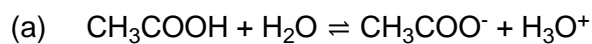
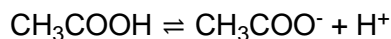


## Mark schemes

1



OR

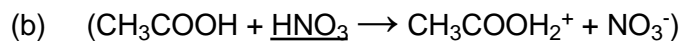


*Must show  $\rightleftharpoons$*

*Allow  $\text{CH}_3\text{CO}_2\text{H}$ ,  $\text{CH}_3\text{CO}_2^-$*

*Ignore state symbols*

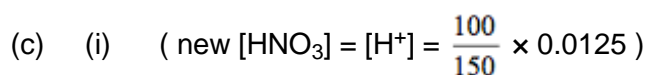
1



*IGNORE  $\rightleftharpoons$*

*Allow  $\text{CH}_3\text{CO}_2\text{H}$ ,  $\text{CH}_3\text{CO}_2\text{H}_2^+$ ,  $\text{CH}_3\text{C}^+(\text{OH})_2$*

1



M1  $[\text{H}^+] = 8.3(3) \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$

OR

$\text{new}[\text{HNO}_3] = \frac{\text{mol HNO}_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2  $\text{pH} = -\log \text{M1 OR } 2.08$

*Must be 2dp*

*Allow correct pH conseq to their  $[\text{H}^+]$  concentration*

1

(ii) M1  $\text{mol NaOH} (= 50 \times 10^{-3} \times 0.0108) = 5.40 \times 10^{-4}$

1

M2 Subtraction of M1 from moles of  $\text{HNO}_3$  ( $1.25 \times 10^{-3}$  or conseq from 1c(i))

Excess mol  $\text{H}^+ = 7.10 \times 10^{-4}$

*M2 allow ecf for subtraction of mol*

***If no subtraction, no further marks***

1

M3  $[\text{H}^+] = \frac{\text{M2}}{150 \times 10^{-3}} \text{ OR } \frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

*M3 if no use of volume, no further marks (pH=3.15)*

*If incorrect volume used, can score M4*

1

M4  $\text{pH} = -\log \text{M3 OR } 2.32$

*M4 Allow 2.33 Must be 2 dp*

1

(d) (i) M1  $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$   
 Penalise ( ) once here Not  $[H^+][A^-] / [HA]$   
 If  $K_a$  expression wrong – Allow correct pH conseq to their  $[H^+]$   
 concentration M4 only

1

M2  $K_a = \frac{[H^+]^2}{[CH_3COOH]}$  or with numbers or with HA

1

M3  $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$   
 Mark for answer

1

M4 pH = 3.33  
 Must be 2dp  
 Allow correct pH conseq to their  $[H^+]$  concentration  
 (pH = 3.83 can score M1, M2 and M4)

1

(ii) Sodium ethanoate  
 Ignore formula  
 Allow sodium acetate

1

(iii) M1  $[H^+] = 1.45 \times 10^{-5}$   
 Accept  $1.445 \times 10^{-5}$  or  $1.4 \times 10^{-5}$

1

M2  $\frac{[\text{salt}]}{[\text{acid}]}$  (OR  $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H^+]}$ ) =  $\frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$

If M1 incorrect CE=0  
 Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)  
 Ignore units  
 $1.4 \times 10^{-5}$  gives 1.24

1

- (e) M1 (Electronegative) chlorine withdraws electrons  
*Allow Cl has negative inductive effect* 1
- M2 Stabilises/reduces charge on COO-  
**OR** weakens O-H bond  
**OR** makes O-H more polar  
*Ignore chloroethanoic acid dissociates more readily*  
*Mark independently* 1
- (f) M1 Strong acids (almost) completely dissociated/ionised  
**OR** not an equilibrium  
**OR** equilibrium lies far to the right  
*Cannot have  $K_a$  value for a reaction not in equilibrium scores both marks* 1
- M2  $K_a$  value for strong acids tends to infinity/is very large  
**OR** can't divide by zero in  $K_a$  1
- 2** (a) Burette [20]  
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  
 $K_w = [H^+][OH^-]$  therefore  $[OH^-] = K_w / [H^+]$  1  
Therefore,  $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$   
*Allow 6.31–6.33  $\times 10^{-3} \text{ (mol dm}^{-3}\text{)}$*  1
- (d) At this point,  $[NH_3] = [H^+]$   
Therefore  $K_a = \frac{[H^+]^2}{[NH_4^+]}$  1

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

1

$$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10} \text{ (mol dm}^{-3}\text{)}$$

$$\text{Allow } 3.15 - 3.16 \times 10^{-10} \text{ (mol dm}^{-3}\text{)}$$

1

(e) When  $[\text{NH}_3] = [\text{NH}_4^+]$ ,  $K_a = [\text{H}^+]$  therefore  $-\log K_a = -\log [\text{H}^+]$

*Answer using alternative value*

1

$$\text{Therefore pH} = -\log_{10}(3.15 \times 10^{-10}) = 9.50$$

$$\text{M2 pH} = -\log_{10}(4.75 \times 10^{-9}) = 8.32$$

*Allow consequential marking based on answer from part (d)*

1

**[12]**

**3**

- (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 δ<sup>+</sup>
- More dissociation into H<sup>+</sup> ions
- Ethanedioic acid is stronger than ethanoic acid

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

*Extended response*

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

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

1

$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$$

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

1

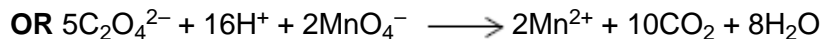
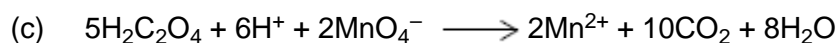
$$[\text{H}^+] = 5.89 \times 10^{-2} \times (4.00 \times 10^{-2} / V) / (6.00 \times 10^{-2} / V) = 3.927 \times 10^{-2}$$

1

$$\text{pH} = -\log_{10}(3.927 \times 10^{-2}) = 1.406 = 1.41$$

*Answer must be given to this precision*

1



1

$$\text{Moles of KMnO}_4 = 20.2 \times 2.00 \times 10^{-2} / 1000 = 4.04 \times 10^{-4}$$

1

$$\text{Moles of H}_2\text{C}_2\text{O}_4 = 5 / 2 \times 4.04 \times 10^{-4} = 1.01 \times 10^{-3}$$

1

Concentration = moles / volume (in dm<sup>3</sup>)

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

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

1

[15]

**4** B

[1]

**5** C

[1]

**6** (a) (i) G

1

(ii) F

1

(iii) H

1

- (b) (i) cresol purple 1
- (ii) yellow to red  
*both colours needed and must be in this order* 1
- (iii) yellow or pale yellow  
*Not allow any other colour with yellow* 1

[6]

7

- (a) [H<sub>2</sub>O] is very high (compared with [H<sup>+</sup>] and [OH<sup>-</sup>])  
**OR**  
Very few H<sup>+</sup> and OH<sup>-</sup> ions  
**OR**  
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
- (c) [H<sup>+</sup>] =  $\sqrt{K_w}$  (or =  $\sqrt{5.48 \times 10^{-14}}$ )  
*Correct pH answer scores 3* 1
- If wrong method no marks  
*Using alternative  $K_w$  ( $1.00 \times 10^{-14}$ ) gives pH = 7.00 which scores 1*
- =  $2.34 \times 10^{-7}$  1
- pH = 6.63  
*Final answer must have 2dp* 1

(d)  $[H^+] = K_w / [OH^-]$  or  $(= 5.48 \times 10^{-14} / 0.12)$

*Correct pH answer scores 3*

1

If wrong method no marks

*If use alternative  $K_w$  ( $1.00 \times 10^{-14}$ ) again, do not penalise repeat error so  $pH = 13.08$  scores 3*

$= 4.566 \times 10^{-13}$

1

$pH = 12.34$

*If use alternative  $K_w$  ( $1.00 \times 10^{-14}$ ) **not** as a repeat error,  $pH = 13.08$  scores 1*

*If AE in  $K_w$  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.*

1

[10]

8

(a)  $[H^+] = \frac{K_a \times [CH_3COOH]}{CH_3COO^-}$  or  $= 1.74 \times 10^{-5} \times \frac{0.186}{0.105}$

*Allow ( )*

M1

1

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

*If  $[HX] / [X^-]$  or  $\frac{0.186}{0.105}$  upside down, or any addition or subtraction lose M1 & M2.*

M2

1

$pH = 4.51$  (correct answer scores 3)

*Can score M3 for correct pH conseq to their  $[H^+]$ , so  $pH = 5.01$  scores one*

*Must be to 2 dp*

M3

1



Alternative using Henderson–Hasselbach Equation

$$\text{pH} = \text{pKa} - \log\left[\frac{[\text{HX}]}{[\text{X}^-]}\right] = -\log(1.74 \times 10^{-5}) - \log\left(\frac{0.186}{0.105}\right)$$

*Allow ( )*

M1

$$\text{pKa} = 4.76 - 0.248$$

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

M2

$$\text{pH} = = 4.51$$

*so pH = 5.01*

*Must be to 2 dp*

M3

(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

$$[H^+] = \left( \frac{K_a \times [CH_3COOH]}{CH_3COO^-} \right) = \frac{1.74 \times 10^{-5} \times 0.266}{0.125}$$

*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*

M3

1

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

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

M4

1

$$\text{pH} = 4.43$$

Correct use of HX and  $X^-$  values from (d) gives  
pH = 4.41 and scores 4

*If wrong method, e.g.  $\sqrt{\quad}$  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

$$\text{mol acid after addition} = 0.251 + 0.015 = 0.266$$

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

M1

$$\text{mol salt after addition} = 0.140 - 0.015 = 0.125$$

*For X<sup>-</sup> if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3*

M2

$$\text{pH} = (\text{pKa} - \log[\text{HX}] / [\text{X}^-]) = -\log(1.74 \times 10^{-5}) - \log(0.266 / 0.125)$$

*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*

M3

$$\text{pH} = 4.76 - 0.328$$

M4

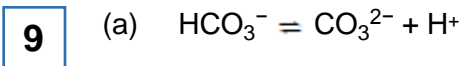
$$\text{pH} = 4.43$$

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

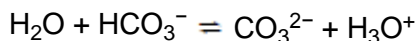
*Allow more but not fewer than 2dp here.*

M5

[8]



or



*Must have equilibrium sign but mark on to (b)*

*Ignore state symbols*

1

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

*Allow  $H^+$  ions react with carbonate ions (to form  $HCO_3^-$ )*

1

Alkali:  $OH^-$  reacts with  $H^+$  ions, equilibrium moves to the right (to replace the  $H^+$  ions)

1

Concentration of  $H^+$  remains (almost) constant

1

**[4]**