**M1.**(a) [H<sub>2</sub>O] is <u>very</u> high (compared with [H<sup>+</sup>] and [OH<sup>-</sup>]) Very few H<sup>+</sup> and OH<sup>-</sup> ions Only / very slightly dissociates OR Equilibrium lies far to the left Not partially dissociates M1 1 [H<sub>2</sub>O] is (effectively) constant OR is incorporated into the constant K Allow changes by only a very small amount M2 1 (b) (Dissociation OR breaking bonds) is endothermic 1 : Equilibrium moves to RHS (at higher T) to absorb heat or to lower T or oppose increase in T Allow to oppose change only if increase T mentioned 1  $= \sqrt{K_w}$  (or  $= \sqrt{5.48} \times 10^{-14}$ ) [H<sup>+</sup>] (c) Correct pH answer scores 3 1 If wrong method no marks Using alternative  $K_w$  (1.00 × 10<sup>-14</sup>) gives pH = 7.00 which scores 1  $= 2.34 \times 10^{-7}$ 1 рΗ = 6.63Final answer must have 2dp 1

 $[H^{+}] = K_w / [OH^{-}] \text{ or } (= 5.48 \times 10^{-14} / 0.12)$ (d) Correct pH answer scores 3 1 If wrong method no marks If use alternative  $K_w$  (1.00 × 10<sup>-14</sup>) again, do not penalise repeat error so pH = 13.08 scores 3  $= 4.566 \times 10^{-13}$ 1 рΗ = 12.34If use alternative  $K_w$  (1.00 × 10<sup>-14</sup>) **not** as a repeat error, pH = 13.08 scores 1 If AE in K<sub>w</sub> value made in part (c) is repeated here, do not penalise again. Final answer must have 2dp, but if dp penalised in (c) allow more than 2dp here but not fewer. [10] **M2.**(a) Burette 1 Because it can deliver variable volumes 1 (b) The change in pH is gradual / not rapid at the end point 1 An indicator would change colour over a range of volumes of sodium hydroxide Allow indicator would not change colour rapidly / with a few drops of NaOH 1 (c)  $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$ 1

$$K_{\rm w}$$
 = [H<sup>+</sup>] [OH<sup>-</sup>] therefore [OH<sup>-</sup>] =  $K_{\rm w}$  / [H<sup>+</sup>]

Therefore,  $[OH^{-}] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3} \text{ (mol dm}^{-3})$ Allow 6.31–6.33 × 10<sup>-3</sup> (mol dm<sup>-3</sup>)

1

1

(d) At this point,  $[NH_3] = [H^+]$   $= [H^+]^2$ Therefore  $K_a$   $[NH_4^+]$ 

1

$$[H^{+}] = 10^{-4.6} = 2.51 \times 10^{-5}$$

1

$$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10} \text{ (mol dm}^{-3})$$
  
Allow 3.15 – 3.16 × 10<sup>-10</sup> (mol dm<sup>-3</sup>)

1

(e) When  $[NH_3] = [NH_4^+]$ ,  $K_a = [H^+]$  therefore  $-\log K_a = -\log [H^+]$ Answer using alternative value

1

Therefore pH = 
$$-\log_{10}(3.15 \times 10^{-10}) = 9.50$$
  
 $M2 \text{ pH} = -\log_{10}(4.75 \times 10^{-9}) = 8.32$   
Allow consequential marking based on answer from part (d)

[12]

**M3.**(a) **M1** 
$$[H^+] = 0.0170$$

1

2 dp

Allow M2 for correct pH calculation from theirwrong [H·] for this pH calculation only

(b) (i) 
$$K_a = \frac{H^+ X^-}{[HX]^2}$$
 Ignore  $K_a = \frac{H^+}{[HX]^2}$ 

Penalize missing [] here **and not elsewhere**Allow HA instead of HX

(ii) **M1** [H<sup>+</sup>] = 
$$10^{-2.79}$$
 OR  $1.6218... \times 10^{-3}$  If [H<sup>+</sup>] wrong, can only score M2

$$\mathbf{M2} \qquad K_{a} = \frac{\left[H^{+}\right]^{2}}{\left[HX\right]} \qquad OR \qquad \frac{\left[1.62 \times 10^{-3}\right]^{2}}{\left[0.0850\right]}$$

Allow HA instead of HX

**M3** K<sub>a</sub> = 
$$3.09 \times 10^{-5}$$
 3sfs min (allow  $3.10 \times 10^{-5}$  if 1.6218 rounded to 1.622) Ignore units

If [HX] used as  $(0.0850 - 1.62 \times 10^{-3})$ 

this gives K<sub>a</sub> =  $3.15 \times 10^{-5}$ 
 $(0.0016)^2/0.085 = 3.01 \times 10^{-5}$  scores 2 for AE

(c) M1 mol OH<sup>-</sup> (= 
$$(38.2 \times 10^{-3}) \times 0.550$$
)  
=  $2.10(1) \times 10^{-2}$  or  $0.0210(1)$   
Mark for answer

**M2** Mol H<sup>-</sup> (= 
$$(25.0 \times 10^{-3}) \times 0.620$$
)  
=  $1.55 \times 10^{-2}$  or  $0.0155$   
Mark for answer

M3 excess mol OH<sup>-</sup> = 
$$5.5(1) \times 10^{-3}$$
  
Allow conseq for M1 – M2  
If wrong method e.g. no subtraction or use of  $\sqrt{}$   
can only score max of M1, M2, M3 and M4.

**M4** [OH-] =  $5.51 \times 10^{-3} \times \frac{10^3}{63.2}$  [ = 0.08718 (0.0872)]

OR 
$$[OH^{-}] = 5.5 \times 10^{-3} \times \frac{10^{3}}{63.2} = 0.0870(2)$$
  
 $(M1 - M2) / vol \ in \ dm^{3} \ mark \ for \ dividing \ by \ volume$   
 $(take \ use \ of \ 63.2 \ without \ 10^{-3} \ as \ AE \ so \ 9.94 \ scores \ 5)$   
If no use or wrong use of vol lose M4 & M6  
Can score M5 for showing  $(10^{-14} / their \ XS \ alkali)$ 

**M5**  $[H^{1}] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$ 

$$OR = \frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$$

**OR** pOH = 1.06 If no use or wrong use of  $K_w$  or pOH no further marks

M6 pH = 12.9(4) allow 3sf

If vol missed score max 4 for 11.7(4)

If acid— alkali reversed max 4 for pH = 1.06

Any excess acid— max 4

Any excess acid – max 4

**M4.**B

[1]

1

1

1

## M5.(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

$$CH_3CH_2COOH + CO_3^{2-} \longrightarrow CH_3CH_2COO^- + HCO_3^-$$

Must be propanoic acid, allow C<sub>2</sub>H₅COOH.

Not molecular formulae.

Allow multiples.

Ignore reversible sign.

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

1

1

1

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

Correct answer for pH with or without working scores 3.

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

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

pH = 12.38 M3

Lose M3 if not 2 decimal places: 12.4 scores 2.

Page 7

12.08 scores 1 (missing × 2); 12.1 scores 0. 11.78 scores 1 (dividing by 2) 11.8 scores 0.

1

(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.

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

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

May score M1 in part (i).

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M2 
$$[H^*] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)}$$
 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  $5.26 \times 10^{-7}$ .

1

$$M3 = \frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$$

And M5 for  $7.57 \times 10^{-5}$  g.

1

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

1

M5 Mass (
$$C_6H_5COONa$$
) = 7.572 × 10<sup>-3</sup> × 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).

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(e) M1  $CO_2$  Allow  $NO_x$  and  $SO_2$ .

1

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

If M1 wrong, no further marks.

1

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  $H_2CO_3 H_2SO_3 H_2SO_4$  etc OR  $H^+$  ions.

[17]