

Acids and bases HL (answers)

IB CHEMISTRY HL

<div>25</div> <div>Mn</div> <div>Manganese 54.938045</div>	<div>16</div> <div>S</div> <div>Sulfur 32.065</div>	<div></div> <div>J</div> <div></div>	<div>6</div> <div>C</div> <div>Carbon 12.0107</div>	<div>2</div> <div>He</div> <div>Helium 4.002602</div>	<div>25</div> <div>Mn</div> <div>Manganese 54.938045</div>
---	--	---	--	--	---

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.

International-mindedness:

- Acid–base theory has developed from the ideas of people from different parts of the world through both collaboration and competition.

Theory of knowledge:

- The same phenomenon can sometimes be explored from different perspectives, and explained by different theories. For example, do we judge competing theories by their universality, simplicity or elegance?

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 , pK_a , K_b and pK_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.

International-mindedness:

- Mathematics is a universal language. The mathematical nature of this topic helps chemists speaking different native languages to communicate more objectively.

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:

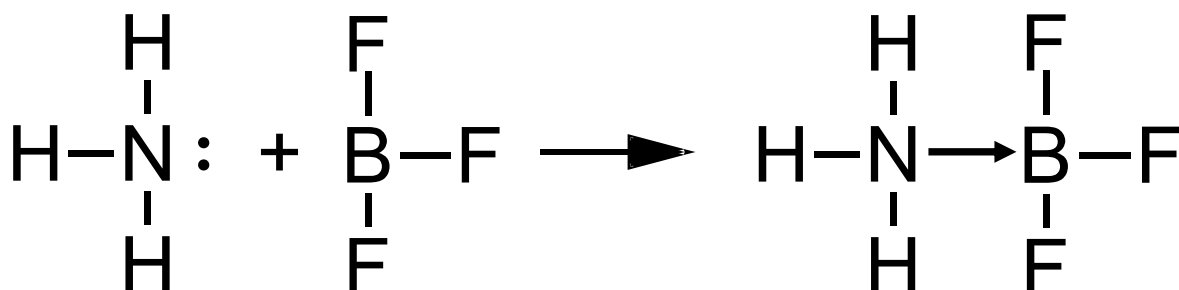
- The general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases with an explanation of their important features.
- Selection of an appropriate indicator for a titration, given the equivalence point of the titration and the end point of the indicator.
- While 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:

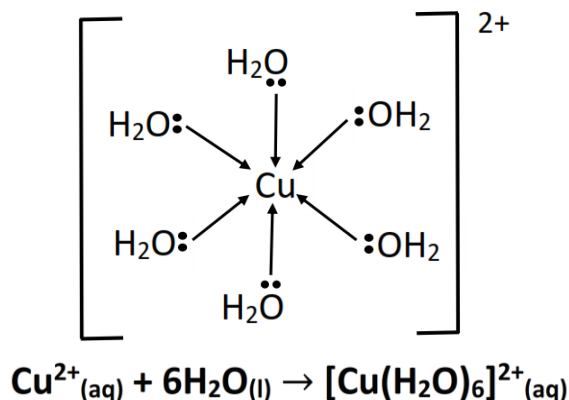
- Only examples involving the transfer of one proton will be assessed. Important features are:
 - intercept with pH axis
 - equivalence point
 - buffer region
 - points where $pK_a = \text{pH}$ or $pK_b = \text{pOH}$.
- For an indicator which is a weak acid:
 - $\text{HIn(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{In}^-(\text{aq})$
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:
 - $\text{BOH(aq)} \rightleftharpoons \text{B}^+(\text{aq}) + \text{OH}^-(\text{aq})$
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.

Lewis acids and bases

- A Lewis acid is a lone pair of electrons acceptor.
- A Lewis base is a lone pair of electrons donor.
- A coordinate covalent bond is formed between the acid and the base.

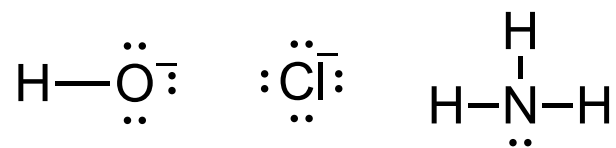


- NH_3 is a Lewis base, as it has a lone pair of electrons to donate.
- BF_3 is a Lewis acid as it has an incomplete octet to accept the lone pair of electrons from NH_3
- A coordinate covalent bond is formed between the two (represented by an arrow).
- Transition metal ions (Cu^{2+}) in solution are Lewis acids.
- Ligands (H_2O) are Lewis bases.
- The diagram below shows the bonding in a complex ion.

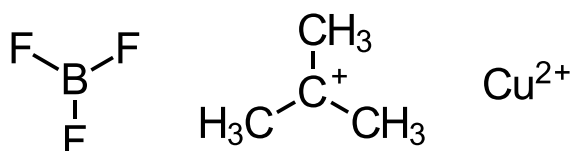


Nucleophiles and electrophiles

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

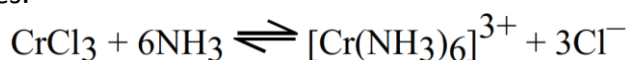


- Electrophiles are electron-deficient species that accept a lone pair of electrons (Lewis acids).
- Examples include the boron trifluoride, carbocations, and the copper ion.



Concept check:

- 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.
- 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.
BF₃ is able to accept a lone pair of electrons.
- Explain why the following reaction cannot be described using the Bronsted-Lowry theory of acids and bases.

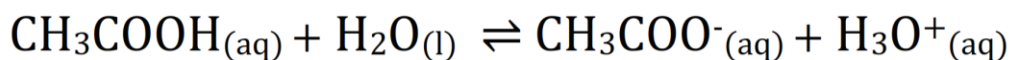


There is no proton transfer in the reaction.

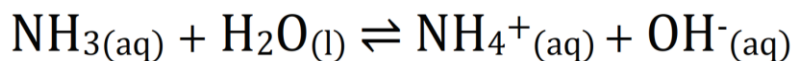
- In the above reaction, explain how the Cr³⁺ is able to act as a Lewis acid.
By accepting a lone pair of electrons. This results in the formation of a coordinate covalent bond between the Lewis base (the ligand) and metal ion (the Lewis acid).

Acid and base dissociation constants (K_a and K_b)

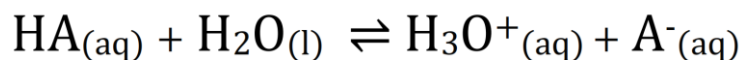
- Weak acids partially dissociate (ionize) in solution.



- Weak bases partially dissociate (ionize) in solution.

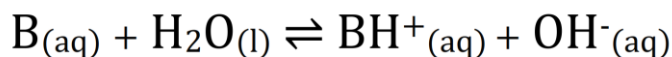


- These are equilibrium reactions in which the equilibrium lies to the left (reactants side).
- K_a (the acid dissociation constant) is an equilibrium constant that refers to the dissociation or ionisation of an acid.
- H_2O is not included in the K_a , or K_b expression as it is more or less a constant.



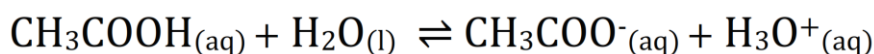
$$K_a = \frac{[\text{H}^{+}][\text{A}^{-}]}{[\text{HA}]}$$

- K_b (the base dissociation constant) is an equilibrium constant that refers to the dissociation or ionisation of a base.

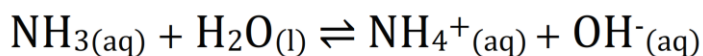


$$K_b = \frac{[\text{BH}^{+}][\text{OH}^{-}]}{[\text{B}]}$$

Exercise: Write expressions for the K_a and K_b for the following reactions:



$$K_a = \frac{[\text{CH}_3\text{COO}^{-}][\text{H}^{+}]}{[\text{CH}_3\text{COOH}]}$$



$$K_b = \frac{[\text{NH}_4^{+}][\text{OH}^{-}]}{[\text{NH}_3]}$$

pK_a and pK_b

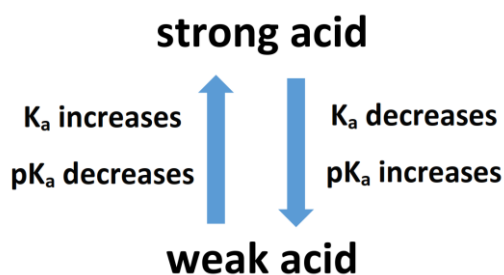
$$pK_a = -\log_{10} K_a \quad pK_b = -\log_{10} K_b$$

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

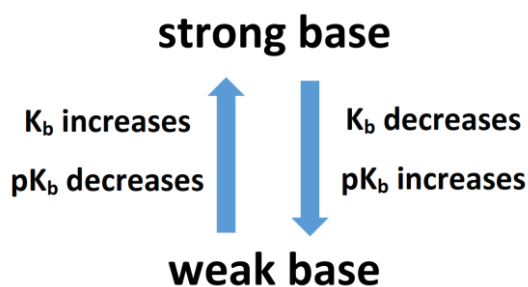
- pK_a and pK_b are usually positive and have no units.
- A change of one unit of pK_a or pK_b represents a ten-fold change in the value K_a or K_b .
- pK_a and pK_b must be quoted at a specific temperature.

K_a and pK_a

- K_a and pK_a (and K_b and pK_b) have an inverse relationship; the stronger the acid, the higher the value of K_a , the lower the value of the pK_a



K_b and pK_b



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

acid	pK_a	base	pK_b
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.

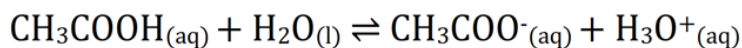
Strongest acid is methanoic acid as it has the lowest value for the pK_a .

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 $K_a \times K_b = K_w$

Example: Determine the K_b for ethanoic acid given that its K_a value is 1.75×10^{-5}



$$K_a \text{ CH}_3\text{COOH} = 1.75 \times 10^{-5}$$

$$\text{At } 298 \text{ K, } K_w = 1.00 \times 10^{-14}$$

$$K_b \text{ CH}_3\text{COO}^{-} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

pK_a, pK_b and pK_w

$$K_a \times K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

$$\text{p}K_w = -\log (1.00 \times 10^{-14}) = 14$$

$$\text{At } 298 \text{ K, } \text{p}K_a + \text{p}K_b = 14$$

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

A 0.750 mol dm⁻³ solution of ethanoic acid has a K_a of 1.8×10^{-5} at 298 K. Calculate the pH of the solution.

	CH ₃ COOH _(aq)	CH ₃ COO ⁻ _(aq)	H ⁺ _(aq)
initial (mol dm ⁻³)	0.750	0.00	0.00
change (mol dm ⁻³)	- x	+ x	+ x
equilibrium (mol dm ⁻³)	0.750 - x	x	x

See video for solution.

Example 2:

A 0.200 mol dm⁻³ solution of ammonia (NH₃) K_b of 1.8×10^{-5} at 298 K. Calculate the pH of the solution.

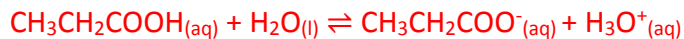
	NH _{3(aq)}	NH ₄ ⁺ _(aq)	OH ⁻ _(aq)
initial (mol dm ⁻³)	0.200	0.00	0.00
change (mol dm ⁻³)	- x	+ x	+ x
equilibrium (mol dm ⁻³)	0.200 - x	x	x

See video for solution.

Exercises:

1. Propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ 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.



$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

b) Calculate the K_a value of propanoic acid. The $\text{p}K_a$ of propanoic acid is 4.87.

$$K_a = 10^{-\text{p}K_a}$$

$$K_a = 10^{-4.87}$$

$$K_a = 1.35 \times 10^{-5}$$

c) Use your answer from (b) to calculate the $[\text{H}^+]$ in an aqueous solution of propanoic acid of concentration $0.0500 \text{ mol dm}^{-3}$, and the pH of this solution.

$$[\text{H}^+] = \sqrt{K_a [\text{CH}_3\text{CH}_2\text{COOH}]}$$

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

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

2. In aqueous solution at 298 K, ammonia is a weak base with a $\text{p}K_b$ value of 4.75

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



b) State the base dissociation constant expression, K_b , for ammonia.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

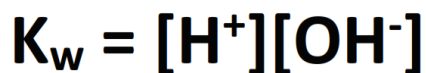
c) Calculate the pH of a $0.250 \text{ mol dm}^{-3}$ solution of ammonia.

$$[\text{OH}^-] = 2.1 \times 10^{-3}$$

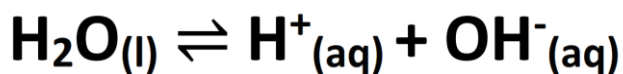
$$\text{pOH} = 2.7 / [\text{H}^+] = 4.8 \times 10^{-12}$$

$$\text{pH} = 11.3$$

Temperature dependence of K_w



$$K_w = 1.00 \times 10^{-14} \text{ at } 298\text{K}$$



- The dissociation of water requires energy (the forward reaction is endothermic and the reverse reaction is exothermic).

Exercise: Predict in which direction the equilibrium will shift when the temperature is increased.
Equilibrium will shift to the right because forward reaction is endothermic.

What effect (if any) will this have on the pH of pure water?

The concentration of H^+ will increase therefore the pH will decrease.

Complete the following table:

Temperature (K)	K_w	$[\text{H}^+]$ in pure water	pH of pure water
273	1.50×10^{-15}	3.87×10^{-8}	7.4
298	1.00×10^{-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 as the $[\text{H}^+] = [\text{OH}^-]$.

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

$$K_w = [\text{H}^+][\text{OH}^-]$$

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

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

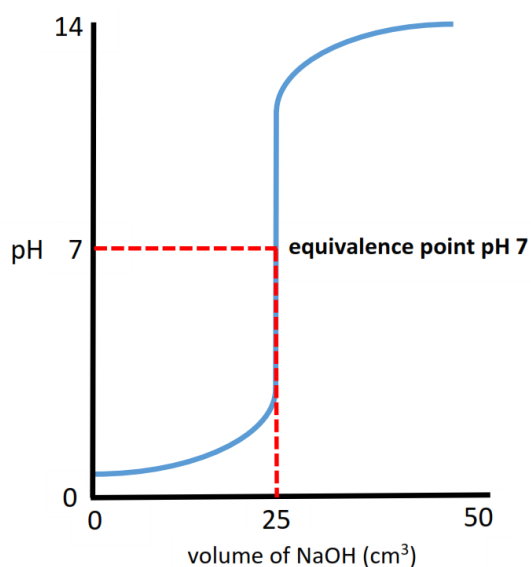
$$= 2.37 \times 10^{-7} \text{ mol dm}^{-3}$$

- c) The value of $[\text{OH}^-]$ in water at 60°C is greater than the value at room temperature. Explain why water is not alkaline at 60°C .

$$[\text{H}^+] = [\text{OH}^-] \text{ (concentrations of } \text{H}^+ \text{ and } \text{OH}^- \text{ are equal)}$$

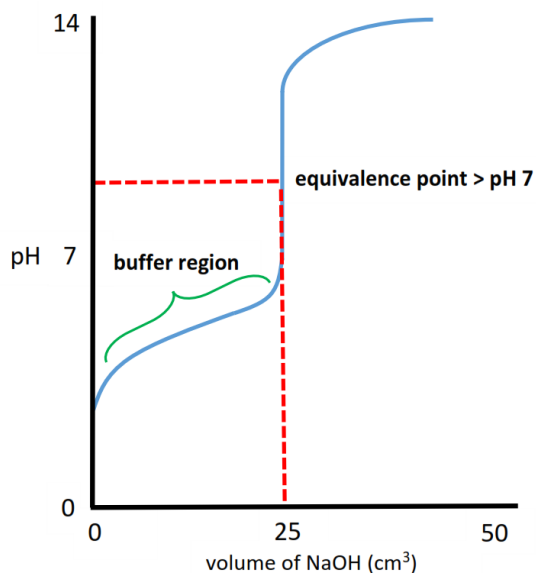
pH curves

Strong acid and strong base (HCl and NaOH)



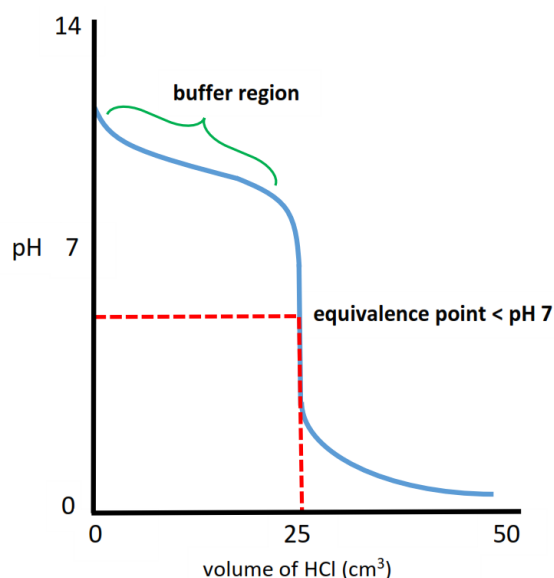
- Initial pH quite (strong acid)
- Very sharp increase in pH from pH 3 to pH 11
- Curve flattens out at high pH 14 (pH of strong base)
- pH at equivalence point = 7

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

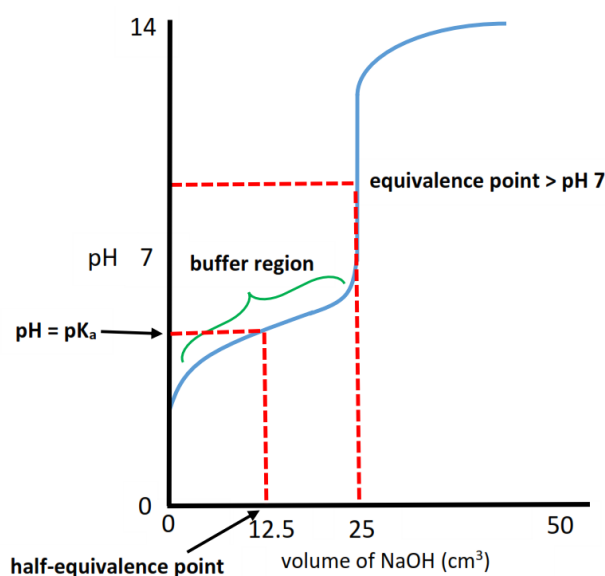
Strong acid and weak base (HCl + NH₃)



- 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

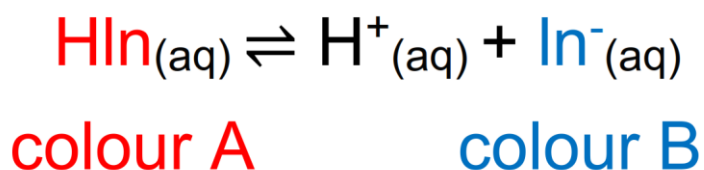
Half-equivalence point

- The 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).
- 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.

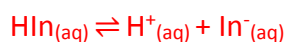


- Litmus turns red in an acidic solution and blue in an alkaline solution.
- In acidic solutions (high $[\text{H}^+]$), the equilibrium shifts to the left and the red colour is seen. In alkaline solutions (high $[\text{OH}^-]$), the equilibrium shifts to the right and the blue colour is seen.

Exercise: The indicator bromophenol blue, $\text{HIn}_{(\text{aq})}$, has a form that is yellow and an $\text{In}^-_{(\text{aq})}$ 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.



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

(ii) on the addition of a strong base.

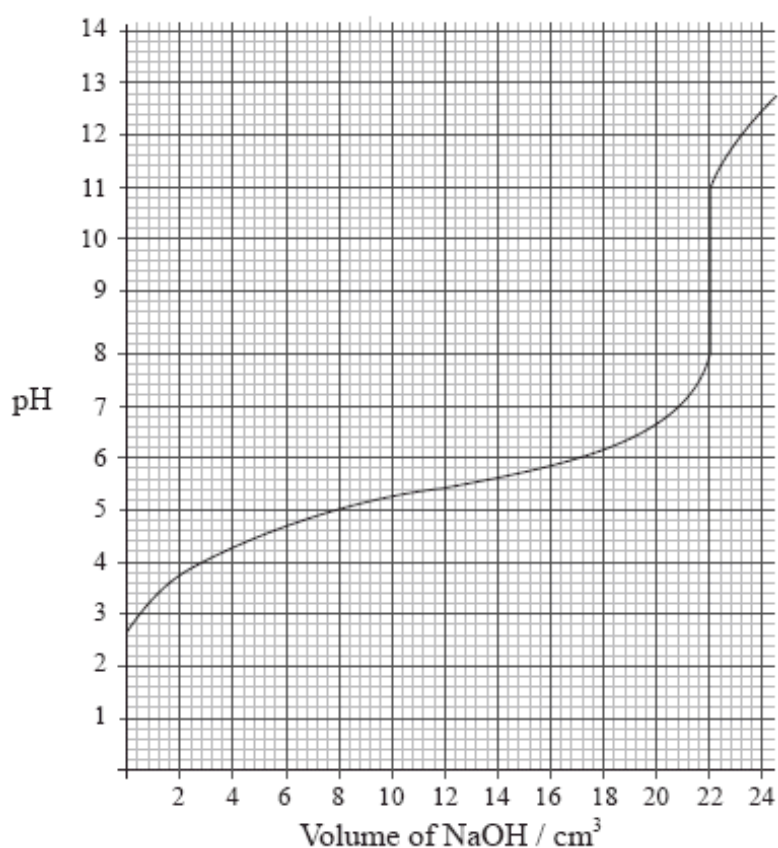
Addition of OH^- , equilibrium shifts to right, blue colour is seen.

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 pK_a
- The colour change can be considered to take place over a range of $pK_a \pm 1$
- 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:

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



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.

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

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

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

- The pH and pOH scales are inverse, which means the higher the $[\text{H}^+]$ or $[\text{OH}^-]$ concentration, the lower the pH or pOH value.
- The relationship between pH and pOH is:

$$\text{pH} + \text{pOH} = 14.00 \text{ at } 298 \text{ K}$$

- $\text{p}K_w$ can be derived from K_w :

$$\text{p}K_w = -\log_{10} (K_w)$$

$$K_w = 10^{-\text{p}K_w}$$

Exercises:

1. Lemon juice has a pH of 2.90 at 298 K. Calculate its $[\text{H}^+]$, $[\text{OH}^-]$ and pOH.

$$10^{-2.90} = 1.26 \times 10^{-3}$$

$$[\text{OH}^-] = 1.00 \times 10^{-14} \div 1.26 \times 10^{-3} = 7.94 \times 10^{-12}$$

$$\text{pOH} = -\log (7.94 \times 10^{-12}) = 11.1 \text{ or } 14.0 - 2.90 = 11.1$$

2. A sample of blood at 298 K has a $[\text{H}^+]$ of $4.60 \times 10^{-8} \text{ mol dm}^{-3}$. Calculate the OH^- and state whether the blood is acidic, neutral or basic.

$$[\text{OH}^-] = 1.00 \times 10^{-14} \div 4.60 \times 10^{-8} = 2.17 \times 10^{-7}$$

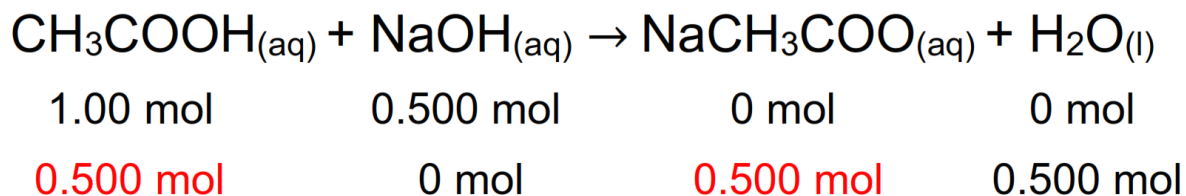
$[\text{OH}^-]$ greater than $[\text{H}^+]$ therefore basic.

How would you expect the pH to be changed at body temperature (37°C)?

pH would decrease as the dissociation of water is endothermic.

Buffer solutions

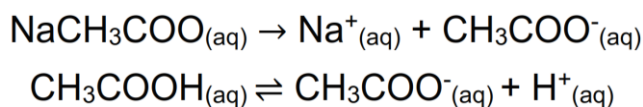
- Buffer solutions resist a change in pH when small amounts of acid or base are added.
- A buffer solution can be prepared by reacting a weak acid with a strong base (or a weak base and strong acid).



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

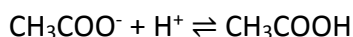
Acidic buffers

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



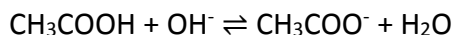
Response to added acid $\text{H}^+_{(\text{aq})}$

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



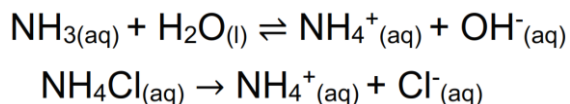
Response to added base $\text{OH}^-_{(\text{aq})}$

- The added OH^- ions react with the CH_3COOH to form CH_3COO^- and H_2O .



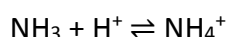
Basic buffers

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



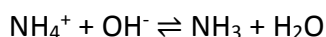
Response to added acid $\text{H}^+_{(\text{aq})}$

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



Response to added base $\text{OH}^-_{(\text{aq})}$

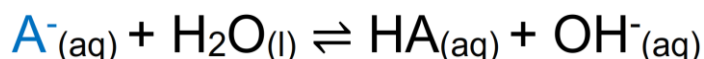
- The added OH^- ions react with the NH_4^+ to form NH_3 and H_2O



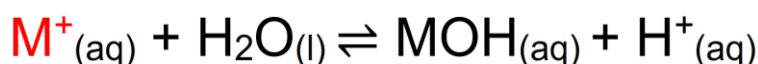
Salt hydrolysis

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

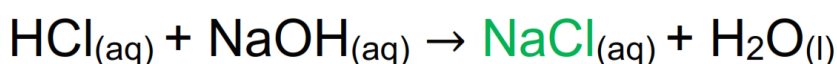
Anion hydrolysis ($\text{pH} > 7$ at 298 K)



Cation hydrolysis ($\text{pH} < 7$ at 298 K)

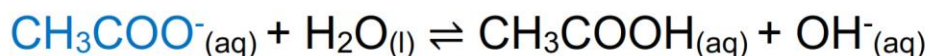
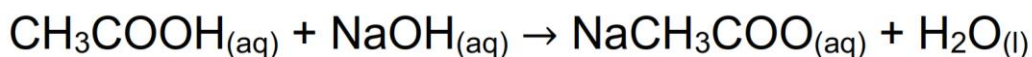


Salt of a strong acid and strong base



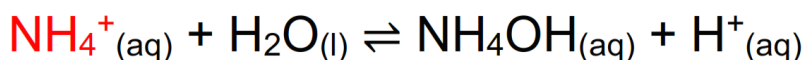
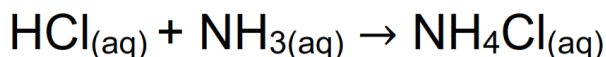
- The salt formed from a strong acid and a strong base (NaCl) has a pH of approximately 7 at 298 K (neither ion hydrolyses).

Salt of a weak acid and strong base



- 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



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