Acids and bases HL

IB CHEMISTRY HL

25	16		6	2	25
Mn	S	J	C	He	Mn
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

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:

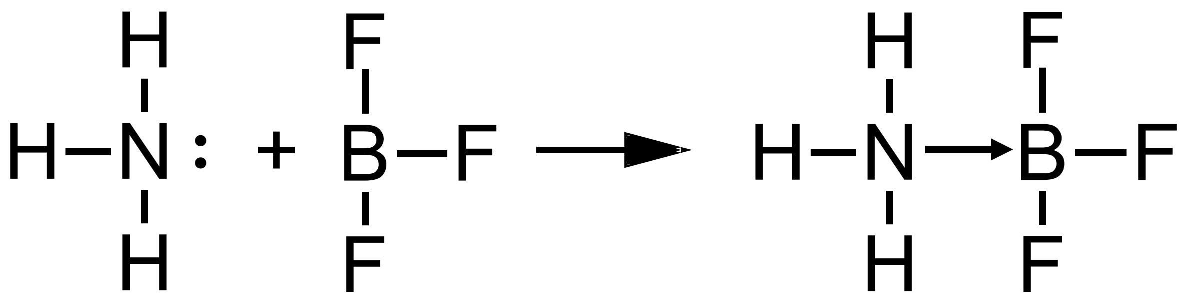
- Only examples involving the transfer of one proton will be assessed. Important features are:
  - intercept with pH axis
  - equivalence point
  - buffer region
  - points where $pK_a = pH$ or $pK_b = pOH$.
- For an indicator which is a weak acid:
  - $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

    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:
  - $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$

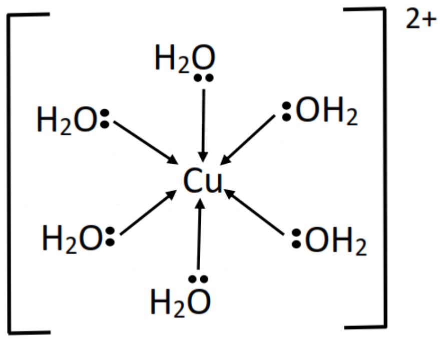
    Colour A   Colour B
- Examples of indicators are listed in the data booklet in section 22.
- Salts formed from the four possible combinations of strong and weak acids and bases should be considered. Calculations are not required.
- The acidity of hydrated transition metal ions is covered in topic 13. The treatment of other hydrated metal ions is not required.

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.



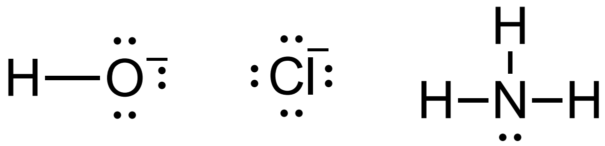
- NH_3 is a Lewis base, as it has a lone pair of electrons to donate.
- BF_3 is a Lewis acid as it has an incomplete octet to accept the lone pair of electrons from NH_3
- A coordinate covalent bond is formed between the two (represented by an arrow).
- Transition metal ions (Cu^{2+}) in solution are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



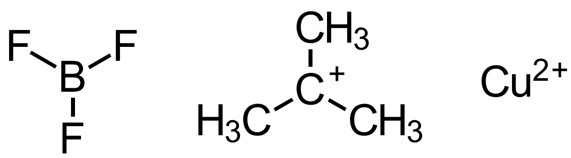
$$\mathbf{Cu^{2+}{}_{(aq)} + 6H_2O_{(l)} \rightarrow [Cu(H_2O)_6]^{2+}{}_{(aq)}}$$

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:

1. Define an acid and base according to the Lewis theory.

2. Draw the Lewis structure of ammonia (NH_3). Explain how it is able to act as a Lewis base.

3. Explain how BF_3 is able to act as a Lewis acid and state the name of the bond formed.

4. Explain why the following reaction cannot be described using the Bronsted-Lowry theory of acids and bases.

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

5. In the above reaction, explain how the Cr^{3+} is able to act as a Lewis acid.

Acid and base dissociation constants (K_a and K_b)

- Weak acids partially dissociate (ionize) in solution.

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

- Weak bases partially dissociate (ionize) in solution.

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

- 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.

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

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

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

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

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

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

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

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

pK_a and pK_b

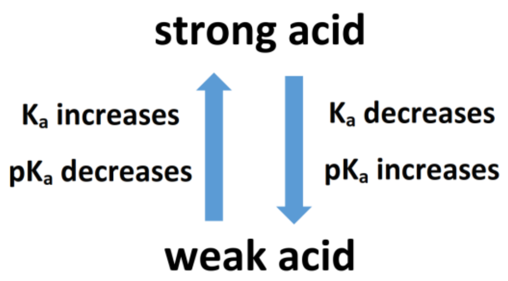
$$pK_a = -\log_{10} K_a \qquad pK_b = -\log_{10} K_b$$

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

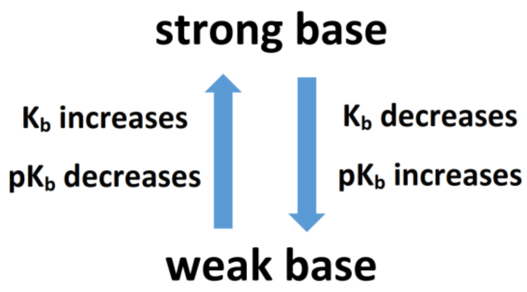
- pK_a and pK_b are usually positive and have no units.
- A change of one unit of pK_a or pK_b represents a ten-fold change in the value K_a or K_b.
- pK_a and pK_b must be quoted at a specific temperature.

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.

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 it K_a value is 1.75×10^{-5}

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

$$K_a\ CH_3COOH = 1.75 \times 10^{-5}$$

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

$$K_b\ CH_3COO^- = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

pK_a, pK_b and pK_w

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = pK_w$$

$$pK_w = -\log(1.00 \times 10^{-14}) = 14$$

$$\text{At 298 K, } pK_a + pK_b = 14$$

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.

	$CH_3COOH_{(aq)}$	$CH_3COO^-_{(aq)}$	$H^+_{(aq)}$
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

Example 2:

A 0.200 mol dm^{-3} solution of ammonia (NH_3) 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

Exercises:

1. Propanoic acid, CH_3CH_2COOH 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.

b) Calculate the K_a value of propanoic acid. The pK_a of propanoic acid is 4.87.

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.

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.

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

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

Temperature dependence of K_w

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

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

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

- 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.

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

Complete the following table:

Temperature (K)	K_w	$[H^+]$ in pure water	pH of pure water
273	1.50×10^{-15}		
298	1.00×10^{-14}		
313	3.00×10^{-14}		

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

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

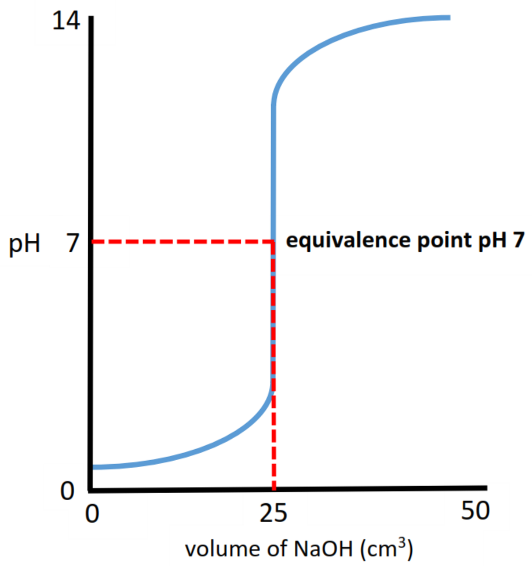
a) State the expression for the K_w

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

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.

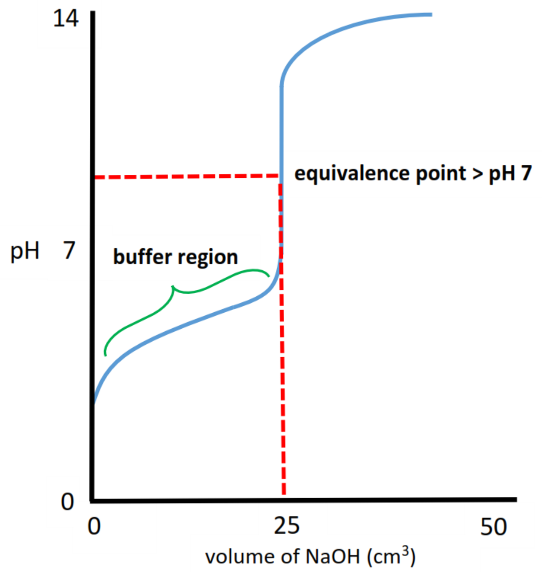
pH curves

Strong acid and strong base (HCl and NaOH)



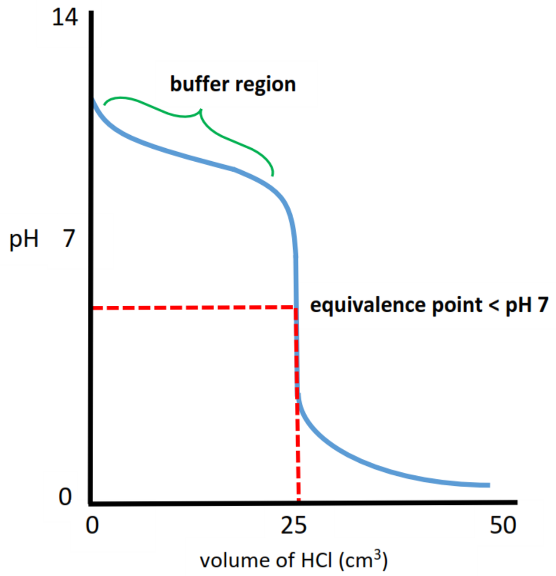
- Initial pH quite (strong acid)
- Very sharp increase in pH from pH 3 to pH 11
- Curve flattens out at high pH 14 (pH of strong base)
- pH at equivalence point = 7

Weak acid and strong base (CH_3COOH 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

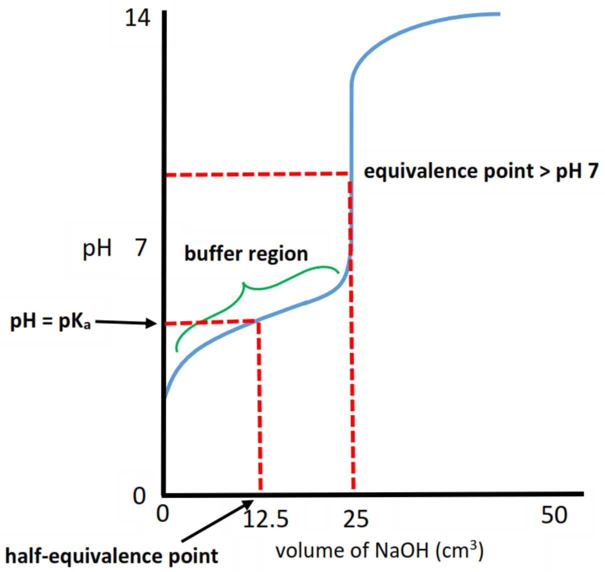
Strong acid and weak base (HCl + NH_3)



- 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.

$$\underset{\text{colour A}}{HIn_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{colour B}}{In^-_{(aq)}}$$

- 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.

(ii) on the addition of a strong base.

End point

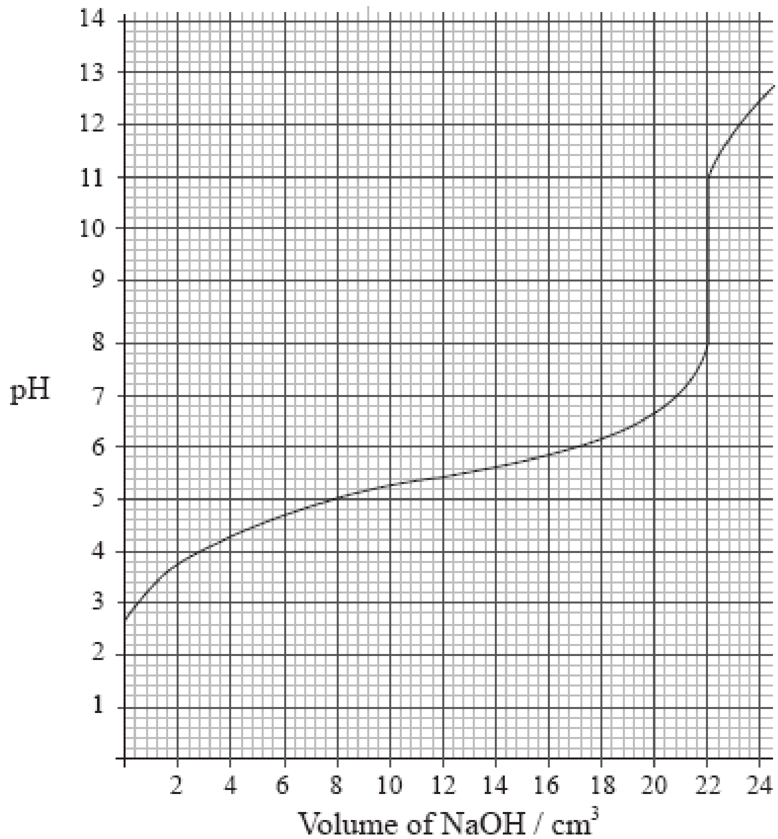
- The end point of an indicator is the pH at which it changes colour.
- An indicator changes colour when the pH is equal to its pK_a
- The colour change can be considered to take place over a range of $pK_a \pm 1$
- A list of acid base indicators can be found in section 22 of the data booklet.

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

a) the pH at the equivalence point

b) the pK_a of the weak acid

c) suggest a suitable indicator for the titration.



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 $[OH^-]$ concentration, the lower the pH or pOH value.
- The relationship between pH and pOH is:

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

- pK_w can be derived from K_w:

$$pK_w = -\log_{10} (K_w)$$

$$K_w = 10^{-pKw}$$

Exercises:

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

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.

   How would you expect the pH to be changed at body temperature (37^{o}C)?

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).

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$$

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.

$$NaCH_3COO_{(aq)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$
$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

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 CH_3COOH to form CH_3COO^- and H_2O.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

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.

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$
$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

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^- 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)

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

Cation hydrolysis (pH < 7 at 298 K)

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

Salt of a strong acid and strong base

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

- 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

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$$

$$NaCH_3COO_{(aq)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

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

- 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

$$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4Cl_{(aq)}$$

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

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