Chapter 4 Acids and bases

Section 4.1 Introducing acids and bases

4.1 KEY QUESTIONS

1   $HBr(g) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$

2   H_2SO_4/HSO_4^- and $H_2NO_3^+/HNO_3$

3   a H_2O
    b H_3O^+
    c CH_3NH_2

4   a NH_4^+
    b CH_3COOH
    c $H_2PO_4^-$
    d HCO_3^-

5   Brønsted–Lowry acid–base reactions are those involving the exchange of a proton (H^+ ion). The acid donates the proton to the base. In the reaction below, the HCl loses a proton to the base.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

The ionic equation provides a clearer way (by eliminating spectator ions) of noting the reaction between the H^+ and OH^- ions neutralising to form water.

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

6   Acting as an acid, whereby the reactant donates one proton:
    a $HCO_3^- + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
    b $HPO_4^{2-} + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$
    c $HSO_4^- + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
    d $H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$

    Acting as a base, whereby the reactant accepts one proton:
    a $HCO_3^- + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$
    b $HPO_4^{2-} + H_2O(l) \rightarrow H_2PO_4^-(aq) + OH^-(aq)$
    c $HSO_4^- + H_2O(l) \rightarrow H_2SO_4(aq) + OH^-(aq)$
    d $H_2O + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

Section 4.2 Strength of acids and bases

4.2 KEY QUESTIONS

1   a $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$
    b $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
    c $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

2   Stage 1: $H_3AsO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2AsO_4^-(aq)$
    Stage 2: $H_2AsO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HAsO_4^{2-}(aq)$
    Stage 3: $HAsO_4^{2-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + AsO_4^{3-}(aq)$

3   A. A strong acid readily donates a proton to a water molecule to form the hydronium ion. The complete ionisation of the acid molecule is indicated by the use of a single arrow, $\rightarrow$.

4   Stronger acids ionise more readily, forming ions in solution. As perchloric acid is a stronger acid, more hydronium ions would be present in solution than in a solution of ethanoic acid, making it a better conductor of electricity.

5   a $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$; $K_a = \dfrac{[H_3O][F^-]}{[HF]}$

    b $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$; $K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

    c $H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$; $K_a = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$

    d $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$; $K_a = \dfrac{[H_3O^+][NH_3]}{[NH_4^+]}$

Section 4.3 Acidity of solutions

Worked example: Try yourself 4.3.1

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 5.6×10^{-6} mol L^{-1} HNO$_3$ solution at 25°C, calculate [H$_3$O$^+$] and [OH$^-$].

Thinking	Working
Find the concentration of hydronium (H$_3$O$^+$) ions.	HNO$_3$ is a strong acid, so it will ionise completely in solution. Each molecule of HNO$_3$ donates one proton to water to form one H$_3$O$^+$ ion: HNO$_3$(aq) + H$_2$O(l) → H$_3$O$^+$(aq) + NO$_3^-$(aq) Because HNO$_3$ is completely ionised in water, 5.6×10^{-6} mol L^{-1} will produce a solution with a concentration of H$_3$O$^+$ ions of 5.6×10^{-6} mol L^{-1}: i.e [H$_3$O$^+$] = 5.6×10^{-6} mol L^{-1}
Use the expression for the ionisation constant of water to calculate the concentration of OH$^-$ ions.	K_w = [H$_3$O$^+$][OH$^-$] = 1.00×10^{-14} $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$ Since [H$_3$O$^+$] = 5.6×10^{-6} mol L^{-1} $[OH^-] = \dfrac{1.00 \times 10^{-14}}{5.6 \times 10^{-6}}$ $= 1.8 \times 10^{-9}$ mol L^{-1}

Worked example: Try yourself 4.3.2

CALCULATING pH OF AN AQUEOUS SOLUTION FROM [H$_3$O$^+$]

What is the pH of a solution in which [H$_3$O$^+$] is 6.0×10^{-9} mol L^{-1}? Express your answer to two significant figures.

Thinking	Working
Write down [H$_3$O$^+$] in the solution.	[H$_3$O$^+$] = 6.0×10^{-9} mol L^{-1}
Substitute the value of [H$_3$O$^+$] into: pH = $-\log_{10}$[H$_3$O$^+$] Use the logarithm function on your calculator to calculate the answer.	pH = $-\log_{10}$[H$_3$O$^+$] $= -\log_{10}(6 \times 10^{-9})$ (use your calculator) $= 8.2$

Worked example: Try yourself 4.3.3

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.01 mol L^{-1} solution of Ba(OH)$_2$ at 25°C?

Thinking	Working
Write down the reaction in which Ba(OH)$_2$ dissociates.	In water, each mole of Ba(OH)$_2$ completely dissociates to release 2 moles of OH$^-$ ions. Ba(OH)$_2$(aq) → Ba^{2+}(aq) + 2OH$^-$(aq)
Determine [OH$^-$].	[OH$^-$] = 2 × [Ba(OH)$_2$] $= 2 \times 0.01$ mol L^{-1} $= 0.02$ mol L^{-1}

Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.02}$ $= 5 \times 10^{-13}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(5 \times 10^{-13})$ (use your calculator) $= 12.3$

Worked example: Try yourself 4.3.4

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 0.50 g KOH in 500 mL of solution?	
Thinking	**Working**
Determine the number of moles of KOH.	$n(KOH) = \dfrac{m}{M}$ $= \dfrac{0.50}{56.0}$ $= 8.9 \times 10^{-3}$ mol
Write the equation for dissocation of KOH.	$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$ KOH is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(OH^-) = n(KOH)$ $= 8.9 \times 10^{-3}$ mol
Use the formula for determining concentration given the number of moles and volume: $c = \dfrac{n}{V}$	$n = 8.9 \times 10^{-3}$ mol $V = 0.500$ L $c = \dfrac{8.9 \times 10^{-3}}{0.500}$ $= 0.0179$ mol L^{-1}
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.0179}$ $= 5.6 \times 10^{-13}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(5.6 \times 10^{-13})$ (use your calculator) $= 12.3$

Worked example: Try yourself 4.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 10.4 at 25°C.	
Thinking	**Working**
Decide which form of the relationship between pH and $[H_3O^+]$ should be used: $pH = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$	As you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-pH}$

Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-pH}$ $= 10^{-10.4}$ $= 3.98 \times 10^{-11} \, mol \, L^{-1}$

Worked example: Try yourself 4.3.6

CALCULATING pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

43.0 mL of 0.200 mol L^{-1} nitric acid is added to 15.0 mL of 0.300 mol L^{-1} barium hydroxide (at 25°C). Calculate the pH of the final solution.

Thinking	Working
Identify the type of reaction and write an equation for the reaction.	acid + base → salt + water $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
Identify the values for the concentrations and volumes of the reactants.	HNO$_3$ Ba(OH)$_2$ $c = 0.200 \, mol \, L^{-1}$ $c = 0.300 \, mol \, L^{-1}$ $V = 43.0 \, mL$ $V = 15.0 \, mL$
Calculate the number of moles of H$^+$ and OH$^-$.	$n(HNO_3) = \dfrac{43}{1000} \times 0.2 = 8.6 \times 10^{-3} \, mol$ $n(Ba(OH)_2) = \dfrac{15}{1000} \times 0.3 = 4.5 \times 10^{-3} \, mol$ Total $n(OH^-) = 2 \times 4.5 \times 10^{-3} = 9 \times 10^{-3} \, mol$
Identify the relationship between the number of moles of H$^+$ and OH$^-$. (This will always be 1:1.)	1 mol of H$^+$ reacts with 1 mol of OH$^-$.
Identify which of H$^+$ and OH$^-$ is in excess.	OH$^-$ is in excess.
Calculate the number of moles of reactant in excess.	$n(OH^-)$ left $= 9 - 8.6 \times 10^{-3} = 4 \times 10^{-4} \, mol$
Calculate the concentration of the excess OH$^-$.	$[OH^-] = \dfrac{4 \times 10^{-4}}{0.058} = 6.897 \times 10^{-3} \, mol \, L^{-1}$
Calculate the concentration of H$^+$ (H$_3$O$^+$).	$[H^+] = \dfrac{K_w}{OH^-}$ $[H^+] = \dfrac{1 \times 10^{-14}}{6.897 \times 10^{-3}} = 1.45 \times 10^{-12} \, mol \, L^{-1}$
Calculate pH using: pH = $-\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	pH = $-\log_{10}[H_3O^+]$ pH = $-\log_{10}(1.45 \times 10^{-12}) = 11.8$

4.3 KEY QUESTIONS

1 $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{0.001} = 1.00 \times 10^{-11} \, mol \, L^{-1}$

2 $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{5.70 \times 10^{-9}} = 1.75 \times 10^{-6} \, mol \, L^{-1}$

3 $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{[OH^-]}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \, mol \, L^{-1}$

4 $pH = -\log_{10}[H_3O^+]$

$= -\log_{10}0.01$

$= 2$

5   As nitric acid is a strong acid, the concentration of H_3O^+ ions is $0.0010\,mol\,L^{-1}$.

$pH = -\log_{10}[H_3O^+]$

$= -\log_{10}0.0010$

$= 3$

6 $[H_3O^+] = 10^{-pH}$

$= 10^{-6}$

$= 1.0 \times 10^{-6}$ (or 0.0000010) $mol\,L^{-1}$

7 $M(HCl) = M(H) + M(Cl)$

$= 1.0 + 35.5$

$= 36.5$

As HCl completely dissociates to H_3O^+ and Cl^-, $n(HCl) = n(H_3O^+)$, therefore $n(H_3O^+) = 0.01\,mol$.

$c = \dfrac{n}{V} = \dfrac{0.01}{0.20} = 0.050\,mol\,L^{-1}$

$[H_3O^+] = 0.050\,mol\,L^{-1}$

$pH = -\log_{10}[H_3O^+]$

$= -\log_{10}0.050 = 1.3$

$= 1.3$

8   HCl

$[H_3O^+] = 10^{-2} = 0.01\,mol\,L^{-1}$

$n(HCl) = c \times V = 0.01 \times 0.1 = 0.001\,mol$

NaOH

$[H_3O^+] = 10^{-11}\,mol\,L^{-1}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{H_3O^+}$

$[OH^-] = 10^{-3}\,mol\,L^{-1}$

$n(NaOH) = c \times V = 0.001 \times 0.2 = 0.002\,mol$

Neutralisation

$NaOH + HCl \rightarrow NaCl + H_2O$
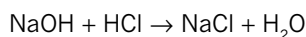
1 mol of HCl react with 1 mol of NaOH; NaOH is in excess.

$n(OH^-)$ remaining $= 0.002 - 0.001 = 0.001\,mol$

$c = \dfrac{n}{V}$

$c = \dfrac{0.001}{0.3} = 0.0033\,mol\,L^{-1}$

$[H_3O^+] = \dfrac{K_w}{[OH^-]}$

$[H_3O^+] = \dfrac{10^{-14}}{0.0033} = 3 \times 10^{-12}$

$pH = -\log_{10}[H_3O^+] = 11.5$

Section 4.4 **Dilution of acids and bases**

Worked example: Try yourself 4.4.1

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of nitric acid when 80.0 mL of water is added to 20.0 mL of 5.00 mol L^{-1} HNO$_3$.	
Thinking	**Working**
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, litres or millilitres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	Remember that 80.0 mL was added to 20.0 mL, so the final volume is 100.0 mL. $c_1 = 5.00$ mol L^{-1} $V_1 = 20.0$ mL $V_2 = 100.0$ mL You are required to calculate c_2, the concentration after dilution.
Transpose the equation and substitute the known values into the equation to find the required value.	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{5.00 \times 20.0}{100.0}$ $= 1.00$ mol L^{-1}

Worked example: Try yourself 4.4.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 15.0 mL of 10.0 mol L^{-1} NaOH to dilute the solution to 2.00 mol L^{-1}?	
Thinking	**Working**
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, although not necessarily litres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	$c_1 = 10.0$ mol L^{-1} $V_1 = 15.0$ mL $c_2 = 2.00$ mol L^{-1} You are required to calculate V_2, the volume of the diluted solution.
Transpose the equation and substitute the known values into the equation to find the required value.	$V_2 = \frac{c_1 \times V_1}{c_2}$ $= \frac{10.0 \times 15.0}{2.00}$ $= 75.0$ mL
Calculate the volume of water to be added.	Volume of dilute solution = 75.0 mL Initial volume of NaOH = 15.0 mL So 75.0 – 15.0 = 60.0 mL of water must be added.

Worked example: Try yourself 4.4.3

CALCULATING pH OF A DILUTED ACID

10.0 mL of 0.10 mol L^{-1} HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.	
Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.10 \text{ mol L}^{-1}$ $V_1 = 10.0 \text{ mL}$ $V_2 = 30.0 \text{ mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \dfrac{c_1 \times V_1}{V_2}$ $= \dfrac{0.10 \times 10.0}{30.0}$ $= 0.03 \text{ mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.03)$ $= 1.5$

Worked example: Try yourself 4.4.4

CALCULATING pH OF A DILUTED BASE

15.0 mL of 0.020 mol L^{-1} KOH is diluted to 60.0 mL. Calculate the pH of the diluted solution.	
Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.020 \text{ mol L}^{-1}$ $V_1 = 15.0 \text{ mL}$ $V_2 = 60.0 \text{ mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of $[OH^-]$ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \dfrac{c_1 \times V_1}{V_2}$ $= \dfrac{0.020 \times 15.0}{60.0}$ $= 0.005 \text{ mol L}^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.005}$ $= 2 \times 10^{-12} \text{ mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(2 \times 10^{-12})$ $= 11.7$

4.4 KEY QUESTIONS

1 $c_1V_1 = c_2V_2$, $c_1 = 0.10\,\text{mol}\,\text{L}^{-1}$, $V_1 = 3.0\,\text{L}$, $V_2 = 4.0\,\text{L}$, $c_2 = ?$

$0.10 \times 3.0 = c_2 \times 4.0$

$c_2 = \dfrac{0.10 \times 3.0}{4.0} = 0.075\,\text{mol}\,\text{L}^{-1}$

2 $c_1V_1 = c_2V_2$, $c_1 = 2.0\,\text{mol}\,\text{L}^{-1}$, $V_1 = 10\,\text{mL}$, $V_2 = ?$, $c_2 = 0.50\,\text{mol}\,\text{L}^{-1}$

$2.0 \times 10 = 0.50 \times V_2$

$V_2 = \dfrac{2.0 \times 10}{0.50} = 40\,\text{mL}$

Final volume – initial volume = 40 – 10 = 30 mL, so 30 mL of water needs to be added.

3 $c_1V_1 = c_2V_2$, $c_1 = 0.60\,\text{mol}\,\text{L}^{-1}$, $V_1 = 20\,\text{mL}$, $V_2 = ?$, $c_2 = 0.10\,\text{mol}\,\text{L}^{-1}$

$0.60 \times 20 = 0.10 \times V_2$

$V_2 = \dfrac{0.60 \times 20}{0.10} = 120\,\text{mL}$

Final volume – initial volume = 120 – 20 = 100 mL, so 100 mL of water needs to be added.

4 This increases the pH by one unit.

5 $c_1V_1 = c_2V_2$, $c_1 = 0.100\,\text{mol}\,\text{L}^{-1}$, $V_1 = 20.0\,\text{mL}$, $V_2 = 50.0\,\text{mL}$, $c_2 = ?$

$0.100 \times 20.0 = c_2 \times 50.0$

$c_2 = \dfrac{0.100 \times 20.0}{50.0} = 0.040\,\text{mol}\,\text{L}^{-1}$

As NaOH dissociates completely to Na^+ and OH^-, [NaOH] = [OH⁻], therefore [OH⁻] = 0.040 mol L⁻¹

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$1.00 \times 10^{-14} = [H_3O^+] \times 0.040$

$[H_3O^+] = \dfrac{1.0 \times 10^{-14}}{0.040} = 2.5 \times 10^{-13}$

$pH = -\log_{10}[H_3O^+]$

$pH = -\log_{10}2.5 \times 10^{-13} = 12.6$

6 **a i** The concentration of H_3O^+ ions equals the concentration of a monoprotic acid = 0.001 mol L⁻¹

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{0.001\,\text{mol}\,\text{L}^{-1}} = 1 \times 10^{-11}\,\text{mol}\,\text{L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(10^{-3}\,\text{mol}\,\text{L}^{-1}) = 3$

   b i $[H_3O^+] = 0.03\,\text{mol}\,\text{L}^{-1}$

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{0.003\,\text{mol}\,\text{L}^{-1}} = 3.33 \times 10^{-13}\,\text{mol}\,\text{L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(0.030\,\text{mol}\,\text{L}^{-1}) = 1.5$

   c i NaOH dissociates completely to Na^+ and OH^-, [NaOH] = [OH⁻], therefore [OH⁻] = 0.010 mol L⁻¹.

   $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{0.010\,\text{mol}\,\text{L}^{-1}} = 1.0 \times 10^{-12}\,\text{mol}\,\text{L}^{-1}$

   ii From part **i**, [OH⁻] = 0.010 mol L⁻¹

   iii $pH = -\log_{10}[H_3O^+] = -\log(10^{-12}\,\text{mol}\,\text{L}^{-1}) = 12$

   d i 10⁻⁴·⁵ mol L⁻¹ HCl = $[H_3O^+]$ = 3.16 × 10⁻⁵ mol L⁻¹

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{3.16 \times 10^{-5}\,\text{mol}\,\text{L}^{-1}} = 3.16 \times 10^{-10}\,\text{mol}\,\text{L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(3.16 \times 10^{-5}\,\text{mol}\,\text{L}^{-1}) = 4.5$

   e i $[OH^-] = 2 \times [Ba(OH)_2] = 2 \times 0.005\,\text{mol}\,\text{L}^{-1} = 0.01\,\text{mol}\,\text{L}^{-1}$

   $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{0.010\,\text{mol}\,\text{L}^{-1}} = 1.0 \times 10^{-12}\,\text{mol}\,\text{L}^{-1}$

   ii From part **i**, [OH⁻] = 0.01 mol L⁻¹

   iii $pH = -\log_{10}[H_3O^+] = -\log(1.0 \times 10^{-12}\,\text{mol}\,\text{L}^{-1}) = 12$

Section 4.5 pH of salt solutions

Worked example: Try yourself 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of calcium hydroxide ($Ca(OH)_2$) and oxalic acid ($H_2C_2O_4$).	
Thinking	**Working**
Write the equation for the neutralisation reaction.	$Ca(OH)_2(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4 (aq) + 2H_2O(l)$
Identify the anion and cation in the salt.	Ca^{2+} and $C_2O_4^{2-}$
Determine whether the ions will react with water in a hydrolysis reaction. (Are the ions neutral, acidic or basic?)	Ca^{2+} cannot accept a proton from water (Ca^{2+} is a neutral ion) $C_2O_4^{2-}(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + OH^-(aq)$ ($C_2O_4^{2-}$ is a basic ion)
If an ion accepts a proton from water, it is basic. If an ion donates a proton to water, it is acidic.	The salt is basic.

4.5 KEY QUESTIONS

1

Reactants	Name of salt formed	Formulae of ions present in the salt solution
Hydrochloric acid + magnesium hydroxide	Magnesium chloride	$Mg^{2+}(aq) + Cl^-(aq)$
Sulfurous acid + zinc hydroxide	Zinc sulfite	$Zn^{2+}(aq) + SO_3^{2-}(aq)$
Phosphoric acid + potassium hydroxide	Potassium phosphate	$K^+(aq) + PO_4^{3-}(aq)$
Ethanoic acid + calcium hydroxide	Calcium ethanoate	$Ca^{2+}(aq) + CH_3COO^-(aq)$
Ammonia + nitric acid	Ammonium nitrate	$NH_4^+(aq) + NO_3^-(aq)$
Phosphoric acid + sodium hydroxide	Sodium dihydrogenphosphate	$Na^+(aq) + H_2PO_4^-(aq)$

2 **a** $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^- (aq) + OH^-(aq)$
  b $ClO_2^-(aq) + H_2O(l) \rightleftharpoons HClO_2 (aq) + OH^-(aq)$
  c $PH_4^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$
  d $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

3 **a** Neutral: KNO_3 is the salt of a strong acid and a strong base (KOH and HNO_3). Neither ion can hydrolyse in aqueous solution.
  b Acidic: NH_4NO_3 is the salt of a strong acid and a weak base (HNO_3 and NH_3). The nitrate ion cannot hydrolyse but the ammonium ion can.
    $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
  c Basic: $Ca(H_3COO)_2$ is the salt of a weak acid (CH_3COOH) and a strong base ($Ca(OH)_2$). The calcium ion cannot hydrolyse but the ethanoate ion can.
    $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
  d Neutral: $MgBr_2$ is the salt of a strong acid (HBr) and a strong base ($Mg(OH)_2$). Neither ion can hydrolyse in aqueous solution.

CHAPTER 4 REVIEW

1 B

NH_4Cl dissolves, producing NH_4^+ and Cl^-.

NH_4^+ hydrolyses, producing NH_3 and H_3O^+.

Cl^- does not hydrolyse in water, therefore is most abundant.

2 D. A base is a proton acceptor. CH_3NH_2 accepts a proton to produce $CH_3NH_3^+$.

3 a NH_4^+

  b HCl

  c HCO_3^-

  d H_3O^+

  e $CH_3COOH(aq)$

4 Remember that if a chemical acts as a base, it will accept a proton. In this question, the proton comes from a water molecule, but this is not always the case. If a chemical acts as an acid, it must be able to donate one or more protons.

  a $PO_4^{3-}(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + OH^-(aq)$

  b The $H_2PO_4^-$ accepts a proton from water, and acts as a base:

  $H_2PO_4^-(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + OH^-(aq)$
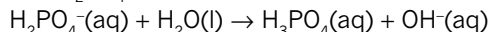
  The $H_2PO_4^-$ donates a proton to the water, and acts as an acid:

  $H_2PO_4^-(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$
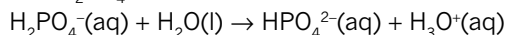
  c $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$

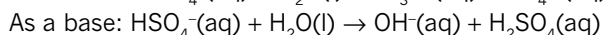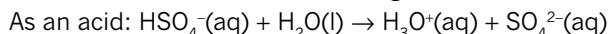**5 a** Cl^-

  b H_2O

  c OH^-

  d SO_4^{2-}

6 a Sulfuric acid (H_2SO_4) is a diprotic acid because each molecule can donate two protons to a base:

  i.e. $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

 $HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$
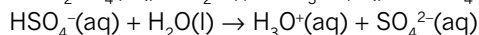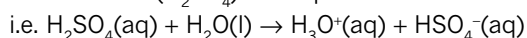
  The HSO_4^- ion, however, is amphiprotic because it can act as either an acid or a base, depending on the environment. In water it will undergo both acid and base reactions. For example:
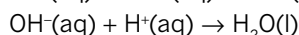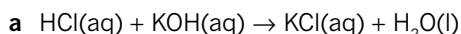
  As an acid: $HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$

  As a base: $HSO_4^-(aq) + H_2O(l) \rightarrow OH^-(aq) + H_2SO_4(aq)$

  b A strong acid is one that ionises completely in solution (e.g. HCl). A concentrated acid is one in which there is a large amount of acid dissolved in a given volume of solution; for example, $5\,mol\,L^{-1}$ HCl and $5\,mol\,L^{-1}$ CH_3COOH are concentrated acids.
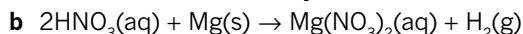
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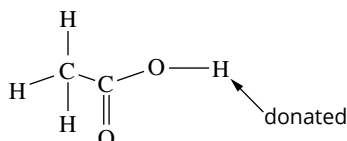
donated

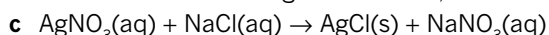**8** The first step, as in the development of any equation, is to write the correct chemical formulas for each of the chemicals involved.

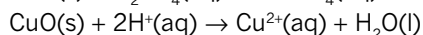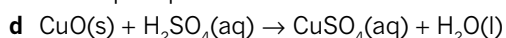 **a** $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$

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

  This is a Brønsted–Lowry acid–base reaction. H^+ donated to OH^-.

  b $2HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$

  This is an acid reacting with a metal, not a Brønsted–Lowry acid–base reaction.

  c $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

  This a precipitation reaction.

  d $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

  $CuO(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l)$

  This is a Brønsted–Lowry acid–base reaction. H^+ donated to O^{2-}.

9 D

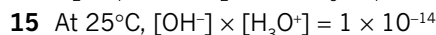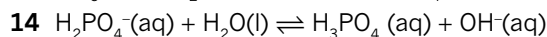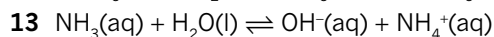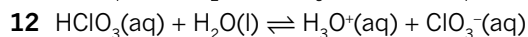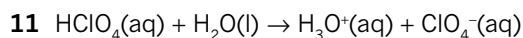K_a is a measure of the extent to which a reaction occurs

K_a for accepting a proton $> K_a$ for donating a proton. This means that $H_2PO_4^-$ more readily accepts a proton than donates a proton in water.

10 C

pH of $0.00001\,mol\,L^{-1}$ H^+ is 5

A monoprotic strong acid (HA) hydrolyses so that $[H^+] = [HA] = 0.00001\,mol\,L^{-1}$

I, II and IV must be diprotic or triprotic and may be strong or weak

11 $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

12 $HClO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_3^-(aq)$

13 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

14 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4\,(aq) + OH^-(aq)$

15 At 25°C, $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$

(Note: [ ] denotes concentration in molar units.)

$\therefore [OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

a $10^{-11}\,mol\,L^{-1}$
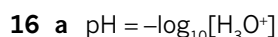
b $10^{-9}\,mol\,L^{-1}$

c $1.8 \times 10^{-6}\,mol\,L^{-1}$

d $2.9 \times 10^{-3}\,mol\,L^{-1}$

e $1.5 \times 10^{-13}\,mol\,L^{-1}$

f $4.48 \times 10^{-2}\,mol\,L^{-1}$

16 a $pH = -\log_{10}[H_3O^+]$

$[H_3O^+] = 10^{-pH}$ (or 10 to the power of pH)

$\qquad = 10^{-1}$

$\qquad = 0.1\,mol\,L^{-1}$

At 25°C, $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$

$\therefore [OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

$\qquad = \dfrac{1.00 \times 10^{-14}}{0.10\,mol\,L^{-1}} = 1.0 \times 10^{-13}\,mol\,L^{-1}$

b $[H_3O^+] = 10^{-3}\,mol\,L^{-1}$

$[OH^-] = 10^{-11}\,mol\,L^{-1}$

c $[H_3O^+] = 10^{-7}\,mol\,L^{-1}$

$[OH^-] = 10^{-7}\,mol\,L^{-1}$

d $[H_3O^+] = 2 \times 10^{-12}\,mol\,L^{-1}$

$[OH^-] = 5 \times 10^{-3}\,mol\,L^{-1}$

17 A solution with a pH of 7.4 is basic.

The concentration of hydroxide ions will be greater than the concentration of hydronium ions.

18 Remember: $pH = -\log_{10}[H_3O^+]$

pH = 3

$\therefore [H_3O^+] = 10^{-3}\,mol\,L^{-1}$

pH = 5

$\therefore [H_3O^+] = 10^{-5}\,mol\,L^{-1}$

$\therefore$ the difference is a factor of 100.

19 a $[H^+] = 10^{-pH} = 0.001\,mol\,L^{-1}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H^+]} = \dfrac{1.00 \times 10^{-14}}{10^{-3}\,mol\,L^{-1}} = 1.0 \times 10^{-11}\,mol\,L^{-1}$

b $[H^+] = 10^{-10}\,mol\,L^{-1}$, $[OH^-] = 10^{-4}$

c $[H^+] = 3.16 \times 10^{-9}\,mol\,L^{-1}$, $[OH^-] = 3.16 \times 10^{-6}\,mol\,L^{-1}$

d $[H^+] = 1.58 \times 10^{-6}\,mol\,L^{-1}$, $[OH^-] = 6.3 \times 10^{-9}\,mol\,L^{-1}$

e $[H^+] = 2.5 \times 10^{-10}\,mol\,L^{-1}$, $[OH^-] = 4.0 \times 10^{-5}\,mol\,L^{-1}$

f $[H^+] = 3.16 \times 10^{-14}\,mol\,L^{-1}$, $[OH^-] = 0.316\,mol\,L^{-1}$

20 $pH = -\log_{10}[H_3O^+] = -\log_{10}5.3$

$[H_3O^+] = 10^{-5.3}$, $[OH^-] = \dfrac{1.00 \times 10^{-14}}{10^{-5.3}\,\text{mol}\,L^{-1}} = 2.0 \times 10^{-9}\,\text{mol}\,L^{-1}$

21 Remember to use $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$ at 25°C and $pH = -\log_{10}[H_3O^+]$.

   a $pH = 2$, $\therefore$ $[H_3O^+] = 10^{-2}$ or $0.01\,\text{mol}\,L^{-1}$

   b The formula for amounts of substance in solution is $n = c \times V$ (where n is the amount in moles, c the concentration in $\text{mol}\,L^{-1}$ and V the volume of the solution in litres).

     $n = 0.01 \times 0.500 = 0.005\,\text{mol}$

22 These three questions have two steps.

   Step 1. Dilution questions are best answered using the formula $c_1V_1 = c_2V_2$, where c is the concentration in $\text{mol}\,L^{-1}$ and V is the volume of the solution. Each of the volume units needs to be the same, although not necessarily litres.

   Step 2. Also remember, $pH = pH = -\log_{10}[H_3O^+]$

   a $c_2 = 0.25 \times \dfrac{10}{50} = 0.05\,\text{mol}\,L^{-1}$

     $\therefore [H_3O^+] = 0.05\,\text{mol}\,L^{-1}$
     $pH = -\log_{10}(0.05\,\text{mol}\,L^{-1}) = 1.3$

   b $c_2 = 0.0050 \times \dfrac{20}{500} = 2 \times 10^{-4}\,\text{mol}\,L^{-1}$

     $\therefore [OH^-] = 2.0 \times 10^{-4}\,\text{mol}\,L^{-1}$
     $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{2 \times 10^{-4}\,\text{mol}\,L^{-1}} = 5.0 \times 10^{-11}\,\text{mol}\,L^{-1}$
     $pH = -\log_{10}(5.0 \times 10^{-11}\,\text{mol}\,L^{-1}) = 10.3$

   c $c_2 = 0.15 \times \dfrac{10}{1500}$ (1.5 L has been converted to mL to maintain identical units)

     $= 0.001\,\text{mol}\,L^{-1}$
     $\therefore [H_3O^+] = 0.001\,\text{mol}\,L^{-1} = 10^{-3}\,\text{mol}\,L^{-1}$
     $\therefore pH = 3$

23 $c_1V_1 = c_2V_2$, $c_1 = 18.0\,\text{mol}\,L^{-1}$, $V_1 = ?$, $c_2 = 2.00\,\text{mol}\,L^{-1}$, $V_2 = 1.00\,L$

   $V_1 = \dfrac{2.00 \times 1.00}{18.0} = 0.111\,L = 111\,\text{mL}$

24 Initial $pH = 2$. $[H_3O^+] = 10^{-pH} = 10^{-2} = 0.010\,\text{mol}\,L^{-1}$

   Final $pH = 4$. $[H_3O^+] = 10^{-pH} = 10^{-4} = 1.00 \times 10^{-4}\,\text{mol}\,L^{-1}$

   $c_1V_1 = c_2V_2$, $c_1 = 0.010\,\text{mol}\,L^{-1}$, $V_1 = 10.0\,\text{mL}$, $c_2 = 1.00 \times 10^{-4}\,\text{mol}\,L^{-1}$, $V_2 = ?$

   $V_2 = \dfrac{0.010 \times 1.00}{1.00 \times 10^{-4}} = 1000\,\text{mL}$

25 $pH(\text{initial}) = -\log_{10}[H_3O^+] = 1.0$

   $c_1V_1 = c_2V_2$, $c_1 = 0.10\,\text{mol}\,L^{-1}$, $V_1 = 40.0\,\text{mL}$, $c_2 = ?$, $V_2 = 500\,\text{mL}$

   $c_2 = \dfrac{0.10 \times 40.0}{500} = 8.0 \times 10^{-3}\,\text{mol}\,L^{-1}$

   $pH(\text{final}) = -\log_{10}(8 \times 10^{-3}) = 2.10$

   Therefore the pH will increase.

26 B

   In A, the ammonium ion hydrolyses to produce an acid and the ethanoate ion hydrolyses to produce a base. The pH of the salt will be close to neutral (pH = 7)
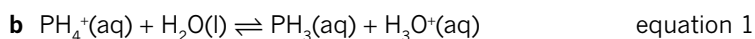
   In B, the ammonium ion hydrolyses to produce an acid. The chloride ion cannot accept a proton because it is the conjugate base of a strong acid. The solution will be acidic with pH < 7.

   In C, the ammonium ion hydrolyses to produce an acid and the phosphate ion hydrolyses to produce a base. The pH of the salt will be close to neutral (pH = 7).

   In D, the sodium ion cannot accept or donate a proton and the bromide is the conjugate base of a strong acid. The solution will be neutral (pH = 7).

27 a

Salt dissolved	Approximate pH (5, 7 or 9)
Potassium nitrate	7
Ammonium chloride	5
Sodium phosphate	9
Potassium hydrogensulfate	5

b $PH_4^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$ equation 1
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ equation 2
Since pH < 7, $[H^+]$ must be greater than $[OH^-]$
And so, the position of equilibrium in equation 1 must be further over to the right-hand side than in equation 2.

28 Solution A: weaker base, few freely moving charged particles—ammonia

Solution B: neutral, no freely moving charged particles—glucose

Solution C: strong base, many freely moving charged particles—sodium hydroxide

Solution D: strong acid, many freely moving charged particles—hydrochloric acid

Solution E: weaker acid, few freely moving charged particles—ethanoic acid
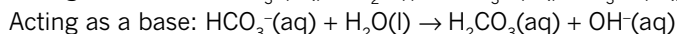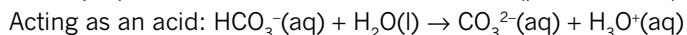
29 a i A Brønsted–Lowry acid is a proton donor.
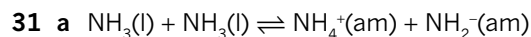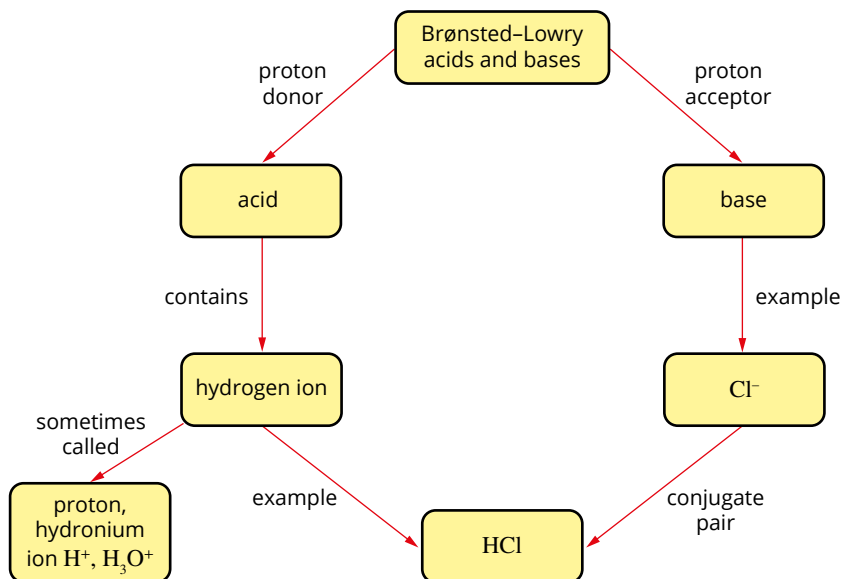   **ii** A strong base is a substance that readily accepts hydrogen ions.
   iii Molarity is a measure of concentration of a solution expressed in $mol\,L^{-1}$.
   iv The conjugate acid of a base contains one more hydrogen ion (proton) than the base.
 b An amphiprotic substance can act as an acid (proton donor) or a base (proton acceptor).
Acting as an acid: $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
Acting as a base: $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$

30

31 a $NH_3(l) + NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$
   acid 1   base 2   acid 2   base 1
 b As the value of K increases, the concentration of ions increases. Heating a reaction in equilibrium favours the endothermic reaction. Thus the forward for the ionisation of ammonia is endothermic.