

# Equilibria, Energetics and Elements

## Acids, Bases & Buffers

1. (i)  $\text{H}^+$ /proton donor (1) 1
- (ii) partially dissociates/ionises (1) 1 [2]
- 
2.  $\text{C}_6\text{H}_5\text{OH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{O}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
           acid 1           base 2                   base 1           acid 2 (1) [1]
- 
3. (i)  $K_a = [\text{C}_6\text{H}_5\text{O}^-(\text{aq})] [\text{H}^+(\text{aq})] / [\text{C}_6\text{H}_5\text{OH}(\text{aq})]$  (1) 1
- (ii)  $M_r \text{C}_6\text{H}_5\text{OH} = 94$  (1)  
 $[\text{C}_6\text{H}_5\text{OH}(\text{aq})] = 4.7/94 = 0.050 \text{ mol dm}^{-3}$  (1)  
 $1.3 \times 10^{-10} \approx [\text{H}^+(\text{aq})]^2 / 0.050 \text{ mol dm}^{-3}$  (1) ('=' sign is acceptable)  
 $[\text{H}^+] = \sqrt{\{(1.3 \times 10^{-10}) \times (0.050)\}} = 2.55 \times 10^{-6} \text{ mol dm}^{-3}$  (1)  
 $\text{pH} = -\log[\text{H}^+] = -\log 2.55 \times 10^{-6} = 5.59$  (1)  
 3 marks:  $[\text{H}^+]$ ; pH expression ; calc of pH from  $[\text{H}^+]$  5 [6]
- 
4.  $[\text{H}^+(\text{aq})] = 1.99 \times 10^{-9} \text{ mol dm}^{-3}$  (1)  
 $[\text{C}_6\text{H}_5\text{O}^-(\text{aq})] = K_a [\text{C}_6\text{H}_5\text{OH}(\text{aq})] / [\text{H}^+(\text{aq})]$  (1)  
 $[\text{C}_6\text{H}_5\text{O}^-(\text{aq})] = 0.13 \text{ mol dm}^{-3}$  (1)
- Calculation should use half the original concentration of phenol to find the concentration of sodium phenoxide in the buffer. This should then be doubled back up again.*
- Do **not** penalise an approach that uses the original concentration of phenol in the expression above.*
- [3]
- 
5. (a) (i) Ionic product (1) 1
- (ii)  $K_w = [\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})]$  (1) *state symbols not needed* 1

(b) moles of HCl =  $\frac{5 \times 10^{-3} \times 21.35}{1000} = 1.067 \times 10^{-4}$  mol (1)

moles of Ca(OH)<sub>2</sub> =  $\frac{1.067 \times 10^{-4}}{2} = 5.34 \times 10^{-5}$  mol (1)

concentration of Ca(OH)<sub>2</sub> =  $40 \times 5.34 \times 10^{-5}$   
 $= 2.136 \times 10^{-3}$  mol dm<sup>-3</sup> (1)

2 marks for  $4.27 \times 10^{-3} / 8.54 \times 10^{-3}$  mol dm<sup>-3</sup>  
 (no factor of 4)

3

(c) [OH<sup>-</sup>] =  $2 \times 2.7 \times 10^{-3} = 5.4 \times 10^{-3}$  mol dm<sup>-3</sup> (1)

[H<sup>+</sup>(aq)] =  $\frac{K_w}{[\text{OH}^-(\text{aq})]} = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-3}} = 1.85 \times 10^{-12}$  mol dm<sup>-3</sup> (1)

pH =  $-\log(1.85 \times 10^{-12}) = 11.73/11.7$  (1)

3

ecf is possible for pH mark providing that the [H<sup>+</sup>]  
 value has been derived from  $K_w/[\text{OH}^-]$

If pOH method is used, pOH = 2.27. would get 1<sup>st</sup> mark,  
 pH = 14 - 2.27 = 11.73 gets 2<sup>nd</sup> mark.

Commonest mistake will be to not double OH<sup>-</sup> and to use  $2.7 \times 10^{-3}$   
 This gives ecf answer of 11.43/11.4, worth 2 marks.

pH = 11.13 from dividing by 2: worth 2 marks

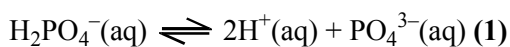
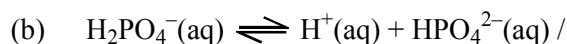
(d) 8 (1)

1

[9]



1



(or equivalent with H<sub>2</sub>O forming H<sub>3</sub>O<sup>+</sup>)

1

- (c) (i)  $\text{HPO}_4^{2-}$  (1) 1
- (ii)  $\text{H}_3\text{PO}_4$  (1) 1
- (iii)  $\text{H}_2\text{PO}_4^-$  produced  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  or on LHS of an attempted equilibrium equation (1)  
 2 equations/equilibria to shown action of buffer (1)(1)  
 from:  
 $\text{H}_2\text{PO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{PO}_4 /$   
 $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} /$   
 $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{HPO}_4^{2-} /$   
 $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$  3

[7]

7. proton donor ✓  
 partially dissociates ✓

[2]

8.  $K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]} / \frac{[\text{H}^+]^2}{[\text{HCOOH}]} / [\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$   
 $1.58 \times 10^{-4} = \frac{[\text{H}^+]^2}{0.025} / \checkmark$   
 $[\text{H}^+] = \sqrt{\{(1.58 \times 10^{-4}) \times (0.025)\}} = 1.99 \times 10^{-3} \text{ mol dm}^{-3} \checkmark$   
 $\text{pH} = -\log[\text{H}^+] = -\log 1.99 \times 10^{-3} = 2.70 \checkmark$   
 5.4034 (no square root) **with working** would score 1 mark.

[3]

9. (i) A solution that minimises pH changes/resists pH changes/opposes pH changes ✓  
 (not pH is kept constant/pH maintained/pH cancelled out. 1
- (ii)  $\text{HCOONa}/\text{HCOO}^-/\text{NaOH}$  ✓  
 $\text{HCOO}^-$  is the conjugate base/  
 $\text{HCOONa}$  is the salt of the weak acid or  $\text{HCOOH}/$   
 $\text{HCOONa}$  supplies  $\text{HCOO}^-$  ✓ 2

- (iii) *Two points from:*  
 Ka /pKa /acid strength/amount of dissociation ✓  
 temperature ✓ (but **not** "temperature & pressure")  
 ratio/amounts/concentrations of weak acid and  
**conjugate base/salt** ✓ (or reverse ratio)  
 (**not** ..... concentration of base as it could imply  
 NaOH)

2 max

[5]

10. Mass of HNO<sub>3</sub> =  $\frac{1400 \times 65}{100} / 910\text{g}$  ✓

Moles of HNO<sub>3</sub> =  $\frac{910}{63} = 14.4$  ✓

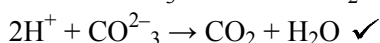
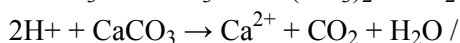
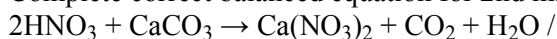
pH =  $-\log[\text{H}^+] = -\log 14.4 = -1.16/1.2$  ✓ calc -1.15836

pH from ignoring 65% pH = -1.35: **with working**, 2 marks.

[3]



Complete correct balanced equation for 2nd mark:



[2]

12. Two species differing by H<sup>+</sup> .... AW ✓

one pair: HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> ✓

other pair: HCOOH and HCOOH<sub>2</sub><sup>+</sup> ✓

[3]

13. moles of NaOH =  $\frac{0.1263 \times 23.75}{1000} / 3.00 \times 10^{-3}$  mol ✓

moles of acid =  $3.00 \times 10^{-3}$  mol ✓

moles of acid in flask =  $10 \times 3.00 \times 10^{-3} = 3.00 \times 10^{-2}$  mol ✓

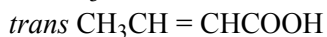
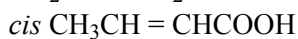
molar mass of compound =  $\frac{\text{mass}}{n} = \frac{2.58}{3.00 \times 10^{-2}} = 86$  ✓ 4

Molecular formula = C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> ✓

A 4 carbon carboxylic acid

(e.g. butanoic acid) shown (bod) ✓

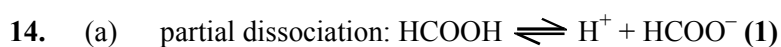
Any 2 possible isomers ✓✓ from:



4

*Accept structural formulae that are unambiguous.*

[8]



1

- (b) (i)  $\text{pH} = -\log(1.55 \times 10^{-3}) = 2.81/2.8$  (1)  
[H<sup>+</sup>] deals with negative indices over a very wide range/  
pH makes numbers manageable  
/removes very small numbers (1)

2

(ii)  $K_a = \frac{[\text{H}^+(\text{aq})][\text{HCOO}^-(\text{aq})]}{[\text{HCOOH}(\text{aq})]}$  (1) (state symbols not needed)

1

(iii)  $K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{HCOOH}(\text{aq})]} = \frac{(1.55 \times 10^{-3})^2}{0.015}$  (1)

$$= 1.60 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}(1)$$

$$\text{p}K_a = -\log K_a = -\log(1.60 \times 10^{-4}) = 3.80$$
 (1)

3

(iv) Percentage dissociating =  $\frac{(1.55 \times 10^{-3}) \times 100}{0.015} = 10.3\%$  /

10% (1)

1

*(working not required)*

[8]



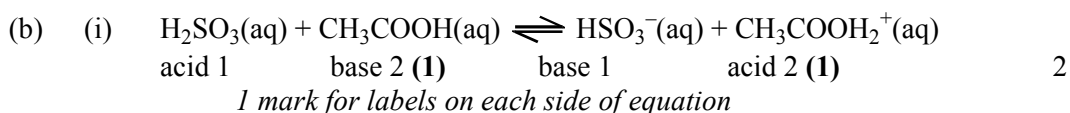
1

*state symbols not needed*

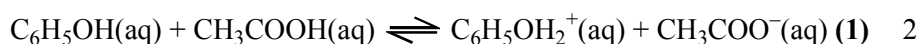
- (ii)  $n(\text{HCOOH}) = 0.0150 \times 25.00/1000 = 3.75 \times 10^{-4}$  (1)  
 volume of NaOH(aq) that reacts is 30 cm<sup>3</sup> (1)  
 so  $[\text{NaOH}] = 3.75 \times 10^{-4} \times 1000/30 = 0.0125 \text{ mol dm}^{-3}$  (1) 2
- (iii)  $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$  (1)  
 $\text{pH} = -\log(1 \times 10^{-14}/0.0125) = 12.10/12.1$  (1)  
 (calc 12.09691001) 3
- (iv) metacresol purple (1)  
 pH range coincides with pH change **during sharp rise** OR  
 pH 6-10 /coincides with equivalence point/end point (1) 2

[8]

16. (a) strength of acid/extent of dissociation/ionisation (1) 1



- (ii)  $\text{CH}_3\text{COOH}$  is the stronger acid/  
 $K_a$   $\text{CH}_3\text{COOH}$  is greater/  
 $\text{CH}_3\text{COOH}$  is more acidic ORA (1)



- (c) For HCl,  $\text{pH} = -\log[\text{H}^+]$  (1) (or with values).  
 Could be awarded below  
 $= -\log 0.045 = 1.35$  (1) (accept 1.3)

For  $\text{CH}_3\text{COOH}$ ,  $[\text{H}^+] = \sqrt{(K_a \times [\text{CH}_3\text{COOH}]}$  /  
 $\sqrt{(1.70 \times 10^{-5} \times 0.045)}$  (1)

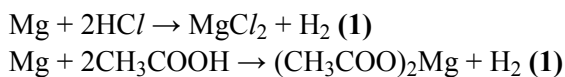
$[\text{H}^+] = 8.75 \times 10^{-4} \text{ mol dm}^{-3}$  (1)

$\text{pH} = -\log 8.75 \times 10^{-4} = 3.058/3.06$  (1) (accept 3.1) 5

[10]

17. HCl and CH<sub>3</sub>COOH have same number of moles/  
 release same number of moles H<sup>+</sup> /  
 1 mole of each acid produce ½ mol of H<sub>2</sub> (1)

[H<sup>+</sup>] in CH<sub>3</sub>COOH < [H<sup>+</sup>] in HCl//  
 CH<sub>3</sub>COOH is a weaker acid than HCl (ora) (1)



or



4

[4]

18. amount of NaOH in titration = 0.175 x 22.05/1000  
 or 3.86 × 10<sup>-3</sup> (1) (calc: 3.85875 x 10<sup>-3</sup>)

amount of A in 25.0 cm<sup>3</sup> = 0.5 × mol NaOH  
 or 1.93 × 10<sup>-3</sup> (1) (calc: 1.929375 × 10<sup>-3</sup>)

amount of A in 250 cm<sup>3</sup> = 10 × 1.93 × 10<sup>-3</sup> or 1.93 × 10<sup>-2</sup> (1)

1.93 × 10<sup>-2</sup> mol A has a mass of 2.82 g

molar mass of A = 2.82/1.93 × 10<sup>-2</sup> = 146 g mol<sup>-1</sup> (1)  
 (or M<sub>r</sub> of A is 146)

Therefore A is adipic acid / HOOC(CH<sub>2</sub>)<sub>4</sub>COOH (1)

5

[5]

19. (i) proton donor (1)

1

(ii) partially dissociates (1)

1

[2]

20. C<sub>6</sub>H<sub>5</sub>OH(aq) + OH<sup>-</sup>(aq) ⇌ C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>(aq) + H<sub>2</sub>O(l)  
 acid 1                  base 2 (1)                  base 1                  acid 2 (1)  
 1 mark for each acid-base pair

[2]

21. (i)  $K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{OH}]} \quad (1)$  1

- (ii) concentration =  $38/94 \quad (1) = 0.40 \text{ mol dm}^{-3} \quad (1)$   
*(first mark for  $M_r$  of phenol – incorrect answer here will give ecf for remainder of question)*

$$1.3 \times 10^{-10} \approx \frac{[\text{H}^+(\text{aq})]^2}{0.40} \quad (1)$$

*(‘=’ sign is acceptable)*

$$[\text{H}^+] = \sqrt{\{(1.3 \times 10^{-10}) \times (0.40)\}} = 7.2 \times 10^{-6} \text{ mol dm}^{-3} \quad (1)$$

$$\text{pH} = -\log[\text{H}^+] = -\log 7.2 \times 10^{-6} = 5.14 \quad (1)$$
 5

**3 marks:**  $[\text{H}^+] \quad (1)$ ; pH expression  $(1)$ ; calc of pH from  $[\text{H}^+] \quad (1)$

**Common errors:**

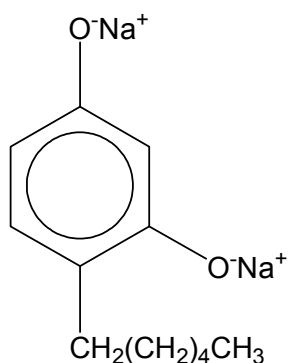
Without square root, answer = 10.28  $(1)(1)(0)$

Use of 38 as molar concentration does not score 1<sup>st</sup> 2 marks.

This gives an answer of 4.15 for 3 marks  $(1)(1)(1)$

[6]

22.



/ NaOH / Na  $(1)$

weak acid/base pair mixture formed  $(1)$

*On structure, 1 mark for O Na on either or both phenol groups.*

2

[2]

23. (i) completely dissociates/ionised  $(1)$   
 proton donor  $(1)$  2

- (ii)  $\text{NO}_3^- \quad (1)$  1

[3]

24. (i)  $\text{pH} = -\log[\text{H}^+] / -\log(0.015) \quad (1) = 1.82 / 1.8 \quad (1)$  (Not 2) 2



(ii)  $[H^+] = 0.0075 \text{ mol dm}^{-3}$   
 $\text{pH} = -\log(0.0075) = 2.12 / 2.1$  (1) 1 [3]

25. (i)  $K_w = [H^+(\text{aq})][OH^-(\text{aq})]$  (1) 1  
*state symbols not needed*

(ii)  $[H^+(\text{aq})] = 10^{-\text{pH}} = 10^{-13.54} = 2.88/2.9 \times 10^{-14} \text{ mol dm}^{-3}$  (1)  
 $[NaOH] / [OH^-(\text{aq})] = \frac{K_w}{[H^+(\text{aq})]} = \frac{1.0 \times 10^{-14}}{2.88 \times 10^{-14}}$   
 $= 0.347 / 0.35 \text{ mol dm}^{-3}$  (1) 2 [3]

26. (i) a solution that minimises/resists/opposes pH changes (1) 1

(ii) The buffer must contain both  $CH_3COOH$  and  $CH_3COONa$  /  
 $CH_3COO^-$  /weak acid and conjugate base(\*) (1)

Solution **A** is a mixture of  $CH_3COOH$ (\*) and  $CH_3COONa$ (\*) /  
 / has an excess of acid /is acidic (1)

Solution **B**, contains only  $CH_3COONa$ / only  $CH_3COO^-$   
 /only the salt/ is neutral (1)

$CH_3COOH(\text{aq}) + NaOH(\text{aq}) \rightarrow CH_3COONa(\text{aq}) + H_2O(\text{l})$  /  
 acid/alkali has been neutralised/  
 $CH_3COOH(\text{aq})$  and  $NaOH$  react together (1) 4 [5]

27.  $[H^+]$  increases (1)  
 $H_2O$  ionises more /  
 for  $H_2O \rightleftharpoons H^+ + OH^-$ , equilibrium moves to the right (1) 2  
*exo/endo is 'noise'* [2]