Acids and bases HL (answers)

IB CHEMISTRY HL













18.1 Lewis acids and bases

Understandings:

- A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.
- When a Lewis base reacts with a Lewis acid a coordinate bond is formed.
- A nucleophile is a Lewis base and an electrophile is a Lewis acid.

Applications and skills:

• Application of Lewis' acid-base theory to inorganic and organic chemistry to identify the role of the reacting species.

Guidance:

- Both organic and inorganic examples should be studied.
- Relations between Brønsted–Lowry and Lewis acids and bases should be discussed.

Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Describe the Lewis theory of			
acids and bases			
Outline the formation of a			
coordinate covalent bond			
formed when a Lewis acid			
reacts with a Lewis base			
Classify nucleophiles and			
electrophiles as Lewis acids			
and bases.			
Outline the relationship			
between Bronsted-Lowry			
theory and Lewis theory			

Lewis acids and bases

- A Lewis acid is an electron pair acceptor.
- A Lewis base is an electron pair donor.
- A coordinate covalent bond is formed between the acid and the base.

$A + : B \rightarrow A - B$

- A is a Lewis acid (it is electron deficient).
- B is a Lewis base (has a lone pair of electrons).
- A–B is an adduct.



- NH₃ acts as a Lewis base as it has a lone pair of electrons to donate.
- BF_3 acts as a Lewis acid as it has an incomplete octet to accept the lone pair of electrons from NH_3
- A coordinate covalent bond is formed between the NH₃ and the BF₃

Complex ions and Lewis acids and bases

- Transition metal ions (Cu²⁺) in solution are Lewis acids.
- Ligands (H₂O) are Lewis bases.
- The diagram below shows the bonding in a complex ion.



Nucleophiles and electrophiles

- Nucleophiles are electron-rich species that donate a lone pair of electrons (Lewis bases).
- Examples include the hydroxide ion, the chloride ion and ammonia.



- Electrophiles are electron-deficient species that accept a lone pair of electrons (Lewis acids).
- Examples include the boron trifluoride, carbocations, and the copper ion.



Exercises:

- Define an acid and base according to the Lewis theory.
 A Lewis acid is an electron pair acceptor, a Lewis base is an electron pair donor.
- 2. Draw the Lewis structure of ammonia (NH₃). Explain how it is able to act as a Lewis base. From its Lewis structure, you can see it has a lone pair of electrons.
- Explain how BF₃ is able to act as a Lewis acid and state the name of the bond formed between a Lewis acid and a Lewis base.
 BF₃ is able to accept a lone pair of electrons (it is electron deficient). The bond formed is a coordinate covalent bond.
- 4. Explain why the following reaction cannot be described using the Bronsted-Lowry theory of acids and bases.

$$CrCl_3 + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 3Cl^{-1}$$

There is no proton transfer in the reaction. The ligands (Lewis bases) donate their lone pairs of electrons to the central metal ion (Lewis acid).

5. In the above reaction, explain how the Cr³⁺ is able to act as a Lewis acid. Cr³⁺ is electron deficient; it acts a Lewis acid by accepting lone pair of electrons. This results in the formation of a coordinate covalent bond between the Lewis base (the ligand) and metal ion (the Lewis acid).

Lewis theory vs Bronsted-Lowry theory

• The definitions of acids and bases for each theory are shown in the table below.

Bronsted-Lowry theory	Lewis theory
An acid is a proton donor	An acid is an electron pair acceptor
A base is a proton acceptor	A base is an electron pair donor

• Bronsted-Lowry theory involves the transfer of protons; if there is no transfer of protons taking place, then the reaction cannot be described using Bronsted-Lowry theory.

Species	Bronsted-Lowry base	Lewis base	Bronsted-Lowry acid	Lewis acid
NH ₃ H ₂ O	Yes	Yes	No	No
HCI HNO₃	No	No	Yes	Yes
BF ₃ AICI ₃	No	No	No	Yes
Cu ²⁺ Cr ³⁺	No	No	No	Yes

- All Bronsted-Lowry acids are also Lewis acids and all Bronsted-Lowry bases are also Lewis bases.
- Not all Lewis acids are Bronsted-Lowry acids (BF₃, Cu²⁺).
- The formation of a complex ion can be described using Lewis theory, but not Bronsted-Lowry theory.

18.2 Calculations involving acids and bases

Understandings:

The expression for the dissociation constant of a weak acid (K_a) and a weak base (K_b).

- For a conjugate acid base pair, $K_a \times K_b = K_w$
- The relationship between K_a and pK_a is $(pK_a = -\log K_a)$, and between K_b and pK_b is $(pK_b = -\log K_b)$.

Applications and skills:

- Solution of problems involving $[H^+_{(aq)}]$, $[OH^-_{(aq)}]$, pH, pOH, K_a , p K_a , K_b and p K_b
- Discussion of the relative strengths of acids and bases using values of K_a , pK_a , K_b and pK_b

Guidance:

- The value K_w depends on the temperature.
- The calculation of pH in buffer solutions will only be assessed in options B.7 and D.4.
- Only examples involving the transfer of one proton will be assessed.
- Calculations of pH at temperatures other than 298 K can be assessed.
- Students should state when approximations are used in equilibrium calculations.
- The use of quadratic equations will not be assessed.

Syllabus checklist

Objective	I am confident with this	I need to review	I need help with this
Determine the strength of an			
acid or base from its K_2 (p K_2) or			
$K_{\rm b}$ (p $K_{\rm b}$) value			
Calculate K_a and K_b value of			
conjugate acids and bases and			
vice versa			
Calculate the pH of a weak			
acid or base using the K_a or K_b			
or pK_a or pK_b and the initial			
concentration			
Calculate K_a and K_b from pK_a			
and pK_b values			
Explain the temperature			
dependence of the ionic			
product constant, K _w			

Acid and base dissociation constants (K_a and K_b)

• Weak acids partially dissociate (ionise) in solution.

$CH_{3}COOH_{(aq)} + H_{2}O_{(l)} \rightleftharpoons H_{3}O^{+}_{(aq)} + CH_{3}COO^{-}_{(aq)}$

• Weak bases partially dissociate (ionise) in solution.

$$\mathsf{NH}_{3(\mathsf{aq})} + \mathsf{H}_2\mathsf{O}_{(\mathsf{I})} \rightleftharpoons \mathsf{NH}_4^+(\mathsf{aq}) + \mathsf{OH}^-(\mathsf{aq})$$

• These are equilibrium reactions in which the equilibrium position lies to the left (reactants side).

K_a (acid dissociation constant)

- K_a is an equilibrium constant that refers to the dissociation or ionisation of an acid.
- H_2O is not included in the K_a expression as it is a constant.

$$HA_{(aq)} + H_2O_{(I)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_{\mathrm{a}} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

- The magnitude of the K_a tells us the extent of dissociation and the strength of the acid.
- The larger the value of the *K*_a, the greater the degree of dissociation and the stronger the acid.

K_b (base dissociation constant)

• *K*_b is an equilibrium constant that refers to the dissociation or ionisation of a base.

$$B_{(aq)} + H_2O_{(I)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$K_{\rm b} = \frac{[\rm BH^+][\rm OH^-]}{[\rm B]}$$

- The magnitude of the K_b tells us the extent of dissociation and the strength of the base.
- The larger the value of the *K*_b, the greater the degree of dissociation and the stronger the base.

Exercise: Write expressions for the K_a or K_b for the following reactions.

1. $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

$$K_{a} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{CH}_{3}\mathrm{COO}^{-}]}{[\mathrm{CH}_{2}\mathrm{COOH}]}$$

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2. $NH_{3(aq)} + H_2O_{(I)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

$$K_{\rm b} = \frac{[\rm NH_4^+][\rm OH^-]}{[\rm NH_3]}$$

Calculating K_a or K_b of a weak acid or weak base

Example 1:

A 0.100 mol dm⁻³ solution of HClO has a pH of 4.23. Calculate the K_a of HClO.

$$\mathrm{HClO}_{(\mathrm{aq})} + \mathrm{H}_{2}\mathrm{O}_{(\mathrm{I})} \rightleftharpoons \mathrm{H}_{3}\mathrm{O}^{+}_{(\mathrm{aq})} + \mathrm{ClO}^{-}_{(\mathrm{aq})}$$

$$K_{\rm a} = \frac{[\rm H_3O^+][\rm CIO^-]}{[\rm HCIO]}$$

[H⁺] = 10^{-pH} [H⁺] = 10^{-4.23} [H⁺] = 5.89 × 10⁻⁵ mol dm⁻³

$$K_{a} = \frac{(5.89 \times 10^{-5})^{2}}{0.100} \qquad K_{a} = \frac{(5.89 \times 10^{-5})^{2}}{(0.100 - 5.89 \times 10^{-5})}$$
$$K_{a} = 3.47 \times 10^{-8}$$

Example 2:

A 0.100 mol dm⁻³ solution of C₆H₅NH₂ has a pH of 8.79. Calculate the K_b of C₆H₅NH₂.

 $\mathbf{C_6H_5NH_{2(aq)}+H_2O_{(l)}\rightleftharpoons C_6H_5NH_3^+_{(aq)}+OH^-_{(aq)}}$

$$K_{\rm b} = \frac{[{\rm C}_{6}{\rm H}_{5}{\rm N}{\rm H}_{3}^{+}][{\rm O}{\rm H}^{-}]}{[{\rm C}_{6}{\rm H}_{5}{\rm N}{\rm H}_{2}]}$$

pH + pOH = 14.00 (at 298 K) pOH = 14.00 - 8.79 = 5.21 $[OH^{-}] = 10^{-5.21}$ $[OH^{-}] = 6.17 \times 10^{-6} \text{ mol dm}^{-3}$

$$K_{\rm b} = \frac{[{\rm C}_{6}{\rm H}_{5}{\rm N}{\rm H}_{3}^{+}][{\rm O}{\rm H}^{-}]}{[{\rm C}_{6}{\rm H}_{5}{\rm N}{\rm H}_{2}]}$$

$$K_{\rm b} = \frac{(6.17 \times 10^{-6})^2}{0.100} \qquad K_{\rm b} = \frac{(6.17 \times 10^{-6})^2}{(0.100 - 6.17 \times 10^{-6})}$$

 $K_{\rm b} = 3.81 \times 10^{-10}$

 pK_a and pK_b

$pK_a = -\log_{10}K_a \quad pK_b = -\log_{10}K_b$

$K_{\rm a} = 10^{-pK_{\rm a}}$ $K_{\rm b} = 10^{-pK_{\rm b}}$

- pK_a and pK_b are usually positive and have no units.
- A change of one unit of pK_a or pK_b represents a ten-fold change in the value K_a or K_b .
- pK_a and pK_b must be quoted at a specific temperature.

K_a and pK_a

• K_a and pK_a have an inverse relationship; the stronger the acid, the higher the value of K_a , the lower the value of the pK_a



 $K_{\rm b}$ and $pK_{\rm b}$

• K_b and pK_b have an inverse relationship; the stronger the base, the higher the value of K_b , the lower the value of the pK_b



K_b increases pK_b decreases pK_b increases

weak base

Exercise: The following table shows pK_a and pK_b values for acids and bases.

acid	рК _а	base	рК _ь
methanoic acid	3.75	ammonia	4.75
ethanoic acid	4.76	methylamine	3.34

Identify the strongest acid and the strongest base from the table.

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Strongest acid is methanoic acid as it has the lowest value for the pK_a . Strongest base is methylamine as it has the lowest value for the pK_b .

K_{a} , K_{b} and K_{w}

- For a conjugate acid-base pair, $K_a \times K_b = K_w$
- At 298 K, K_a × K_b = 1.00 × 10⁻¹⁴

pK_a , pK_b and pK_w

- $pK_a + pK_b = pK_w$
- $pK_w = -\log_{10}K_w$
- At 298 K, pK_a + pK_b = 14

pH and pOH scales

- The pH scale gives a measure of the [H⁺] ions in solution.
- The pOH scale gives a measure of the [OH⁻] ions in solution.

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

- The pH and pOH scales are inverse, which means the higher the [H⁺] or [OH⁻], the lower the pH or pOH value.
- The relationship between pH and pOH is:

pH + pOH = 14.00 at 298 K

Exercises:

1. Lemon juice has a pH of 2.90 at 298 K. Calculate its [H⁺], [OH⁻] and pOH.

 $\begin{aligned} 10^{-2.90} &= 1.26 \times 10^{-3} \\ [OH^{-}] &= 1.00 \times 10^{-14} \div 1.26 \times 10^{-3} = 7.94 \times 10^{-12} \\ pOH &= -\log \left(7.94 \times 10^{-12}\right) = 11.1 \text{ or } 14.0 - 2.90 = 11.1 \end{aligned}$

2. A sample of blood at 298 K has a [H⁺] of 4.60 × 10⁻⁸ mol dm⁻³. Calculate the [OH⁻] and state whether the blood is acidic, neutral or basic.
[OH⁻] = 1.00 × 10⁻¹⁴ ÷ 4.60 × 10⁻⁸ = 2.17 × 10⁻⁷
[OH⁻] > [H⁺] therefore blood is basic.

Calculating the pH of a weak acid or a weak base Example 1:

A 0.500 mol dm⁻³ solution of CH₃COOH has a K_a of 1.8 × 10⁻⁵. Calculate the pH of the solution.

 $CH_{3}COOH_{(aq)} + H_{2}O_{(l)} \rightleftharpoons H_{3}O^{+}_{(aq)} + CH_{3}COO^{-}_{(aq)}$

$$K_{a} = \frac{[H_{3}O^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$$
$$1.8 \times 10^{-5} = \frac{x^{2}}{0.500}$$

 $x = \sqrt{9.0 \times 10^{-6}}$ $x = 3.0 \times 10^{-3}$ Assumption is that [CH₃COOH]_{eq} = [CH₃COOH]_{initial}

$$x = 3.0 \times 10^{-3}$$

[H⁺] = 3.0 × 10⁻³ mol dm⁻³
pH = -log[H⁺]
pH = -log(3.0 × 10⁻³)
pH = 2.5

Example 2:

A 0.200 mol dm⁻³ solution of NH₃ has a K_b of 1.8 × 10⁻⁵. Calculate the pH of the solution.

 $NH_{3(aq)} + H_2O_{(I)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

$$K_{\rm b} = \frac{[\rm NH_4^+][\rm OH^-]}{[\rm NH_3]}$$

1.8 × 10⁻⁵ = $\frac{x^2}{0.200}$
 $x = \sqrt{3.6 \times 10^{-6}}$ $x = 1.9 \times 10^{-3}$

Assumption is that [NH₃]_{eq} = [NH₃]_{initial}

$$x = 1.9 \times 10^{-3}$$

[OH⁻] = 1.9 × 10⁻³ mol dm⁻³
pOH = -log[OH⁻]
pOH = -log(1.9 × 10⁻³)
pOH = 2.7
pH + pOH = 14.00
pH = 14.00 - 2.7 = 11.3

Exercises:

1. Propanoic acid, CH₃CH₂COOH is an example of a weak acid.

a) Write the equation for the ionization of propanoic acid in water and deduce the expression for the acid dissociation constant, K_a , of propanoic acid.

 $CH_3CH_2COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2COO^{-}_{(aq)} + H_3O^{+}_{(aq)}$

 $CH_3CH_2COOH_{(aq)} \rightleftharpoons CH_3CH_2COO^{-}_{(aq)} + H^{+}_{(aq)}$

 $\boldsymbol{K}_{\mathsf{a}} = \frac{[CH_{3}CH_{2}COO^{-}][H^{+}]}{[CH_{3}CH_{2}COOH]}$

- b) Calculate the K_a value of propanoic acid. The p K_a of propanoic acid is 4.87.
- $K_{\rm a} = 10^{-\rm pKa}$

 $K_{\rm a} = 10^{-4.87}$

- $K_{\rm a} = 1.35 \times 10^{-5}$
- c) Use your answer from (b) to calculate the [H⁺] in an aqueous solution of propanoic acid of concentration 0.0500 mol dm⁻³, and the pH of this solution.

 $[H^+] = \sqrt{K_a[CH_3CH_2COOH]}$

 $[H^+] = 8.21 \text{ or } 8.22 \times 10^{-4} \text{ mol dm}^{-3}$

 $pH = -log [H^+] = -log (8.22 \times 10^{-4}) = 3.1 \text{ or } 3.09$

2. In aqueous solution at 298 K, ammonia is a weak base with a pK_b value of 4.75

a) Write an equation for the reaction of ammonia with water.

 $NH_{3(aq)} + H_2O_{(I)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

b) State the base dissociation constant expression, *K*_b, for ammonia.

$$K_{b} = \frac{[\mathrm{NH}_{4}^{+}][\mathrm{OH}^{-}]}{[\mathrm{NH}_{3}]}$$

c) Calculate the pH of a 0.250 mol dm⁻³ solution of ammonia.

[OH⁻] = 2.1 × 10⁻³ pOH = 2.7/[H⁺] = 4.8 × 10⁻¹² pH = 11.3

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Temperature dependence of K_w

• Water dissociates according to the following equation:

$H_2O_{(I)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

- The dissociation of water requires energy (the forward reaction is endothermic and the reverse reaction is exothermic).
- As the temperature increases, the equilibrium position shifts to the right and the [H⁺] and [OH⁻] increase.
- This causes the pH of the water to increase, however it is still neutral because [H⁺] = [OH⁻].

Exercise: Predict in which direction the equilibrium position will shift when the temperature is decreased. What effect will this have on the pH of pure water?

Equilibrium position will shift to the left because reverse reaction is exothermic. The $[H^+]$ will decrease therefore the pH will increase.

Complete the following table:

Temperature (K)	Kw	[H ⁺] in pure water	pH of pure water
273	$1.50 imes 10^{-15}$	3.87 × 10 ⁻⁸	7.4
298	$1.00 imes 10^{-14}$	1.00×10^{-7}	7
313	3.00×10^{-14}	1.73 × 10 ⁻⁷	6.7

Summary:

- K_w is temperature dependent, therefore the pH of pure water is only 7 at 298 K.
- Pure water is still neutral at lower and higher temperatures because [H⁺] = [OH⁻].

Exercise: The value of the ionic product constant of water, K_w , at 60°C is 5.60 × 10⁻¹⁴

a) State the expression for the K_w

 $K_{\mathsf{w}} = [\mathsf{H}^+][\mathsf{OH}^-]$

b) Calculate the values of $[H^+]$ and pH in water at a temperature of 60°C.

$$[\text{H}^{+}] = \sqrt{K_{\text{W}}} / \sqrt{5.60 \times 10^{-14}};$$

 $[H^+] = 2.37 \times 10^{-7} \text{ mol dm}^{-3}$

 $pH = -log(2.37 \times 10^{-7}) = 6.63$

c) The value of [OH⁻] in water at 60°C is greater than the value at room temperature. Explain why water is not alkaline at 60°C.

 $[H^+] = [OH^-]$ (concentrations of H^+ and OH^- are equal).

18.3 pH curves

Understandings:

- The characteristics of the pH curves produced by the different combinations of strong and weak acids and bases.
- An acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colours.
- The relationship between the pH range of an acid–base indicator, which is a weak acid, and its pK_a value.
- The buffer region on the pH curve represents the region where small additions of acid or base result in little or no change in pH.
- The composition and action of a buffer solution.

Applications and skills:

- The general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases with an explanation of their important features.
- Selection of an appropriate indicator for a titration, given the equivalence point of the titration and the end point of the indicator.
- While the nature of the acid-base buffer always remains the same, buffer solutions can be prepared by either mixing a weak acid/base with a solution of a salt containing its conjugate, or by partial neutralization of a weak acid/base with a strong acid/base.
- Prediction of the relative pH of aqueous salt solutions formed by the different combinations of strong and weak acid and base.

Guidance:

- Only examples involving the transfer of one proton will be assessed. Important features are:
 - intercept with pH axis
 - equivalence point
 - buffer region
 - points where $pK_a = pH$ or $pK_b = pOH$.
- For an indicator which is a weak acid:
 - HIn(aq) H⁺(aq) + In⁻(aq)
 Colour A Colour B
 - The colour change can be considered to take place over a range of $pK_a \pm 1$.

- For an indicator which is a weak base:
 - B(aq) + H₂O \rightleftharpoons HB⁺(aq) + OH⁻(aq) Colour A Colour B
- Examples of indicators are listed in the data booklet in section 22.
- Salts formed from the four possible combinations of strong and weak acids and bases should be considered. Calculations are not required.
- The acidity of hydrated transition metal ions is covered in topic 13. The treatment of other hydrated metal ions is not required.

Syllabus checklist

Objective	I am confident	I need to review	I need help with
	with this	this	this
Describe the different pH			
curves for titrations of strong			
and weak acids and bases			
Identify the important parts of			
a pH curve such as equivalence			
point, half-equivalence point			
and buffer region			
Select the correct indicator for			
a titration given the end-point			
of the titration and its			
equivalence point			
Describe the action of a pH			
indicator			
Outline the two ways in which			
a buffer solution can be made			
Predict the pH of an aqueous			
salt solution based on the			
identity of the parent acid and			
base			

pH curves

- The equivalence point occurs when stoichiometrically equivalent amounts of acid and base have reacted (the solution contains only salt and water).
- The pH of the equivalence point depends on whether the salt produced is acidic or basic (salt hydrolysis).



Strong acid and strong base (HCl and NaOH)

- Initial pH quite (strong acid)
- Very sharp increase in pH from pH 3 to pH 11
- Curve flattens out at high pH 14 (pH of strong base)
- pH at equivalence point = 7

Weak acid and strong base (CH₃COOH and NaOH)



- Initial pH quite low (weak acid)
- pH stays relatively constant (buffer region)
- Sharp increase in pH from pH 7 to pH 11
- Curve flattens out at high pH 14 (pH of strong base)
- pH at equivalence point > 7

Weak base and strong acid (HCl + NH₃)



- Initial pH is quite high (weak base)
- pH stays relatively constant (buffer region)
- Sharp decrease in pH from pH 7 to pH 3
- Curve flattens out at pH 1 (pH of strong acid)
- pH at equivalence point < 7

Half-equivalence point

- The half-equivalence point is the point where half the acid has been neutralised by base and converted into salt.
- At the half-equivalence point, the pH is equal to the pK_a
- A buffer solution resists a change in pH when small amounts of acid or base are added.
- The buffer region on a pH curve represents the region where small additions of acid or base result in little or no change in pH.



Acid-base indicators

• Acid-base indicators are weak acids or bases in which the undissociated and dissociated forms have different colours.

 $Hln_{(aq)} \rightleftharpoons H^+_{(aq)} + ln^-_{(aq)}$ colour A colour B

- Litmus turns red in an acidic solution and blue in an alkaline solution.
- In acidic solutions (high [H⁺]), the equilibrium shifts to the left and the red colour is seen.
 In alkaline solutions (high [OH⁻]), the equilibrium shifts to the right and the blue colour is seen.

Exercise: The indicator bromophenol blue, $HIn_{(aq)}$, has a form that is yellow and an $In_{(aq)}^{-}$ form that is blue. Write an equation to show how bromophenol blue acts as an indicator.

State and explain the colour of bromophenol blue:

(i) on the addition of a strong acid.

 $HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In_{(aq)}^-$

Addition of H⁺, equilibrium shifts to left, yellow colour is seen.

(ii) on the addition of a strong base.

Addition of OH⁻, equilibrium shifts to right, blue colour is seen.

End-point

- The end-point of an indicator is the pH at which it changes colour.
- An indicator changes colour when the pH is equal to its pKa
- The colour change can be considered to take place over a range of pK_a ± 1
- A list of acid base indicators can be found in section 22 of the data booklet.

Exercise: use the following pH curve (weak acid and strong base) to determine:

- a) the pH at the equivalence point. pH 9.5
- b) the p K_a of the weak acid. At 11 cm³, pH = 5.4, pK_a = 5.4
- c) suggest a suitable indicator for the titration. Phenolphthalein (pH range 8.3 10.0)



Buffer solutions

- Buffer solutions resist a change in pH when small amounts of acid or base are added.
- A buffer solution can be prepared by reacting a weak acid with a strong base (or a weak base and strong acid).

CH ₃ COOH _(aq) -	+ NaOH _(aq) →	NaCH ₃ COO _(aq)	+ H ₂ O _(I)
1.00 mol	0.500 mol	0 mol	0 mol
0.500 mol	0 mol	0.500 mol	0.500 mol

• The final solution has equal amounts of weak acid and the salt of the weak acid and strong base (buffer solution).

Acidic buffers

• An acidic buffer can be made by mixing together a weak acid and the salt of the weak acid and a strong base.

$$NaCH_{3}COO_{(aq)} \rightarrow Na^{+}_{(aq)} + CH_{3}COO^{-}_{(aq)}$$
$$CH_{3}COOH_{(aq)} \rightleftharpoons CH_{3}COO^{-}_{(aq)} + H^{+}_{(aq)}$$

Response to added acid $H^+_{(aq)}$

• The added H⁺ ions react with the CH_3COO^- to form CH_3COOH .

 $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

Response to added base OH⁻(aq)

• The added OH⁻ ions react with the CH₃COOH to form CH₃COO⁻ and H₂O. CH₃COOH + OH⁻ \rightleftharpoons CH₃COO⁻ + H₂O

Basic buffers

• A basic buffer can be made by mixing together a weak base and the salt of the weak base and a strong acid.

$$NH_{3(aq)} + H_2O_{(I)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$
$$NH_4CI_{(aq)} \rightarrow NH_4^+{}_{(aq)} + CI^-{}_{(aq)}$$

Response to added acid H⁺_(aq)

• The added H^+ ions react with the NH_3 to form NH_4^+ :

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

Response to added base OH⁻_(aq)

- The added $OH^{\scriptscriptstyle -}$ ions react with the NH_4^+ to form NH_3 and H_2O

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

Salt hydrolysis

• Salt hydrolysis refers to the reaction of a cation or an anion with water which ionizes the water molecule into H⁺ and OH⁻

Anion hydrolysis (pH > 7 at 298 K)

$$A^{-}_{(aq)} + H_2O_{(I)} \rightleftharpoons HA_{(aq)} + OH^{-}_{(aq)}$$

Cation hydrolysis (pH < 7 at 298 K)

$$M^+_{(aq)} + H_2O_{(I)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$$

Salt of a strong acid and strong base

$$\begin{split} HCI_{(aq)} + NaOH_{(aq)} &\rightarrow NaCI_{(aq)} + H_2O_{(I)} \\ NaCI_{(aq)} &\rightarrow Na^+_{(aq)} + CI^-_{(aq)} \end{split}$$

• The salt formed from a strong acid and a strong base (NaCl) has a pH of approximately 7 at 298 K (neither ion hydrolyses).

Salt of a weak acid and strong base

$$CH_{3}COOH_{(aq)} + NaOH_{(aq)} \rightarrow NaCH_{3}COO_{(aq)} + H_{2}O_{(l)}$$

$$NaCH_{3}COO_{(aq)} \rightarrow Na^{+}_{(aq)} + CH_{3}COO^{-}_{(aq)}$$

$$CH_{3}COO^{-}_{(aq)} + H_{2}O_{(l)} \rightleftharpoons CH_{3}COOH_{(aq)} + OH^{-}_{(aq)}$$

• The salt formed from a weak acid and a strong base has a pH of > 7 at 298 K (the anion hydrolyses).

Salt of a strong acid and weak base

$$\begin{aligned} HCI_{(aq)} + NH_{3(aq)} &\rightarrow NH_4CI_{(aq)} \\ NH_4CI_{(aq)} &\rightarrow NH_4^+_{(aq)} + CI^-_{(aq)} \\ NH_4^+_{(aq)} + H_2O_{(I)} &\rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)} \end{aligned}$$

• The salt formed from a strong acid and a weak base has a pH of < 7 at 298 K (the cation hydrolyses).

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