M1.(a) 
$$[H^{+}] = \frac{K_a \times [CH_3COOH]}{CH_3COO^{-}}$$
 or = 1.74 × 10 <sup>-5</sup> ×  $\frac{0.186}{0.105}$ 

Allow ()

M1

 $= 3.08 \times 10^{-5}$ 

M2

pH = 4.51 (correct answer scores 3)

Can score M3 for correct pH conseq to their  $[H^{\dagger}]$ , so pH = 5.01 scores one Must be to 2 dp

М3

1

1

Alternative using Henderson-Hasselbach Equation

pH = pKa - log[HX] / X<sup>-</sup>] = -log(1.74 × 10<sup>-5</sup>) - log(
$$\frac{0.186}{0.105}$$
)

Allow ()

M1

pKa = 4.76 - 0.248

If [HX] / [X] or  $\frac{0.186}{0.105}$  upside down, can only score 1

M2

pH = 4.51

so pH = 5.01Must be to 2 dp

М3

(b) mol HX after addition (= 0.251 + 0.015) = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

1

mol  $X^{-}$  after subtraction (= 0.140 - 0.015) = 0.125

FOR X- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

1

$$[H^{+}] = (\frac{K_a \times [CH_3COOH]}{CH_3COO^{-}}) = \frac{1.74 \times 10^{-s} \times 0.266}{0.125}$$

If errors above in both addition AND subtraction can only score M3 for insertion of their numbers in rearranged expression. One exception, if addition and subtraction reversed then pH =4.58 scores 2

М3

1

 $[H^{\dagger}] = 3.703 \times 10^{-5} \text{ (mol dm}^{-3})$ 

If  $[HX] / [X^-]$  upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their  $[H^+]$ , so if M1 & M2 correct, pH = 5.09 scores 3.

M4

1

pH = 4.43

Correct use of HX and X<sup>-</sup> values from (d) gives pH= 4.41 and scores 4

If wrong method, e.g.  $\sqrt{}$  or no use of rearranged  $K_a$  expression, may score M1 & M2 but no more.

Allow more but not fewer than 2dp here.

M5

1

Alternative using Henderson-Hasselbach Equation

mol acid after addition = 0.251 + 0.015 = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

mol salt after addition = 0.140 - 0.015 = 0.125

For  $X^-$  if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

pH = (pKa –  $log[HX] / [X^-]$ ) =  $-log(1.74 \times 10^{-5})$  – log(0.266 / 0.125)If errors above in both addition AND subtraction can only score M3 for insertion of their numbers – except if addition and subtraction reversed then pH = 4.58 scores 2

М3

pH = 4.76 - 0.328

M4

pH = 4.43

If  $[HX] / [X^-]$  upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their working, so if M1 & M2 correct, pH = 5.09 scores 3.

Allow more but not fewer than 2dp here.

M5

[8]

**M2.**(a) 
$$HCO_3^- = CO_3^{2-} + H^+$$

or

$$H_2O + HCO_3^- = CO_3^{2-} + H_3O^+$$

Must have equilibrium sign but mark on to (b) Ignore state symbols

(b) Acid: Increase in concentration of  $H^{+}$  ions, equilibrium moves to the left.

Allow H<sup>+</sup> ions react with carbonate ions (to form HCO<sub>3</sub>)

Alkali: OH<sup>-</sup> reacts with H<sup>+</sup> ions, equilibrium moves to the right (to replace the H<sup>+</sup> ions)

Concentration of H<sup>+</sup> remains (almost) constant

[4]

1

1

1

1

**M3.**(a) **Z** 

Mark independently.

1

The idea that the solution contains both HA and A-

1

(b) pH

1

 $[\mathsf{H}\mathsf{A}] = [\mathsf{A}^{\scriptscriptstyle{-}}]$ 

Accept solution half neutralised.

1

1

 $pH = pK_a$ 

Accept  $[H^{+}] = K_a$ 

[5]

M4.(a) (only) slightly or partially dissociated / ionised

Ignore 'not fully dissociated'.

Allow low tendency to dissociate or to lose / donate a proton.

Allow shown equilibrium well to the left.

Otherwise ignore equations.

1

(b)  $2CH_3CH_2COOH + Na_2CO_3 \longrightarrow 2CH_3CH_2COONa + H_2O + CO_2$ 

OR

 $2CH_3CH_2COOH + CO_3^{2-} \longrightarrow 2CH_3CH_2COO^- + H_2O + CO_2$ 

OR

**OR** 

Must be propanoic acid, allow C₂H₅COOH.

Not molecular formulae.

Allow multiples.

Ignore reversible sign.

Not H<sub>2</sub>CO<sub>3</sub>.

(c) 
$$[OH^{-}] = 2 \times 0.0120 = 0.0240$$
 M1

Correct answer for pH with or without working scores 3.

$$[H^{+}] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13} \, \text{OR} \, \text{pOH} = 1.62$$
 M2

If  $\times$  2 missed or used wrongly can only score M3 for correct calculation of pH from their [H $^{+}$ ].

1

1

1

1

1

Lose M3 if not 2 decimal places: 12.4 scores 2. 12.08 scores 1 (missing × 2); 12.1 scores 0.

11.78 scores 1 (dividing by 2) 11.8 scores 0.

(d) (i) 
$$K_a = \frac{[H^+][C_6H_5COO^+]}{[C_6H_5COOH]}$$

Ignore () here but brackets must be present.

Must be correct acid and salt.

If wrong, mark part (ii) independently.

(ii) M1 
$$K^a = \frac{[H^+]^2}{[C_6H_5COOH]}$$
 OR with numbers

Page 6

Correct answer for pH with or without working scores 3. Allow HX, HA and ignore () here.

May score M1 in part (i).

1

M2 
$$[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)} \text{ or } \sqrt{(K_a \times [C_6H_5COOH])}$$
  
 $(= \sqrt{(7.572 \times 10^{-7} = 8.70 \times 10^{-4})}$ 

pH = 6.12 may score 2 if correct working shown and they show the square root but fail to take it.

But if no working shown or wrong  $K^a = \frac{[H^+]}{[C_6 H_5 COOH]}$  used which also leads to 6.12, then zero scored.

1

M3 pH = 
$$3.\underline{06}$$

Must be 2 decimal places ie 3.1 loses M3.

1

(iii) M1 
$$[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$$

Correct answer for mass with or without working scores 5. Allow  $1 \times 10^{-4}$ .

1

M2 
$$[X^{-}] = \frac{\text{Ka x } [HX]}{[H^{+}]}$$

Ignore () here.

If [HX] / [X $^{-}$ ] upside down, can score M1 plus M4 for 5.26 × 10 $^{-7}$ .

1

$$M3 = \frac{6.31 \times 10^{-6} \times 0.0120}{1.00 \times 10^{-4}}$$

And M5 for 7.57 × 10<sup>-5</sup> g.

1

M4 = 
$$7.572 \times 10^{-3}$$

M5 Mass ( $C_6H_5COONa$ ) = 7.572 ×  $10^{-3}$  × 144 =1.09 g or 1.1 g

Wrong method, eg using [H<sup>+</sup>]<sup>2</sup> may only score M1 and M5 for correct multiplication of their M4 by 144 (provided not of obviously wrong substance).

(e) M1 CO<sub>2</sub>

Allow NOx and SO2.

M2 <u>pH (It) falls / decreases</u>

If M1 wrong, no further marks.

M3 mark M2 & M3 independently

acidic (gas)

OR reacts with alkali(ne solution) / OH-

**OR** 
$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$$

OR  $CO_2 + OH^- \longrightarrow HCO_3^-$ 

Not forms H<sub>2</sub>CO<sub>3</sub> H<sub>2</sub>SO<sub>3</sub> H<sub>2</sub>SO<sub>4</sub> etc OR H<sup>+</sup> ions.

[17]

1

1

1

1

1

**M5.**(a) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 and stage 2 to stage 3. Steps in stage 3 must be complete, ordered and include a comparison.

Level 3 5 – 6 marks

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows a progression from stage 1 and stage 2 to stage 3.

Level 2 3 – 4 marks

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes some isolated statements, but these are not presented in a logical order or show confused reasoning.

Level 1 1 – 2 marks

Insufficient correct Chemistry to warrant a mark.

Level 0 0 marks

## **Indicative Chemistry content**

Stage 1: difference in structure of the two acids

- The acids are of the form RCOOH
- but in ethanoic acid R = CH<sub>3</sub>
- whilst in ethanedioic acid R = COOH

## Stage 2: the inductive effect

- The unionised COOH group contains two very electronegative oxygen atoms
- therefore has a negative inductive (electron withdrawing)effect
- The CH<sub>3</sub> group has a positive inductive (electron pushing) effect

## **Stage 3:** how the polarity of OH affects acid strength

- The O–H bond in the ethanedioic acid is more polarised / H becomes more  $\delta^{\scriptscriptstyle +}$
- More dissociation into H<sup>+</sup> ions
- Ethanedioic acid is stronger than ethanoic acid

6

(b) Moles of NaOH = Moles of HOOCCOO<sup>-</sup> formed =  $6.00 \times 10^{-2}$  Extended response

1

Moles of HOOCCOOH remaining =  $1.00 \times 10^{-1} - 6.00 \times 10^{-2}$ 

 $= 4.00 \times 10^{-2}$ 

1

$$K_a = [H^+][A^-] / [HA]$$

$$[H^+] = K_a \times [HA] / [A^-]$$

1

$$[H^{+}] = 5.89 \times 10^{-2} \times (4.00 \times 10^{-2} / V) / (6.00 \times 10^{-2} / V) = 3.927 \times 10^{-2}$$

1

pH = 
$$-\log_{10}(3.927 \times 10^{-2})$$
 = 1.406 = 1.41  
Answer must be given to this precision

1

(c) 
$$5H_2C_2O_4 + 6H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

**OR**  $5C_2O_4^{2-}$  +  $16H^+$  +  $2MnO_4^ \longrightarrow$   $2Mn^{2+}$  +  $10CO_2$  +  $8H_2O$ 

1

Moles of KMnO<sub>4</sub> = 
$$20.2 \times 2.00 \times 10^{-2} / 1000 = 4.04 \times 10^{-4}$$

1

Moles of 
$$H_2C_2O_4 = 5 / 2 \times 4.04 \times 10^{-4} = 1.01 \times 10^{-3}$$

1

Concentration = moles / volume (in dm³)

= 
$$1.01 \times 10^{-3} \times 1000 / 25 = 4.04 \times 10^{-2}$$
 (mol dm<sup>-3</sup>)

If 1:1 ratio or incorrect ratio used, M2 and M4 can be scored

[15]