TOPIC 7.2 Ionic Equilibria

PAPER 1

Section A

1. **C**

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

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

$[H^+]^2 = K_w$ since $[H^+] = [OH^-]$

$\therefore [H^+] = \sqrt{1.44 \times 10^{-14}}$

$= 1.20 \times 10^{-7}$ mol dm^{-3}

$pH = -\log_{10}[H^+]$

$= -\log_{10}(1.20 \times 10^{-7})$

$= 6.92 \qquad \therefore pH < 7$

2. **B**

For a weak acid HA,

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

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

$pH = pK_a$ when $K_a = [H^+]$ i.e. when $[A^-] = [HA]$

This occurs at the point of half-neutralisation when volume of NaOH $= \frac{10}{2} = 5$ cm^3

3. **B**

The main buffer in blood plasma is the hydrogen carbonate (HCO_3^-) and carbonic acid (H_2CO_3) buffer system.

Contaminating $H^+(aq)$ ions are removed by HCO_3^- ions based on the equation:

$HCO_3^- + H^+ \rightarrow H_2CO_3$

4. **D**

K_a, the acid dissociation constant, is only affected by changes in temperature. It is not affected by changes in volume, V.

5. **D**

A buffer solution is a solution whose pH remains almost unchanged on dilution or when small amounts of acid or base are added to it.

Soft drinks are considered acidic buffers of weak citric acid and sodium citrate (salt of the acid).

If a small amount of acid, H^+ ions, is added to the buffer solutions, the additional H^+ ions are removed by the large concentration of citrate ions from the salt. Hence, pH remains almost unchanged.

If a small amount of base, OH^- ions, is added to the buffer solutions, the additional OH^- ions are removed by the large concentration of citric acid present in the buffer.

Hence, pH remains almost unchanged.

Section B

6. **B**

Results from student A:

$AgNO_3(aq) + CH_3COO^-Na^+(aq) \rightarrow$

$CH_3COO^-Ag^+(s) + NaNO_3(aq)$

white PPT

$CH_3COO^-Ag^+(s) + KBr(aq) \rightarrow$

$AgBr(s) + CH_3COO^-K^+(aq)$

cream PPT

Results from student B:

$AgNO_3(aq) + KBr(aq) \rightarrow AgBr(s) + KNO_3(aq)$

cream PPT

$AgBr(s) + CH_3COO^-Na^+(aq) \rightarrow$ No Reaction

(i.e. no $CH_3COO^-Ag^+$ formed)

1 – From the results, silver ethanoate ($CH_3CO_2^-Ag^+$) is an insoluble white PPT.

2 – From the results, AgBr is less soluble than $CH_3COO^-Ag^+$.

3 – Bromide is not oxidised by ethanoate.

PAPER 2

1. (a) $K_{sp} = [Ag^+][Br^-]$

(b) $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

$7.1 \times 10^{-7} \quad 7.1 \times 10^{-7} \qquad 7.1 \times 10^{-7}$

$K_{sp} = [Ag^+][Br^-]$

$= (7.1 \times 10^{-7})^2$

$= 5.0 \times 10^{-3}$ mol^2 dm^{-6}

PAPER 3

1. (a) $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

(b)
$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$4.9 \times 10^{-10} = \frac{[H^+]^2}{0.100}$$

$[H^+]^2 = 49 \times 10^{-12}$

$[H^+] = 7.00 \times 10^{-6}$ mol dm^{-3}

$$\therefore \text{\% of HCN ionised} = \frac{7.00 \times 10^{-6}}{0.100} \times 100\%$$

$= 0.007\%$

(c) $HCN \rightleftharpoons H^+ + CN^-$ ...... (1)

$NaCN \rightarrow Na^+ + CN^-$

common ion

The addition of NaCN will increase the $[CN^-]$.

Presence of this common ion will shift the position of equilibrium in (1) to the left i.e. less HCN molecules dissociate. Thus; the % of HCN molecules that ionised is decreased.

2. (a) Let the lactic acid be HA.

$HA \rightleftharpoons H^+ + A^-$

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

Since the degree of dissociation for weak acid is very small, $[HA]_{eqm} = [HA]_{initial}$. From the dissociation equation, $[H^+] = [A^-]$.

$$\therefore \quad K_a = \frac{[H^+]^2}{[HA]}$$

$$[H^+]^2 = K_a[HA] = (1.38 \times 10^{-4})(0.20)$$

$$[H^+] = 5.25 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \quad pH = -\log_{10}[H^+]$$

$$= -\log_{10}(5.25 \times 10^{-3})$$

$$= 2.28$$

(b) (i) A buffer solution is a solution that resists any pH change when small amounts of acid or base is added to it.

(ii) Mixture is a solution of acidic buffer.

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log_{10}K_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log_{10}(1.38 \times 10^{-4}) + \log_{10}\left(\frac{0.30}{0.20}\right)$$

$$= 4.04$$

(iii)

$$\underset{\text{(from acidic buffer)}}{CH_3CH(OH)COO^-} + \underset{\text{(from HCl)}}{H^+} \rightarrow CH_3CH(OH)COOH$$

3. $$K_C = \frac{[\text{gluconic acid}]}{[\text{GDL}][H_2O]}$$

$$\text{No. of moles of GDL} = \frac{\text{Mass}}{M_r}$$

$$= \frac{1.00 \text{ g}}{178}$$

$$= 5.62 \times 10^{-3} \text{ mol}$$

$$[\text{GDL}] = \frac{5.62 \times 10^{-3} \text{ mol}}{\left(\frac{50}{1000}\right) \text{dm}^3}$$

$$= 0.112 \text{ mol dm}^{-3}$$

	GDL +	$H_2O \rightleftharpoons$	gluconic acid
Initial/mol dm^{-3} :	0.112	55.5	0
Equilibrium/mol dm^{-3} :	0.112 – 0.0670 = 0.0450	55.5	0.0670

$$\therefore \quad K_c = \frac{[\text{gluconic acid}]}{[\text{GDL}][H_2O]}$$

$$= \frac{(0.0670)}{(0.0450)(55.5)}$$

$$= 0.0268 \text{ dm}^3 \text{ mol}^{-1}$$

4. (a) $HA \rightleftharpoons H^+ + A^-$ (where HA = Malonic acid)

From the above equation, $[H^+] = [A^-]$ and since the degree of dissociation is very small, $[HA]_{eqm} = [HA]_{initial}$.

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+]^2}{[HA]}$$

$$\boxed{\begin{array}{l} pK_a = 2.85 \\ \therefore K_a = 10^{-2.85} \end{array}}$$

$$[H^+] = \sqrt{K_a[HA]}$$

$$= \sqrt{(10^{-2.85})(0.10)}$$

$$= \sqrt{1.4125 \times 10^{-4}}$$

$$\therefore \quad pH = -\log_{10}[H^+]$$

$$= -\log_{10}(\sqrt{1.4125 \times 10^{-4}})$$

$$= 1.925$$

$$\approx 1.93 \text{ (to 3 s.f.)}$$

(b) Key features of titration curve sketch:

Ⓐ Initial pH = 1.93 at 0 cm^3 (as calculated in part (a)).

Ⓑ pH at $MBC_1 = pK_1 = 2.85$ at 5 cm^3 $(V_{MBC_1} = \frac{1}{2}V_{\text{Equivalence}})$

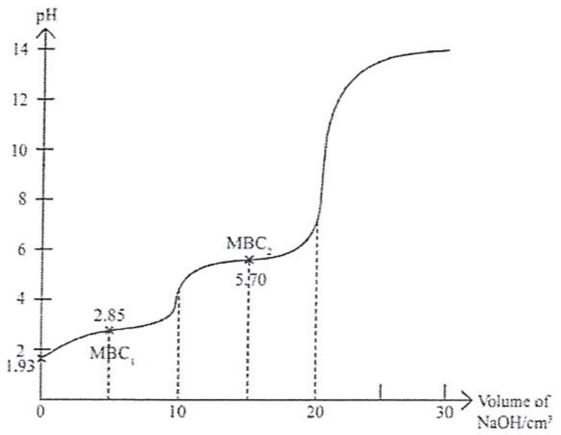
$[HO_2CCH_2CO_2^-] = [HO_2CCH_2CO_2H]$

Ⓒ pH at $MBC_2 = pK_2 = 5.70$ at 15 cm^3

$[HO_2CCH_2CO_2^-] = [^-O_2CCH_2CO_2^-]$

Ⓓ 1st equivalence point @ 10 cm^3

Ⓔ 2nd equivalence point @ 20 cm^3



5. (a) (i) $[Ca^{2+}] = \frac{0.0080}{40.1}$

$= 2.00 \times 10^{-4}$ mol dm^{-3}

$[Mg^{2+}] = \frac{0.0049}{24.3}$

$= 2.00 \times 10^{-4}$ mol dm^{-3}

$[Cl^-] = \frac{0.0071}{33.5}$

$= 2.00 \times 10^{-4}$ mol dm^{-3}

$[HCO_3^-] = \frac{0.0366}{[1.0 + 12.0 + 3(16.0)]}$

$= 6.00 \times 10^{-4}$ mol dm^{-3}

Formulae of the salts and their relative amounts:

$$\begin{array}{ccccccc} CaCl_2 & : & MgCl_2 & : & Ca(HCO_3)_2 & : & Mg(HCO_3)_2 \\ 1 & : & 1 & : & 3 & : & 3 \end{array}$$

Tips

Ionic Equilibrium–Revision–Extra Question:

$[Ca^{2+}] = \frac{0.0080}{40.1} = 2.00 \times 10^{-4}$ mol dm^{-3}

$[Mg^{2+}] = \frac{0.0049}{24.3} = 2.00 \times 10^{-4}$ mol dm^{-3}

$[Cl^-] = \frac{0.0071}{35.5} = 2.00 \times 10^{-4}$ mol dm^{-3}

$[HCO_3^-] = \frac{0.0366}{[1.0 + 12.0 + 3(16.0)]} = 6.00 \times 10^{-4}$ mol dm^{-3}

∴ Relative amounts of soluble salts is:

$$\begin{array}{ccccccc} CaCl_2 & : & MgCl_2 & : & Ca(HCO_3)_2 & : & Mg(HCO_3)_2 \\ 1 & : & 1 & : & 3 & : & 3 \end{array}$$

Solution:

$$\begin{array}{ccccccc} CaCl_2 & : & MgCl_2 & : & Ca(HCO_3)_2 & : & Mg(HCO_3)_2 \\ 1 & : & 1 & : & 3 & : & 3 \end{array}$$

$$\underbrace{\left\{\begin{array}{cccc} 1\ Ca^{2+} & 1\ Mg^{2+} & 3\ Ca^{2+} & 3\ Mg^{2+} \\ 2\ Cl^- & 2\ Cl^- & 6\ HCO_3^- & 6\ HCO_3^- \end{array}\right.}$$

∴ total available mole of ions are:

$$\left.\begin{array}{l} 4\ Ca^{2+} \\ 4\ Mg^{2+} \\ 4\ Cl^- \\ 12\ HCO_3^- \end{array}\right\} \div 2 \left\} \begin{array}{l} 2\ Ca^{2+} \\ 2\ Mg^{2+} \\ 2\ Cl^- \\ 6\ HCO_3^- \end{array}\right\} \text{★same as the molar concentration of ions we have calculated}$$

Comments:

- Both chlorides and hydrogencarbonates of magnesium and calcium had to be present. Besides the above 4 salts, $MgCl(HCO_3)$ was also accepted as one of the salts.
- Salts such as $MgCO_3$ and $CaCO_3$ should not be present.
- Relative amounts of salts need to fit with the ionic ratios calculated.

(ii) Calcium carbonate.

Since $CaCO_3$ is more insoluble than $MgCO_3$, the K_{sp} value for $CaCO_3$ is smaller than that for $MgCO_3$.

When the sample of mineral water was partially evaporated, $[HCO_3^-]$ increased. This caused the position of the equilibrium $CO_2(g) + H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons 2HCO_3^-(aq)$ to shift to the LHS, forming more $CO_3^{2-}(aq)$.

The increased $[CO_3^{2-}]$ caused the ionic product $[Ca^{2+}][CO_3^{2-}]$ to increase to a value more than the $K_{sp}(CaCO_3)$ first, with the ionic product $[Mg^{2+}][CO_3^{2-}]$ remaining less than the $K_{sp}(MgCO_3)$.

Thus, $CaCO_3$ solid is precipitated out first.

(iii) Rocks of hills and mountains are probably made up of calcium carbonate and magnesium carbonate.

Carbon dioxide from the air is dissolved inside rainwater and the rainwater comes into contact with CO_3^{2-} ions:

$$CO_2(g) + H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons 2HCO_3^-(aq)$$

When rainwater percolates through the rock, carbon dioxide reacts with some of the dissolved CO_3^{2-} ions from the partial dissolution of calcium carbonate and magnesium carbonate to form HCO_3^- as present in the mineral water.

This will cause a decrease in $[CO_3^{2-}]$ and thus shifts the position of the equilibrium below to the RHS:

$$XCO_3(s) \rightleftharpoons X^{2+}(aq) + CO_3^{2-}(aq) \text{ (where X= Ca or Mg)}$$

This causes more metal carbonate to dissolve which produces the metal cations of $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$ ions in the mineral water.

(b) (i)

$$6Ca_5(PO_4)_3F + SiO_2 + H_2O \rightarrow SiF_4 + 2HF + 3CaO + 9Ca_3(PO_4)_2$$

∴ a = 1

b = 1

c = 1

d = 2

e = 3

f = 9

(ii) $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ units: mol^5 dm^{-15}

Tips

$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

(iii) $$\begin{array}{ccccc} Ca_3(PO_4)_2 & \rightleftharpoons & 3Ca^{2+} & + & 2PO_4^{3-} \\ x & & 3x & & 2x \end{array}$$

∴ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$1 \times 10^{-26} = (3x)^3(2x)^2$

$1 \times 10^{-26} = 108x^5$

∴ $x = 2.47 \times 10^{-6}$

Hence, $[Ca^{2+}] = 3x = 3(2.47 \times 10^{-6})$

$= 7.42 \times 10^{-6}$ mol dm^{-3}