point question score.

• $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, so $K_a = [H^+]^2 \div [CH_3COOH]$. Assuming $[CH_3COOH] \approx 0.100$: $[H^+] = \sqrt{(1.74 \times 10^{-5} \times 0.100)} = 1.319 \times 10^{-3}$ mol L^{-1}, pH = 2.88. [1 mark]

• Check: $[H^+] \div 0.100 = 1.3\%$, less than 5% of the initial concentration, so ignoring the ionisation of the acid in the denominator is justified. [1 mark]

KEY TAKEAWAY

For a weak acid use $K_a = [H^+]^2/c$; always check the approximation by comparing $[H^+]$ with c (under 5%).

(b) Calculate the pH of the mixture after 15.0 mL of the NaOH solution has been added. Name the type of solution formed and explain why its pH changes only slightly when a small amount of strong base is added.

(b) Answer: pH = 4.94

• Scholarship band (5-6): the part needs your own method and accurate reasoning.

• $n(CH_3COOH) = 0.100 \times 25.0 = 2.50$ mmol; $n(OH^-) = 0.100 \times 15.0 = 1.50$ mmol. After reaction $n(CH_3COOH) = 1.00$ mmol and $n(CH_3COO^-) = 1.50$ mmol. [1 mark]

• A buffer. $pH = pK_a + \log([A^-] \div [HA]) = 4.76 + \log(1.50 \div 1.00) = 4.76 + 0.18 = 4.94$ (the volume cancels in the ratio). [1 mark]

• The buffer holds a weak acid (to remove added OH^-: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$) and its conjugate base (to remove added H^+). Because the ratio $[A^-]/[HA]$ changes only a little, and pH depends on the logarithm of that ratio, the pH hardly changes. [1 mark]

TEST PAPER - NOT FOR SALE OR REDISTRIBUTION

KEY TAKEAWAY

After partial neutralisation work in moles first (limiting reagent), then use pH = pKa + log(base ÷ acid); buffers resist change because pH depends on a ratio, not on amounts.

(c) Calculate the pH at the equivalence point. A student suggests methyl orange (colour change over pH 3.1 to 4.4) as the indicator. Show by calculation why this would be unsuitable, and name a suitable indicator from Table 3 with a reason.

(c) Answer: pH(equivalence) = 8.73; methyl orange ends at 7.6 mL; use phenolphthalein

- Outstanding band (7-8): the part needs insight and a complete, well-supported argument.
- At equivalence the volume of NaOH is 25.0 mL, total volume 50.0 mL and $[CH_3COO^-] = 2.50 \text{ mmol} \div 50.0 \text{ mL} = 0.0500 \text{ mol L}^{-1}$. $K_b = K_w \div K_a = 5.75 \times 10^{-10}$. $[OH^-] = \sqrt{(K_b \times c)} = 5.361 \times 10^{-6} \text{ mol L}^{-1}$, pOH = 5.27, so pH = 8.73. [1 mark]
- Methyl orange has finished changing at pH 4.4. [A⁻] ÷ [HA] = 10^(4.4 − 4.76) = 0.437, so n(OH^-) added = 2.50 × 0.437 ÷ (1 + 0.437) = 0.76 mmol, i.e. V = 7.6 mL, only 30% of the volume needed. The end-point would appear far too early. [1 mark]
- The equivalence pH of 8.73 is basic because the conjugate base CH_3COO^- hydrolyses. Phenolphthalein (colour change 8.3 to 10.0) changes within the steep rise around pH 8.7, so its end-point is within a drop or two of equivalence. [1 mark]

KEY TAKEAWAY

At equivalence a weak acid/strong base titration gives a BASIC solution (conjugate base hydrolysis); choose an indicator whose range includes the equivalence-point pH.

LOS: Aqueous equilibria and titration (93102)

Question 3 (8 marks) [Organic structure and spectroscopy]

(a) Compound X has the molecular formula $C_4H_8O_2$. Its spectra are shown in the table (spectroscopic data in Table 5 of the resource booklet). Calculate the number of rings plus double bonds in X, and use the infrared data to decide which functional group is present and which common groups are absent.

(a) Answer: 1 double bond (C=O); an ester, not a carboxylic acid or alcohol

- Entry step: worth marks in the 1-4 range of the 8-point question score.
- Degree of unsaturation = (2 × 4 + 2 − 8) ÷ 2 = 1, so X contains one C=O or C=C double bond or one ring. [1 mark]
- The strong absorption at 1743 cm^{-1} is C=O, in the ester range (1735 to 1750 cm^{-1}). There is no broad O–H absorption (2500 to 3300 cm^{-1} for an acid, 3200 to 3550 cm^{-1} for an alcohol), so X is not a carboxylic acid or an alcohol; it is an ester. [1 mark]

KEY TAKEAWAY

Count unsaturations from the formula first, then use the IR fingerprint to name the group; the ABSENCE of an O–H band rules out acids and alcohols.

(b) Use the ^1H NMR and ^{13}C NMR data to deduce the structure of X. Explain the splitting and the chemical shift of each signal, and name X.

(b) Answer: $CH_3COOCH_2CH_3$, ethyl ethanoate

- Scholarship band (5-6): the part needs your own method and accurate reasoning.

TEST PAPERS HUB · NOT FOR REDISTRIBUTION

• Three ^{1}H signals in the ratio 2 : 3 : 3 give eight H ($C_4H_8O_2$), so the group $CH_3–CH_2$ is present: the 3H triplet at δ 1.26 is a CH_3 next to a CH_2 (n + 1 rule: 2 neighbours give a triplet) and the 2H quartet is the CH_2 next to the CH_3 (3 neighbours give a quartet). [1 mark]

• The CH_2 is at δ 4.12, a high shift for CH_2, because it is bonded to the electronegative ester oxygen ($–O–CH_2–$). The 3H singlet at δ 2.04 is a CH_3 with no hydrogens on adjacent atoms and a shift typical of CH_3 next to C=O ($CH_3–C=O$). [1 mark]

• Putting $CH_3–C(=O)–O–CH_2–CH_3$ together gives $C_4H_8O_2$ (M = 88). The four ^{13}C signals fit four carbon environments: C=O at 171, $O–CH_2$ at 60, $CH_3–C=O$ at 21 and $CH_3–C$ at 14. X is ethyl ethanoate. The base peak at m/z 43 is CH_3CO^+. [1 mark]

KEY TAKEAWAY

Build the structure from the 1H data: integration counts the H, splitting joins the fragments, shift tells you what each fragment is attached to; then check the 13C count.

(c) A second ester, Y, is an isomer of X and is shown. Predict the ^{1}H NMR spectrum of Y (shift, integration and splitting of each signal) using Table 5, and state how many ^{13}C signals Y gives. The splitting patterns of X and Y are the same. Explain how they can nevertheless be distinguished using the ^{1}H NMR chemical shifts, and name one fragment ion that would be prominent in the mass spectrum of Y but not X.

(c) Answer: Y: δ ≈ 3.7 (3H, s), 2.3 (2H, q), 1.1 (3H, t); 4 ^{13}C signals; Y gives m/z 57

• Outstanding band (7-8): the part needs insight and a complete, well-supported argument.

• Y is methyl propanoate, $CH_3CH_2C(=O)OCH_3$. Predicted: δ ≈ 3.7 (3H, singlet, $CH_3–O$, no neighbouring H); δ ≈ 2.3 (2H, quartet, CH_2 next to C=O and CH_3); δ ≈ 1.1 (3H, triplet, CH_3 next to CH_2). Four carbon environments, so four ^{13}C signals. [1 mark]

• Both X and Y show a 3H singlet, a 2H quartet and a 3H triplet, so splitting and integration cannot tell them apart. The shifts can: in X the quartet is at δ 4.1 (CH_2 attached to O) and the singlet at δ 2.0 (CH_3 attached to C=O), whereas in Y the quartet is at δ ≈ 2.3 (CH_2 attached to C=O) and the singlet at δ ≈ 3.7 (CH_3 attached to O). The positions of the O-bonded group are swapped. [1 mark]

• Fragmentation of the C–C(=O) bond differs: X gives CH_3CO^+ at m/z 43 (the base peak) while Y gives $CH_3CH_2CO^+$ at m/z 57. [1 mark]

KEY TAKEAWAY

Isomers can have identical splitting patterns; the chemical shift shows which side of the ester link each alkyl group is on ($O–CH_2$ near 4, $C(=O)–CH_2$ near 2.3).

LOS: Organic structure and spectroscopy (93102)

TESTPAPERSHUB - NOT FOR RESALE OR REDISTRIBUTION