A-Level Chemistry

Ionic Product of Water (Kw)

Mark Scheme

Time available: 55 minutes
Marks available: 49 marks

1. (a) completely dissociates/ionises (to form H^+ ions)

1

(b) **M1** moles HCl = 1.035×10^{-3} and moles $Ba(OH)_2$ = 3.75×10^{-3}

If M1 incorrect, lose M1 and M6

1

M2 moles OH^- = 2 × ($3.75 \times 10^{-3} = 7.50 \times 10^{-3}$)

If M2 not x2, lose M2 and M6

1

M3 XS n OH^- = 7.50×10^{-3} - 1.035×10^{-3} = 6.465×10^{-3} mol in 35.35 cm^3

If no subtraction for M3, lose M3 and M6

1

M4 [OH] = 6.465×10^{-3} / 35.35×10^{-3} = 0.182885 mol dm^{-3}

= M3/35.35 × 10^{-3}

If M4 not /35.35 × 10^{-3}, lose M4 and M6

However, if divided by 35.35 only lose M4 and allow M6 (ecf = 10.09)

1

M5 $[H^+] = K_w/[OH^-]$ = 1.47×10^{-14} /0.182885 = 8.0378 × 10–14 mol dm^{-3}

= 1.47×10^{-14} / M4

If incorrect rearrangement or wrong equation, lose M5 and M6

If $K_w = 1.00 \times 10^{-14}$ used only lose M5 and allow M6 (ecf = 13.26)

1

M6 pH = 13.09 to 13.10

Must be 2dp

1

Alternative MS to get M2:

Starting amounts are 1.035×10^{-3} mol HCl and 3.75×10^{-3} mol $Ba(OH)_2$ M1

So the HCl will react with 5.175×10^{-4} mol of the $Ba(OH)_2$ leaving an excess of 3.2325×10^{-3} mol of $Ba(OH)_2$ (as alternative M2)

So n OH^- = 2 × 3.2325×10^{-3}= 6.465×10^{-3} mol M3

Credit other methods eg limiting reagent method since HCl limiting reagent

(c) $[H^+] = [OH^-]$

1

(d) SO_2

1

(e) $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

1

(f) **M1** moles HCl added = 0.01 mol and moles CH_3COOH = 0.035 mol

1

M2 moles CH_3COO^- = 0.025 – 0.01 (= 0.015)

M2 mol CH_3COO^- = 0.025 - M1(HCl)

1

M3 moles CH_3COOH = 0.035 + 0.01 (= 0.045)

M3 mol CH_3COOH = M1(CH_3COOH) + M1(HCl)

1

M4 $[H^+] = 1.76 \times 10^{-5} \times \frac{M3\ (/\ V)}{M2\ (/\ V)}$ (= 5.28×10^{-5})

M4 is conditional on an attempt at an addition/subtraction in M2 OR M3

1

M5 pH = 4.28

M5 must be 2dp

If used 0.07 mol for CH_3COOH can score M2, M3 and M4 (pH = 4.03)

1

[15]

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

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

1

M2: $[H^+]$ (= 10^{-pH}) = 2.138×10^{-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 (= $\frac{19.5}{2}$ cm^3) = 9.75 (cm^3)

***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}) = $10^{-4.9}$ = 1.26×10^{-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: = 1.25×10^{-5}

*Alternative **M1** if calculation incorrect:*

Allow pH = pK_a or $[H^+] = K_a$ at <u>half equivalence</u>

(c) cresolphthalein

1

(d)

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

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

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

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 $\frac{[HX]}{[X^-]}$

Allow inverse expression

1

[15]

3. (a) Ans = C

1

(b) $[H^+] = \sqrt{K_w} = \sqrt{2.93 \times 10^{-15}}$ (= 5.41 × 10^{-8})

1

pH = (− log (5.41 × 10^{-8}) = $\underline{7.27}$

Must be 2dp

7.27 scores 2 marks

1

(c) $[H^+]$ = [OH-]

allow description in words

equal moles / quantities / numbers / ratio of H^+ and OH^-

1

(d) $[OH^-]$ = 0.0131 × 2 = 0.0262

pH = 12.95 scores 3 marks

pH = 12.42 scores 2 marks ($K_w = 1 \times 10^{-14}$)

pH = 12.65 scores 1 mark (not multiplied by 2)

pH = 12.35 scores 1 mark (divided by 2)

pH = 12.12 scores 0 marks (no × 2 and wrong K_w)

1

$[H^+] = (K_w / [OH^-]) = 2.93 \times 10^{-15} / 0.0262$ (= 1.118×10^{-13})

1

pH = (− log (1.118×10^{-13}) = 12.9514 = 12.95
Or
$[OH^-]$ = 0.0131 × 2 = 0.0262
pOH = (−log 0.0262) = 1.5817
pH =(−log K_w − pOH = −log 2.93×10^{-15} −1.58 = 14.53 − 1.58) = 12.95

allow to 2dp or more

1

(e) smaller / lower pH / less alkaline / more acidic

If not smaller CE = 0/2

Allow pH number between 8 and 12

1

(magnesium hydroxide) is less soluble / sparingly soluble/ solubility of hydroxide increases down group II

M2 dependent on M1 but if blank mark on

Ignore concentration and dissociation

Ignore incorrect formula

Do not allow $Mg(OH)_2$ is insoluble

1

[9]

4. (a) $[H_2O]$ is very high (compared with $[H^+]$ and $[OH^-]$)
OR
Very few H^+ and OH^- ions
OR
Only / very slightly dissociates
OR
Equilibrium lies far to the left

Not partially dissociates

M1

1

$[H_2O]$ 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) $[H^+]$ $= \sqrt{K_w}$ (or $= \sqrt{5.48 \times 10^{-14}}$)

Correct pH answer scores 3

1

If wrong method no marks

Using alternative K_w (1.00×10^{-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 (1.00×10^{-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 (1.00×10^{-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]