Mark schemes

Q1.

(a) $[H_2O]$ is (almost) constant

> ***Allow***
>
> *$[H_2O]$ is (very) large in comparison (to $[H^+]$ and $[OH^-]$)*
>
> ***or** $[H_2O]$ is incorporated in K_w*
> ***or** $K_w = K_c[H_2O]$*
> ***or** the equilibrium lies <u>very</u> much to the left.*
>
> ***Ignore** water has negligible dissociation*
> ***Ignore** $[H_2O] = 1$ or $[H_2O]$ is very small 1*

1

(b)   M1 Equilibrium is endothermic (in forward direction)

1

      M2 <u>Equilibrium</u> shifts to the RHS to minimise/oppose temperature increase

> ***Ignore** more H^+ and OH^- formed*

1

(c)   M1 $pH = -\log_{10}[H^+]$

> *M1 Allow $pH = -\log[H^+]$*

1

      M2 $[H^+] = \sqrt{5.48 \times 10^{-14}}$ $(= 2.34 \times 10^{-7})$

> *M2 $[H^+]^2 = 5.48 \times 10^{-14}$*

1

      M3 $pH = -\log_{10} 2.34 \times 10^{-7} = 6.63$

> *M3 $pH = -\log_{10}$ M2*

1

      M4 $[H^+] = [OH^-]$
          or
          Dissociation of each water molecule gives one H^+ and one OH^-

> *M4 Allow equal amounts of H^+ and OH^-*

1

(d)   5.55

> *Allow 5.5 to 5.6*

1

(e)   Different solutions must not contaminate each other

> *pH of previous solution doesn't contaminate new solution*

      or

To wash off any residual solution/substance (which could interfere with the reading)

> *Ignore to make neutral/neutralise*
>
> *Ignore so as not to affect concentrations*

1

(f)   To avoid missing the end point

Or

(Very little pH change per cm^3 added at start) large change in pH (near end point)

1

(g)   All have a colour change/pH range within the <u>steep/vertical</u> part of the titration curve

> *Colour change/pH range between pH 3 and 11*

1

(h)   M1   Amount of $OH^- = 36.25 \times 0.200 \div 1000 = 7.25 \times 10^{-3}$ mol
<u>and</u> Amount of $H^+ = 25.0 \times 0.150 \div 1000 = 3.75 \times 10^{-3}$ mol

1

M2   Amount of excess $OH^- = 7.25 \times 10^{-3} - 3.75 \times 10^{-3} = 3.50 \times 10^{-3}$ mol

1

M3 $[OH^-] = (3.50 \times 10^{-3}) \div (61.25 \times 10^{-3})$ $(= 5.71 \times 10^{-2}$ mol$)$

> *M3 $[OH^-] = (M2) \div (61.25 \times 10^{-3})$*

1

M4 $[H^+] = \underline{1.00 \times 10^{-14}} \div 5.71 \times 10^{-2} = 1.75 \times 10^{-13}$

> *M4 $[H^+] = 1.00 \times 10^{-14} \div M3$*

1

M5   pH = 12.76

> *M5 Allow pH = 12.8*
>
> *M5 $pH = -log_{10}(M4)$*
>
> *Alternative Method*
>
> *M4 p OH = 1.24*
>
> *M5 pH = 14 − 1.24 = 12.76*

1

[16]

Q2.

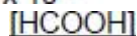$K_a = 10^{-3.75} = 1.78 \times 10^{-4}$ mol dm^{-3}

$$pH = pK_a - log\ \frac{[HCOOH]}{[HCOO^-]}$$

1

$[H^+] = 10^{-4.05} = 8.91 \times 10^{-5}$ mol dm^{-3}

$$log\ \frac{[HCOOH]}{[HCOO^-]} = pK_a - pH = 3.75 - 4.05 = -0.30$$

1

$$[Salt] = \frac{1.78 \times 10^{-4} \times 0.100}{8.91 \times 10^{-5}} = 0.200$$

$$\frac{[HCOOH]}{[HCOO^-]} = 10^{-0.30} = 0.50 \text{ (and } [HCOOH] = 0.1)$$

(so [HCOO⁻] = 0.200 mol dm⁻³)

1

amount = vol x conc = 0.200 x 25/1000 = 0.00500 mol
OR
amount acid = 0.0025 mol so amount salt = 0.005 mol

amount = vol x conc = 0.200 x 25/1000 = 0.00500 mol

1

mass = amount x M_r = 0.00500 x 68.0 = 0.339 / 0.34 g

mass = amount x M_r = 0.00500 x 68.0 = 0.339 g

1

[5]

Q3.

(a)   (Acid) partially or slightly ionises/dissociates (in water to form H⁺ ions)

Allow – does not fully ionise/dissociate

1

(b)

$$(K_a) = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

Allow [H₃O⁺] for [H⁺]
Do not allow ( )

1

(c)   **M1** $[C_2H_5COOH]$ = 0.125 (mol dm⁻³)

Allow consequential marking from wrong M1
If [C₂H₅COOH] = 0.0125 (mol dm⁻³) lose M1,
allow M2, M3 = 4.108 x 10⁻⁴ and M4 = 3.39

1

M2 $[H^+] = \sqrt{Ka \times [C_2H_5COOH]}$ OR $[H^+] = \sqrt{1.35 \times 10^{-5} \times 0.125}$

1

M3 $[H^+]$ = 1.30 x 10⁻³ (mol dm⁻³)

1

M4   pH = – log₁₀ (1.30 x 10⁻³) = 2.89

Allow M4 = -log₁₀ M3
Answer must be to 2 decimal places

1

(d)   **M1** $[H^+]$ = 10⁻⁴·⁵ = 3.16 x 10⁻⁵ (mol dm⁻³)

1

M2
$$[C_2H_5COO^-] = \frac{[C_2H_5COOH] K_a}{[H^+]}$$

OR
$$[C_2H_5COO^-] = \frac{0.250 \times 1.35 \times 10^{-5}}{3.16 \times 10^{-5}}$$

M2: Rearrangement

If rearrangement incorrect, could score M1 M4 M5 and M6

1

M3 $[C_2H_5COO^-] = 0.1068$ (mol dm⁻³)

1

M4 M_r sodium propanoate = 96

1

M5   n (sodium propanoate) = 0.1068 x 0.5 = 0.0534

1

M6   mass (sodium propanoate, x) = 0.0534 x 96 = 5.13 (g)
           M6 Allow 5.09 to 5.14 (g)

Alternative **M5** and **M6**

M5   0.1068 x 96 = 10.25 (g)
           M5 = M3 x M4

M6   Mass (sodium propanoate, x) = $\frac{10.25}{2}$ = 5.13 (g)
           10.25 g scores 4 marks
           If Henderson Hasselbach used
           M1 pKa = −log(1.35 x 10⁻⁵) = 4.87
           M2 log[A⁻] = pH -pKₐ + log[HA]
           M3 log[A⁻] = 4.50 −4.87 + (−0.60206) = −0.9717
           M4 [CH₃CH₂COO⁻] = 10⁻⁰·⁹⁷¹⁷ = 0.1067
           M5 Mᵣ = 96(.0)
           M6 x = 96.0 x 0.1067/2 = 5.12 g

1

[12]

Q4.
   B

[1]

Q5.
   A

[1]

Q6.

D

[1]

Q7.

(a) **M1**: $[H^+] = [OH^-]$

M1: accept equal number/amounts of H^+ and OH^-

1

M2: $[H^+] (= 10^{-pH}) = 2.138 \times 10^{-7}$

M2: allow 2.14×10^{-7}

1

M3: $K_w = [H^+]^2$ or $(2.138 \times 10^{-7})^2$

*M3: allow (**M2**)²*

1

M4: $K_w = 4.57 \times 10^{-14}$

M4: allow 4.58×10^{-14}

*M4 is dependent on (an answer)² in **M3***

1

(b) View with Figure X (ie graph) as they may show working there.

Ignore calculations of mols of salt or acid

M1: Determines volume at half equivalence (= $\frac{19.5}{2}$ cm³) = 9.75 (cm³)

*M1: Allow reading on graph to be from 19.4 to 19.7 giving **M1** = 9.7 to 9.85*

1

M2: pH = 4.80 to 4.95

M2: Reads off pH at half equivalence

1

M3: $K_a (= 10^{-pH}) = 10^{-4.9} = 1.26 \times 10^{-5}$

M3: Allow 1.12×10^{-5} to 1.58×10^{-5}

M3: Allow 2sf or more

1

Alternative method

M1: pH of pure acid = 3

M2: $K_a = (10^{-3})^2 / 0.080$

M3: $= 1.25 \times 10^{-5}$

*Alternative **M1** if calculation incorrect:*
Allow $pH = pK_a$ or $[H^+] = K_a$ at <u>half equivalence</u>

(c) cresolphthalein

1

(d)

M1: $K_a = \dfrac{[H^+][X]}{[HX]}$ or $[H^+] = \dfrac{K_a \times [HX]}{[X^-]}$

M1: allow $[H^+] = \dfrac{K_a \times [acid]}{[salt]}$

1

M2: amount of HX = 0.0500 mol

1

M3: amount of HX after add^n of KOH = 0.05 − $\underline{3 \times 10^{-4}}$ = 0.0497 mol

M3: = M2 − 3 × 10^{-4}

1

M4: amount of KX after add^n of KOH = 0.0136 + $\underline{3 \times 10^{-4}}$ = 0.0139 mol

1

M5: $[H^+] = \left(\dfrac{1.41 \times 10^{-5} \times 0.0497}{0.0139}\right) = \underline{5.04(15) \times 10^{-5}}$

1

M6: pH = -log$_{10}$ 5.04(15) × 10^{-5} = 4.30

Answer to 2 decimal places

1

If no attempt at M3 and M4 max 2 marks

If M3 or M4 attempted using 3 × 10^{-4} max 4 (M1, M2, M3 or M4 and M6)
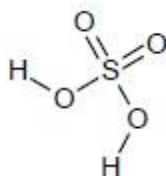
(e)

ratio $\dfrac{[HX]}{[X^-]}$

Allow inverse expression

1

[15]

Q8.

(a)

Ignore shape / bond angles
Ignore lone pair(s) on O atoms
NOT lone pair(s) on S atom

1

(b)   Equation 1: $H_2SO_4 \rightarrow HSO_4^- + H^+$ / $H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$

Equation 1: NOT ⇌

1

Equation 2: $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$ / $HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$

Equation 2: NOT → or ↔

Allow ⇋ or ⇌ or ⇋

1

Ignore state symbols in both equations

Allow multiples in both equations

(c) **M1** weigh solid and transfer using a method that Allows exact mass to be known (there should be two weighings, one of which could be zeroing, and method could be by difference or with washings or directly weighed into container)

M1 Ignore any mass quoted

NOT if any other solid added

1

M2 <u>dissolve</u> in water in suitable container (NOT in 250 cm³ of water)

M2 NOT if any other solution added

1

M3 transfer with washings into 250 cm³ volumetric/graduated flask

M3 Reference to 250 cm³ can appear anywhere

1

M4 make up to mark / 250 cm³ AND THEN shake / invert / mix

M4 Allow if conical flask used

NOT if beaker used

1

Alternative method (M2-4)

M2 in 250 cm³ volumetric/graduated flask

M3 dissolve (NOT in 250 cm³ of water)

M4 make up to mark / 250 cm³ AND THEN shake/invert/mix

(d) **M1** $[H^+] = 10^{-1.72}$ (= 0.0191 (mol dm⁻³))

1

M2 amount NaHSO₄ = 0.605/120.1 (= 5.04 x 10⁻³ (mol))

1

M3 initial [NaHSO₄] = [HSO₄⁻] = **M2** x 10 (= 5.04 x 10⁻² (mol dm⁻³))

$$K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \quad \text{or} \quad K_a = \frac{[H^+]^2}{[HSO_4^-]}$$

1

M4 $K_a = \dfrac{0.0191^2}{0.0504 - 0.0191}$

1

M5 K_a = 1.17 x 10⁻² (1.15 – 1.18 x 10⁻²) must be 3sf

1

M6 mol dm^{-3}

1

> *Correct answer scores **M1-5** (must be 3sf)*
> ***Alternative method** that does not subtract 0.0191:*
> *7.21 x 10^{-3} (7.15 – 7.26 x 10^{-3}) scores **M1-5***
>
> (where **M4** $K_a = \frac{0.0191^2}{0.0504}$)
>
> *If not correct answer:*
> *For **M1-3**, if answer is shown, it must be correct (Ignore sf)*
> *Allow ECF from **M1/2/3** to **M4**/5 (but not from **M3** to **M5** if omission of **M3** gives negative **M5**)*
> *NOT ECF from incorrect K_a expression in **M4** to **M5***
> ***M6** If not mol dm^{-3}, Allow ECF for units from incorrect K_a expression in **M4***
> *7.21 x 10^{-2} (7.15 – 7.26 x 10^{-2}) gives **M1,2,4,5** (by alternative method omitting **M3**)*

(e) **M1** ($HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$) equilibrium moves/shifts left (to counteract / remove increased $[SO_4^{2-}]$)

> ***M1** Allow H^+ reacts with SO_4^{2-}/sulfate*
> *Ignore favours the reverse / left / backwards reaction*
> *NOT base / A^- / sodium sulfate in place of SO_4^{2-}/sulfate*

M2 so $[H^+]$ decreases

1

> ***M2** Allow fewer H^+ (ions) or amount of H^+ lower or removes H^+*
> ***M2** independent of **M1***

1

[15]

Q9.

B

[1]

Q10.

(a) $[H^+] = (10^{-3.87} =) 1.3489 \times 10^{-4}$

> *Allow 1.35×10^{-4}. If M1 wrong can only score M2.*

1

$$[CH_3COOH] = \frac{[H^+]\left[CH_3COO^-\right]}{[Ka]} = \left(\frac{\left[1.3489 \times 10^{-4}\right][0.136]}{\left[1.74 \times 10^{-5}\right]} = 1.05436\right)$$

Mark is for correctly rearranged equation.

1

1.05 – 1.06 (mol dm⁻³)
            3 sf or more

1

(b) **If 0.007 moles in 500 cm³ seen follow Mark Scheme 1**

Mark Scheme 1

moles ethanoic acid = 0.130

1

moles sodium ethanoate = 0.0605

1

mol CH_3COOH after addition = (0.130 - 0.007) = 0.123

1

mol CH_3COO^- after addition = (0.0605+0.007) = 0.0675

1

$$[H^+] = (\frac{[Ka][CH_3COOH]}{[CH_3COO^-]}) = \frac{[1.74 \times 10^{-5}][0.123]}{[0.0675]} (=3.171 \times 10^{-5})$$

1

pH = <u>4.50</u> (must be 2dp)

1

Method 1
For M3 allow M1 – 0.007
For M4 allow M2 + 0.007

If 0.014 moles in 1 dm³ follow Mark Scheme 2

Mark Scheme 2

moles CH_3COOH after addition = (0.260 - 0.014) = 0.246 (This scores 2 marks)
moles CH_3COO^- after addition = (0.121 + 0.014) = 0.135 (This scores 2 marks)

$$[H^+] = (\frac{[Ka][CH_3COOH]}{[CH_3COO^-]}) = \frac{[1.74 \times 10^{-5}][0.246]}{[0.135]}$$

pH = <u>4.50</u> (must be 2dp)

Method 1 and 2
M5 = expression with their numbers
M6 = answer to 2 dp

pH = 4.50 scores 6 marks

If √used in K_a expression, stop at M4
If divide by 2 after M5, lose M6

Allow solutions which use Henderson-Hasselbach Equation

[9]

Q11.

(a)   7–10.2

any range (i.e. 2 values) within this range

1

(b) $K_a = \dfrac{[H^+][X^-]}{[HX]}$

ALLOW H_3O^+ for H^+ and A for X
IGNORE $[H^+]^2/[HX]$
must be square brackets
IGNORE state symbols

1

(c)   Amount NaOH = (24.0 × 0.100)/1000 = 2.40 × 10⁻³ mol

(= amount HX)

Conc HX = 2.40 × 10⁻³/0.025 = 0.0960 mol dm⁻³
ecf for M1/0.025

(d)   (K_a = 2.62 × 10⁻⁵ = $[H^+]^2$/0.0960)

$[H^+]$ = √(2.62 × 10⁻⁵ × 0.0960) (= 1.59 × 10⁻³ mol dm⁻³)
ecf from part (c) $[H^+]$ = √(2.62 × 10⁻⁵ × ans to part (c))
From alternative data
$[H^+]$ = √(2.62 × 10⁻⁵ × 0.600) (= 3.96 × 10⁻³ mol dm⁻³)

(pH = –log 1.59 × 10⁻³ =) 2.80 (must be 2 or more dp)

1

pH = 2.40 (must be 2 or more dp)
M2 dependent on a calculation of $[H^+]$

1

(e)   (pH at half-neutralisation = pK_a)

= –log 2.62 × 10⁻⁵ = 4.58 (must be 2 or more dp)
ALLOW 1dp if already penalised in part (d)

1

(f)   Both points plotted correctly and line touches both points
ecf from (d) and (e) within 1 small square

1

<u>Line steeper at start</u> then levels (to show buffering)
Mark independently

1

[9]

Q12.
  B

[1]

Q13.
  B

[1]

Q14.
  B

[1]

Q15.
  (a) Proton donor

1

  (b) Completely ionises to give H^+ ions in water

1

  (c) 0.058 mol dm^{-3}

1

       1.24

1

  (d) Amount of NaOH $= 5.25 \times 10^{-3}$

1

       Since 1:1 reaction amount of OH^- ions in excess

       $= 5.25 \times 10^{-3} - 1.45 \times 10^{-3}$ mol

       $= 3.80 \times 10^{-3}$ moles OH^-

1

       $[OH^-] = 3.80 \times 10^{-3} \times 1000/60 = 0.0633$

1

       $K_w = [H^+][OH^-$ so $H^+ = \dfrac{10^{-14}}{0.0633} = 1.58 \times 10^{-13}$

1

       pH $= 12.80$

1

  (e) Amount of OH^- added $1.5 / 40 = 0.0375$ mol

1

       Use of 1:1 ratio to calculate amount of A^- formed $= 0.0375$ mol

1

Amount of weak acid initially = 1 × 0.15 = 0.150 mol so amount of weak acid after addition of NaOH = 0.150 − 0.0375 = 0.1125
If M3 incorrect can only score max of 3 marks

1

$[H^+] = K_a [HA]/[A^-]$ or $[H^+] = 1.79 \times 10^{-5} \times 0.1125/0.0375$

1

$= 5.37 \times 10^{-5}$

1

pH = 4.27

1

[15]

Q16.

(a)   Formula of any strong acid (e.g. HCl)

1

Formula of a weak alkali (e.g. NH_3)

1

(b)   Place a fixed volume of alkali in a flask or beaker

1

Add acid in small portions from a burette

1

Stir and use a pH meter to record the pH after each addition of acid

1

(c)   Repeat the experiment with each indicator

1

Select the indicator that changes colour rapidly when the pH changes from about 7 to 4

1

[7]

Q17.

(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

$K_w = [H^+][OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

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

1

(d)   At this point, $[NH_3] = [H^+]$

Therefore K_a $= \dfrac{[H^+]^2}{[NH_4^+]}$

1

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

1

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

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 pH = – log₁₀(4.75 × 10⁻⁹) = 8.32
         Allow consequential marking based on answer from part (d)

1

[12]

Q18.
  C

[1]

Q19.
  B

[1]

Q20.
  C

[1]