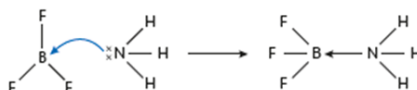
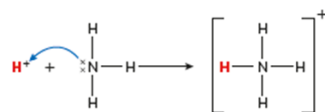
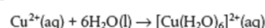
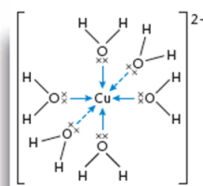


18.1 Lewis acids and bases

Lewis acid - *Electron pair acceptor*Lewis base - *Electron pair donor*

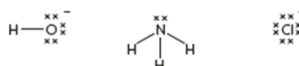
Ligands, as donors of lone pairs, are therefore acting as Lewis bases.

For example, Cu^{2+} in aqueous solution reacts as follows: Cu^{2+} is a Lewis acid and H_2O is a Lewis base.Typical ligands found in complex ions include H_2O , CN^- , and NH_3 . Note that these all possess lone pairs of electrons, the defining feature of their Lewis base properties.

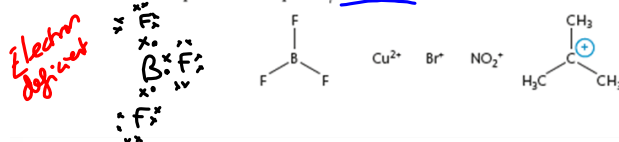
We can relate these terms to those of "nucleophile" and "electrophile" found in organic chemistry:

A **nucleophile** ('likes nucleus') is an electron-rich species that donates a lone pair to form a new covalent bond in a reaction.An **electrophile** ('likes electrons') is an electron-deficient species that accepts a lone pair from another reactant to form a new covalent bond.

• Examples of nucleophiles / Lewis bases:



• Examples of electrophiles / Lewis acids:

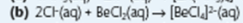
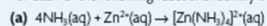


Comparison of Brønsted-Lowry and Lewis theories of acids and bases

Theory	Definition of acid	Definition of base
Brønsted-Lowry	proton donor	proton acceptor
Lewis	electron pair acceptor	electron pair donor

Exercises

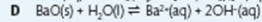
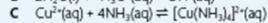
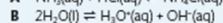
19 For each of the following reactions identify the Lewis acid and the Lewis base.



20 Which of the following could not act as a ligand in a complex ion with a transition metal?

A Cl^- B NCl_3 C PCl_3 D CH_4

21 Which of the following reactions represents an acid-base reaction according to Lewis theory but not according to Brønsted-Lowry theory?

19 (a) Lewis acid Zn^{2+} ; Lewis base NH_3 (b) Lewis acid BeCl_2 ; Lewis base Cl^- (c) Lewis acid Mg^{2+} ; Lewis base H_2O 20 D, CH_4 because it does not possess a lone pair.21 C, there is no exchange of H^+ .

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, $K_a \times K_b = K_w$.

Guidance

- The value K_w depends on the temperature.
- Only examples involving the transfer of one proton will be assessed.
- Calculations of pH at temperatures other than 298 K can be assessed.
- The relationship between K_a and pK_a is $pK_a = -\log K_a$ and between K_b and pK_b is $pK_b = -\log K_b$.

K_w is temperature dependent

The ionic product constant of water, K_w , was derived on pages 358–359.

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

$$pK_w = pH + pOH$$

The dissociation of water is an endothermic reaction (as it requires breaking a bond).

How will an increase in temperature affect K_w ? How will it affect pH?



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

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

Temperature / °C	K_w	$[H^+]$ in pure water ($\sqrt{K_w}$)	pH of pure water ($-\log_{10} [H^+]$)
0	1.5×10^{-15}	0.39×10^{-7}	7.47
10	3.0×10^{-15}	0.55×10^{-7}	7.27
20	6.8×10^{-15}	0.82×10^{-7}	7.08
25	1.0×10^{-14}	1.00×10^{-7}	7.00
30	1.5×10^{-14}	1.22×10^{-7}	6.92
40	3.0×10^{-14}	1.73×10^{-7}	6.77
50	5.5×10^{-14}	2.35×10^{-7}	6.63

In other words, the pH of pure water is 7.00 only when the temperature is 298 K. Note that at temperatures above and below this, despite changes in the pH value, water is still a neutral substance as its $H^+(aq)$ concentration is equal to its $OH^-(aq)$ concentration. It does not become acidic or basic as we heat it and cool it respectively!

pH and pOH scales are inter-related

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

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

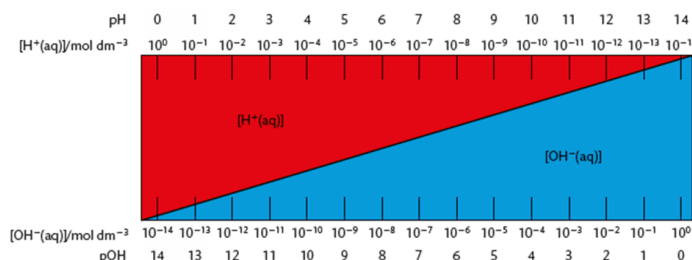
- $pH = -\log_{10} [H^+]$;
- $[H^+] = 10^{-pH}$

From the relationship $[H^+][OH^-] = K_w = 1.00 \times 10^{-14}$ at 298 K, it follows that

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

By taking the negative logarithm to base 10 of both sides, we get

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



In the same way as the negative logarithms to base 10 of H^+ and OH^- are known as pH and pOH respectively, the same terminology can be applied to K_w to derive pK_w .

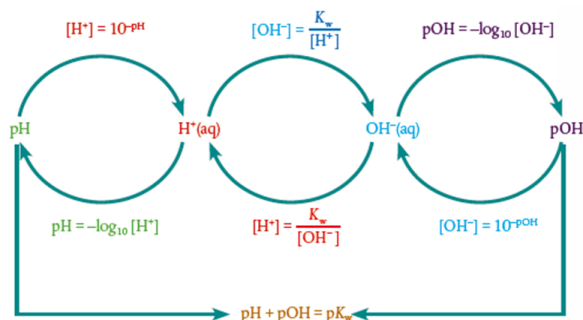
- $pK_w = -\log_{10} (K_w)$
- $K_w = 10^{-pK_w}$

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

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

So we can rewrite the expression above in a form that will apply to all temperatures:

$$pH + pOH = pK_w$$



Converting H^+ and OH^- into pH and pOH

Many calculations on acids and bases involve inter-conversions of $[H^+]$ and pH, as we saw in section 8.3, and we can extend these now to include $[OH^-]$ and pOH.

Worked example

Lemon juice has a pH of 2.90 at 25 °C. Calculate its $[H^+]$, $[OH^-]$, and pOH.

Solution

298K

- $[H^+] = 10^{-pH} = 10^{-2.90} = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$
- $pH + pOH = 14.00$ at 298 K, so $pOH = 14.00 - 2.90 = 11.10$
- $[OH^-] = 10^{-pOH} = 10^{-11.10} = 7.7 \times 10^{-12} \text{ mol dm}^{-3}$
- or $K_w = [H^+][OH^-]$ so $1.00 \times 10^{-14} = (1.3 \times 10^{-3}) \times [OH^-]$
 $[OH^-] = 7.7 \times 10^{-12} \text{ mol dm}^{-3}$

$$[H^+] = 10^{-pH} \\ pH + pOH = 14.00$$

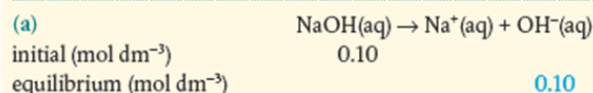
Strong acids and bases: pH and pOH can be deduced from their concentrations

Worked example

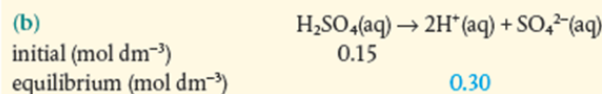
Calculate the pH of the following at 298 K:

- (a) $0.10 \text{ mol dm}^{-3} \text{ NaOH(aq)}$ $\rightarrow [\text{OH}^-] = 0.10 \text{ mol dm}^{-3}$
 (b) $0.15 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4\text{(aq)}$ $\rightarrow [\text{H}^+] = 0.30 \text{ mol dm}^{-3}$

Solution



$\text{pOH} = -\log_{10}(0.10) = 1.0$, therefore $\text{pH} = 13.0$



$\text{pH} = -\log_{10}(0.30) = 0.52$

Exercises

- 22 At the temperature of the human body, 37°C , the value of $K_w = 2.4 \times 10^{-14}$. Calculate $[\text{H}^+]$, $[\text{OH}^-]$, pH, pOH, and $\text{p}K_w$ of water at this temperature. Is it acidic, basic, or neutral?
- 23 The pH of a sample of milk is 6.77 at 298 K. Calculate its pOH, $[\text{H}^+]$, and $[\text{OH}^-]$. Deduce whether it is acidic, basic, or neutral.
- 24 Calculate the pH of the following solutions:
 (a) $0.40 \text{ mol dm}^{-3} \text{ HCl}$
 (b) $3.7 \times 10^{-4} \text{ mol dm}^{-3} \text{ KOH}$ $\rightarrow \text{pOH} =$
 (c) $5.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ Ba(OH)}_2$ $\text{pOH} + \text{pH} = 14$
- 25 Which values are correct for a solution of NaOH of concentration $0.010 \text{ mol dm}^{-3}$ at 298 K?
- A $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $\text{pH} = 2.00$
 B $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $\text{pH} = 12.00$
 C $[\text{H}^+] = 1.0 \times 10^{-12} \text{ mol dm}^{-3}$ and $\text{pOH} = 12.00$
 D $[\text{OH}^-] = 1.0 \times 10^{-12} \text{ mol dm}^{-3}$ and $\text{pOH} = 2.00$

$$K_w = [\text{H}^+][\text{OH}^-] = 2.4 \times 10^{-14}$$

$$\text{pH} + \text{pOH} = \text{p}K_w$$

$$[\text{H}^+]^2 = 2.4 \times 10^{-14}$$

$$[\text{H}^+] = \sqrt{2.4 \times 10^{-14}}$$

22 $[\text{H}^+] = [\text{OH}^-] = 1.55 \times 10^{-7} \text{ mol dm}^{-3}$
 $\text{pH} = \text{pOH} = 6.81$
 $\text{pH} + \text{pOH} = \text{p}K_w = 13.62$
 neutral

23 $\text{pOH} = 7.23$
 $[\text{H}^+] = 1.7 \times 10^{-7} \text{ mol dm}^{-3}$
 $[\text{OH}^-] = 5.9 \times 10^{-8} \text{ mol dm}^{-3}$
 acidic

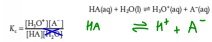
24 (a) 0.40 (b) 10.57
 (c) 10.00

25 B

Dissociation constants express the strength of weak acids and bases

As weak acids and bases only partially dissociate, we cannot calculate $[H^+]$ or $[OH^-]$ from knowing their initial concentrations. So we must use equilibrium expressions to do so:

Consider the generic weak acid HA dissociating in water:



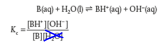
Given that the concentration of water is considered to be a constant, we can combine this with K_a to produce a modified equilibrium constant known as K_a :

$$K_a [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\text{Therefore } K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- K_a is the acid dissociation constant
- A higher value = more dissociation = stronger acid

Similarly, we can consider the ionization of a base using the generic weak base B:



Again we can combine the constants to give a modified equilibrium constant K_b :

$$K_b [H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

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

K_b is known as the base dissociation constant. It will have a fixed value for a particular base at a specified temperature.

- K_b is the base dissociation constant
- A higher value = more dissociation = stronger base

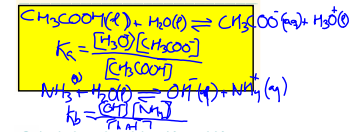
Worked example 1

Write the expressions for K_a and K_b for the following acid and base:

(a) $CH_3COOH(aq)$

(b) $NH_3(aq)$

Solution



Calculations involving K_a and K_b

Important points:

- Given concentrations are initial concentrations.
- Concentration values of $pH/pOH/K_a/K_b$ must be equilibrium concentrations (when equilibrium has been reached).

When the extent of dissociation is very small (very low value for K_a or K_b) it is appropriate to use the approximations:

$$[acid]_{\text{initial}} \approx [acid]_{\text{equilibrium}}$$

$$[base]_{\text{initial}} \approx [base]_{\text{equilibrium}}$$

1 Calculation of K_a and K_b from pH and initial concentration

Worked example 2

Calculate K_a at 298 K for a 0.01 mol dm^{-3} solution of ethanoic acid (CH_3COOH). It has a pH of 3.4 at this temperature.

Solution

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium. As in Chapter 7, numbers in black are data that were given in the question, numbers in blue have been derived.

From the pH we get the $[H^+]$ at equilibrium:

$$pH = 3.4 \Rightarrow [H^+] = 10^{-3.4} = 4.0 \times 10^{-4} \text{ mol } dm^{-3}$$

From the stoichiometry of the reaction we know that $[H^+] = [CH_3COO^-]$

	$CH_3COOH(aq)$	\rightleftharpoons	$CH_3COO^-(aq)$	$+ H^+(aq)$
initial (mol dm^{-3})	0.01		0.00	0.00
change (mol dm^{-3})	-4×10^{-4}		$+4 \times 10^{-4}$	$+4 \times 10^{-4}$
equilibrium (mol dm^{-3})	$0.01 - (4 \times 10^{-4})$		4×10^{-4}	4×10^{-4}
	≈ 0.01			

The approximation $0.01 - 0.0004 = 0.0096$ is valid within the precision of this data.

Write the expression for K_a and substitute the equilibrium values.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(4 \times 10^{-4})^2}{0.01} = 1.6 \times 10^{-5}$$

Worked example 3

Calculate the K_b for a 0.100 mol dm^{-3} solution of methylamine, CH_3NH_2 , at 25 °C. Its pH is 11.80 at this temperature.

Solution

At 25 °C (298 K), $pH + pOH = 14.00$. Therefore $pH = 11.80 \Rightarrow pOH = 2.20$

$$[OH^-] = 10^{-2.20} = 6.3 \times 10^{-3}$$

From the stoichiometry of the reaction $[OH^-] = [CH_3NH_3^+]$

	$CH_3NH_2(aq)$	$+ H_2O(l)$	\rightleftharpoons	$CH_3NH_3^+(aq)$	$+ OH^-(aq)$
initial (mol dm^{-3})	0.100			0.000	0.000
change (mol dm^{-3})	-0.0063			$+0.0063$	$+0.0063$
equilibrium (mol dm^{-3})	0.0937			0.0063	0.0063

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.0063)(0.0063)}{0.0937} = 4.22 \times 10^{-4}$$

2 Calculation of $[H^+]$ and pH, $[OH^-]$ and pOH from K_a and K_b

Worked example 4

A 0.75 mol dm^{-3} solution of ethanoic acid has a value for $K_a = 1.8 \times 10^{-5}$ at a specified temperature. What is its pH at this temperature?

Solution

To calculate pH we need to know $[H^+]$ at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the 'change' amount in the reaction.

So let the change in concentration of $CH_3COOH = -x$

Therefore change in concentration of CH_3COO^- and $H^+ = +x$

	$CH_3COOH(aq)$	\rightleftharpoons	$CH_3COO^-(aq)$	$+ H^+(aq)$
initial (mol dm^{-3})	0.75		0.00	0.00
change (mol dm^{-3})	$-x$		$+x$	$+x$
equilibrium (mol dm^{-3})	$0.75 - x$		x	x

As K_a is very small, x , the amount of dissociation, is also extremely small and it is valid to approximate $[CH_3COOH]_{\text{initial}} \approx [CH_3COOH]_{\text{equilibrium}}$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.75} = 1.8 \times 10^{-5}$$

$$\text{Therefore } x = \sqrt{1.8 \times 10^{-5} \times 0.75} = 3.7 \times 10^{-3}$$

$$[H^+] = 3.7 \times 10^{-3} \Rightarrow pH = 2.4$$

Worked example 5

A 0.20 mol dm^{-3} aqueous solution of ammonia has K_b of 1.8×10^{-5} at 298 K. What is its pH?

Solution

Let the change in concentration of NH_4^+ and $OH^- = +x$

	$NH_3(aq)$	$+ H_2O(l)$	\rightleftharpoons	$NH_4^+(aq)$	$+ OH^-(aq)$
initial (mol dm^{-3})	0.20			0.00	0.00
change (mol dm^{-3})	$-x$			$+x$	$+x$
equilibrium (mol dm^{-3})	$0.20 - x$			x	x

As K_b is very small, x , the amount of dissociation is also extremely small, and so it is valid to approximate $[NH_3]_{\text{initial}} \approx [NH_3]_{\text{equilibrium}}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.20} = 1.8 \times 10^{-5}$$

$$\text{Therefore } x = \sqrt{1.8 \times 10^{-5} \times 0.20} = 1.9 \times 10^{-3}$$

$$[OH^-] = 1.9 \times 10^{-3}$$

$$pOH = -\log_{10}(1.9 \times 10^{-3}) = 2.72$$

$$\text{Therefore at 298 K, } pH = 14.00 - 2.72 = 11.28$$

Note that the term acid dissociation constant is sometimes used interchangeably with the term acid ionization constant. You should be comfortable to recognize either terminology in textbooks and questions.

$$0.01 - (4 \times 10^{-4}) = 0.0096$$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

$$pH = -\log[H^+]$$

$$pOH + pH = \frac{pK_b}{14}$$

pK_a and pK_b

As with $[H^+]$, $[OH^-]$ and K_w we can use a logarithmic function to make numbers much easier to handle:

$$pK_a = -\log_{10} K_a$$

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

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

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

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

Acid	Formula	K_a	pK_a
methanoic	HCOOH	1.8×10^{-4}	3.75
ethanoic	CH ₃ COOH	1.8×10^{-5}	4.76
propanoic	C ₂ H ₅ COOH	1.4×10^{-5}	4.87

Base	Formula	K_b	pK_b
ammonia	NH ₃	1.8×10^{-5}	4.75
methylamine	CH ₃ NH ₂	4.6×10^{-4}	3.34
ethylamine	C ₂ H ₅ NH ₂	4.5×10^{-4}	3.35

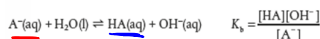
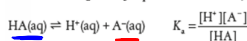
2 The relationship between K_a and pK_a and between K_b and pK_b is inverse.

Stronger acids or bases with higher values for K_a or K_b have lower values for pK_a or pK_b .



Relationship between K_a and K_b , pK_a and pK_b for a conjugate pair

Consider the K_a and K_b expressions for a conjugate acid-base pair HA and A⁻.



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

$$\text{Therefore } K_a \times K_b = [H^+] \times [OH^-] = K_w$$

By taking negative logarithms of both sides:

$$pK_a + pK_b = pK_w$$

$$\text{At } 298 \text{ K, } K_w = 1.00 \times 10^{-14} \text{ so } pK_w = 14.00$$

$$\text{Therefore } pK_a + pK_b = 14.00 \text{ at } 298 \text{ K}$$

High K_a of conjugate acid \rightarrow Lower K_b of conjugate base (and vice-versa)

strongest acid	Acid	Base	weakest base
	HClO ₄	ClO ₄ ⁻	
	HCl	Cl ⁻	
	H ₂ SO ₄	HSO ₄ ⁻	
	H ₂ O	H ₂ O	
	CH ₃ COOH	CH ₃ COO ⁻	
	H ₂ S	SH ⁻	
	NH ₄ ⁺	NH ₃	
	H ₃ O ⁺	OH ⁻	
	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	

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

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

Exercises

32 A weak acid HA has a pK_a of 4.92. What will be the $[H^+]$ and pH of a 0.030 mol dm⁻³ solution of this acid?

33 What is the relationship between K_a and pK_a ?

A $pK_a = -\log K_a$

B $pK_a = \frac{1.0 \times 10^{-14}}{K_a}$

C $pK_a = \log K_a$

D $pK_a = \frac{1.0}{K_a}$

34 The pK_a of HCN is 9.21 and that of HF is 3.17. Which is the stronger acid?

35 Look at the data in Q34. What are the pK_b values of CN⁻ and F⁻? Which is the stronger base?

36 (a) The pK_a of ethanoic acid, CH₃COOH, at 298 K is 4.76. What is the pK_b of its conjugate base CH₃COO⁻? $pK_b = 9.24$

(b) The pK_a of methanoic acid, HCOOH, at 298 K is 3.75. Is its conjugate base weaker or stronger than that of ethanoic acid?

$$pK_b \text{ methanoic acid} = 10.25$$

K_a scale

Very small

Weak acid

Very large

Strong acid

Small

Strong acid

Large

Weak acid

Small

Strong acid

Large

Weak acid

Small

Strong acid

Large

Weak acid

Small

Strong acid

Large

Weak acid

Small

Strong acid

Large

Weak acid

Small

Strong acid

Large

Weak acid



$$K_a = \frac{[H^+][Cl^-]}{[HCl]}$$

Buffer solutions

A buffer solution is resistant to changes in pH on the addition of small amounts of acid or alkali.

To understand the importance of buffers, it is useful to see how added acid or alkali changes the pH of a non-buffered solution. This is shown below.



The 2 main types - those that maintain an acidic solution and those that maintain a basic one. Buffer solutions are made using a mixture of 2 solutions that between them contain a conjugate acid-base pair.

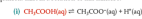
1 Acidic buffers

Composition of the buffer solution

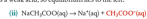
Made by mixing an aqueous solution of a weak acid with a solution of its salt of a strong alkali. For example:



The following equilibria exist in a solution of this mixture:



$\text{CH}_3\text{COOH(aq)}$ is a weak acid, so equilibrium lies to the left.



$\text{CH}_3\text{COO}^-\text{(aq)}$ is a soluble salt, so is fully dissociated in solution.

So the mixture contains relatively high concentrations of both CH_3COOH and CH_3COO^- , that is an acid and its conjugate base. These can be considered as 'reservoirs', ready to react with added OH^- and H^+ respectively in neutralization reactions.

Response to added acid and base

• Addition of acid (H^+):
 H^+ will combine with the base CH_3COO^- to form CH_3COOH , therefore removing most of the added H^+ .



• Addition of base (OH^-):
 OH^- will combine with the acid CH_3COOH to form CH_3COO^- and H_2O , so removing most of the OH^- .



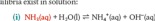
2 Basic buffers

Composition of the buffer solution

Made by mixing an aqueous solution of a weak base with its salt of a strong acid. For example:



The following equilibria exist in solution:



$\text{NH}_3\text{(aq)}$ is a weak base, so equilibrium lies to the left.



$\text{NH}_4^+\text{(aq)}$ is a soluble salt, so is fully dissociated in solution.

So here the mixture contains relatively high concentrations of both $\text{NH}_3\text{(aq)}$ and $\text{NH}_4^+\text{(aq)}$ - that is a base and its conjugate acid. These species will again act as reservoirs, ready to react with added H^+ and OH^- respectively in neutralization reactions.

Response of buffer to added acid or alkali

• Addition of acid (H^+):
 H^+ will combine with the base NH_3 to form NH_4^+ , therefore removing most of the added H^+ .



• Addition of base (OH^-):
 OH^- will combine with the acid NH_4^+ and form NH_3 and H_2O , so removing most of the OH^- .



Making buffer solutions

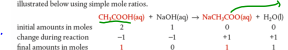
The pH of a buffer is determined by the interactions of its components. Specifically it depends on:

- 1 the pK_a or pK_b of its acid or base;
- 2 the ratio of the initial concentrations of acid and salt, or base and salt, used in its preparation.

Buffer solutions can be prepared by starting with an acid or base that has a pK_a or pK_b value as close as possible to the required pH or pOH of the buffer. This is then either:

- mixed with a solution of a salt containing its conjugate or
- partially neutralized by a strong base or acid.

The neutralization reaction should ensure that approximately one half of the starting acid or base is converted into salt. After reaction, the mixture will contain the unreacted acid or base and its salt in equimolar amounts. An example of this is illustrated below using simple molar ratios.



initial amounts in moles 2 1 0 0
change during reaction -1 -1 +1 +1
final amounts in moles 1 0 1 1

The final mixture, containing equal amounts of the weak acid CH_3COOH and its salt NaCH_3COO , is a buffer solution.

Worked example Equal amounts of a conjugate pair (conjugate)

State whether each of the following mixtures will form a buffer solution when dissolved in 1.00 dm³ of water.

- (a) 0.20 mol NaHCO_3 and 0.20 mol Na_2CO_3 ✓ $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$
(b) 0.20 mol CH_3COOH and 0.10 mol HCl ✗ 0.10 0.20
(c) 0.20 mol NH_3 and 0.10 mol HCl ✓ 0 0.10
(d) 0.10 mol H_3PO_4 and 0.20 mol NaOH ✗ 0 0.10 0.10 0.10

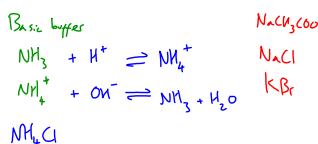
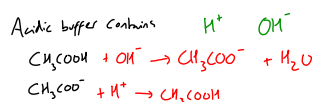
Solution
(a) Solution contains HCO_3^- and CO_3^{2-} , a conjugate pair, so it is a buffer.
(b) Solution contains two acids - it is not a buffer.
(c) NH_3 and HCl react together forming 0.10 mol NH_4Cl and 0.10 mol NH_3 unreacted; it is a buffer.
(d) H_3PO_4 and NaOH react together forming 0.20 mol Na_2HPO_4

Exercises

- 37 Which mixture would produce a buffer solution when dissolved in 1.0 dm³ of water?
A 0.50 mol of CH_3COOH and 0.50 mol of NaOH
B 0.50 mol of CH_3COOH and 0.25 mol of NaOH
C 0.50 mol of CH_3COOH and 1.00 mol of NaOH
D 0.50 mol of CH_3COOH and 0.25 mol of Ba(OH)_2
- 38 A buffer solution can be prepared by adding which of the following to 50 cm³ of 0.10 mol dm⁻³ $\text{CH}_3\text{COOH(aq)}$?
I 50 cm³ of 0.10 mol dm⁻³ $\text{NaCH}_3\text{COO(aq)}$
II 25 cm³ of 0.10 mol dm⁻³ NaOH(aq)
III 50 cm³ of 0.10 mol dm⁻³ NaOH(aq)
A I only B I and II only C II and III only D I, II, and III
- 39 State and explain which of the following has the greater buffering capacity:
(i) 100 cm³ 0.30 mol dm⁻³ HNO_2 and 0.30 mol dm⁻³ NaNO_2 or
(ii) 100 cm³ 0.10 mol dm⁻³ HNO_2 and 0.10 mol dm⁻³ NaNO_2

37 B 38 B

39 (i) Because it has a higher concentration of the acid and its conjugate base.



Factors that can affect buffer solutions

1. **Dilution:** Although diluting a weakly acidic or basic buffer solution would reduce the concentration of H^+ or OH^- ion, because their concentrations are so low (as they are weak) the effect on changing pH or pOH can be ignored. For this reason we consider that dilution does not affect the pH or pOH.

This table shows the effect on pH when diluting an ethanoic acid buffer solution from 0.1 M to 0.0001 M.

However, the "buffering capacity" (ability to maintain pH) will be reduced because the concentrations are less.

0.1M	4.76
0.01M	4.76
$10^{-3}M$	4.79
$10^{-4}M$	4.95

2. **Temperature:** As temperature affects K_a and K_b , it will affect the $[H^+]$ and $[OH^-]$ and therefore it will affect the pH of a buffer.

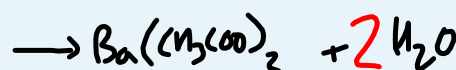


Exercises

37 Which mixture would produce a buffer solution when dissolved in 1.0 dm^3 of water?

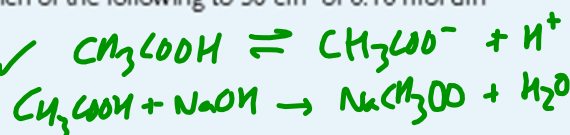
- A 0.50 mol of CH_3COOH and 0.50 mol of $NaOH$
 B 0.50 mol of CH_3COOH and 0.25 mol of $NaOH$ ✓
 C 0.50 mol of CH_3COOH and 1.00 mol of $NaOH$
 D 0.50 mol of CH_3COOH and 0.25 mol of $Ba(OH)_2$

Salt + Water



38 A buffer solution can be prepared by adding which of the following to 50 cm^3 of 0.10 mol dm^{-3} $CH_3COOH(aq)$?

- I 50 cm^3 of 0.10 mol dm^{-3} $NaCH_3COO(aq)$ ✓
 II 25 cm^3 of 0.10 mol dm^{-3} $NaOH(aq)$ ✓
 III 50 cm^3 of 0.10 mol dm^{-3} $NaOH(aq)$ ✗



- A I only **(B) I and II only** C II and III only D I, II, and III

39 State and explain which of the following has the greater buffering capacity:

- (i)** 100 cm^3 0.30 mol dm^{-3} HNO_2 and 0.30 mol dm^{-3} $NaNO_2$ or
 (ii) 100 cm^3 0.10 mol dm^{-3} HNO_2 and 0.10 mol dm^{-3} $NaNO_2$.

37 B 38 B

39 (i) Because it has a higher concentration of the acid and its conjugate base.

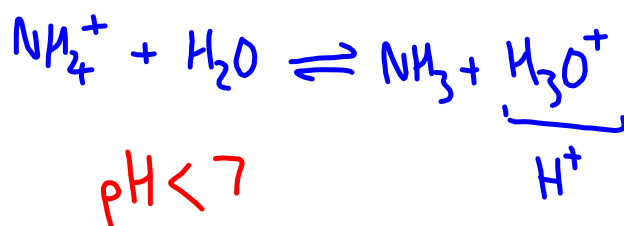
Salt hydrolysis1. Weak acid + Strong base \rightarrow Salt + Water

$\downarrow \text{Na}^+$
Not going to react
with water

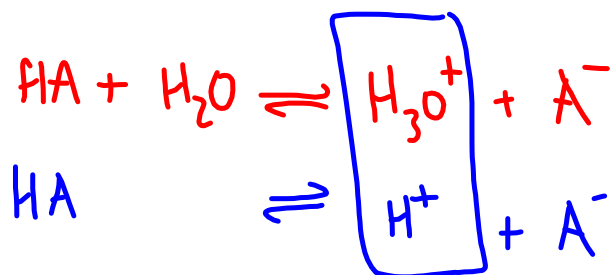
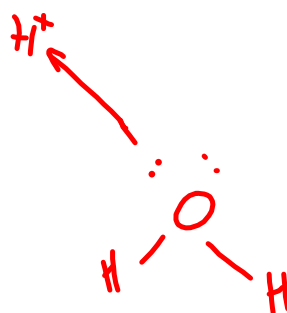
$\downarrow \text{CH}_3\text{COO}^-$
Strong conjugate base
 $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 $\text{pH} > 7$

2. Strong acid + weak base \rightarrow Salt + Water

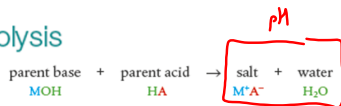
$\downarrow \text{NH}_4^+$
Relatively strong conjugate
acid so:



$\downarrow \text{Cl}^-$
Very stable so does
not react with water.



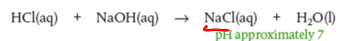
Salt hydrolysis



Not all salts form neutral aqueous solutions. It depends on the extent to which the ions can react with water and hydrolyse it.

Salt of strong acid and strong base – no hydrolysis

The reaction between a strong acid and a strong base forms a salt in which both the conjugate acid and the conjugate base are weak. As a result there is virtually no hydrolysis of ions, and the pH is close to neutral. For example:

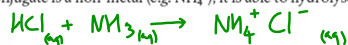


Na^+ x react with H_2O
 Cl^- x react with H_2O

Solutions of salts of strong acids with strong bases have a pH ≈ 7 at 298 K.

Salt of strong acid and weak base – cation hydrolysis

The cation (M^+) is a conjugate of the parent base. When the base is weak and this conjugate is a non-metal (e.g. NH_4^+), it is able to hydrolyse water:



$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
 Cl^- x react with H_2O

The release of H^+ causes the pH of the solution to decrease.

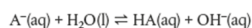
For example:

Solutions of salts of strong acids with weak bases have a pH < 7 at 298 K.

When the cation is a metal ion, the situation is a little more complex as it depends on the metal's charge density. Metal ions that have a high charge density, such as Al^{3+} and Fe^{3+} , carry out hydrolysis, releasing H^+ from water. As a result they form acidic solutions.

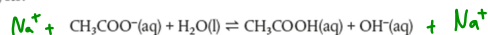
Salt of weak acid and strong base – anion hydrolysis

The anion (A^-) is a conjugate base of the parent acid. When the acid is weak this conjugate base is strong enough to cause hydrolysis:



The release of OH^- causes the pH of the solution to increase.

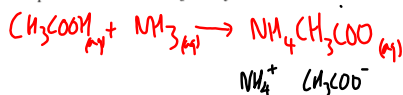
For example, the salt NaCH_3COO , containing the conjugate base CH_3COO^- , causes hydrolysis:



Solutions of salts of weak acids with strong bases have a pH > 7 at 298 K.

Salt of weak acid and weak base

When a weak acid reacts with a weak base, they form a salt in which both the conjugates are relatively strong and carry out hydrolysis. The pH of the solution therefore depends on the relative K_a and K_b values of the acids and bases involved.



Neutralization reaction	Example of parent acid and base	Salt formed	Hydrolysis of ions	Type of salt solution	pH of salt solution
strong acid and strong base	$\text{HCl(aq)} + \text{NaOH(aq)}$	NaCl(aq)	neither ion hydrolyses	neutral	7
weak acid and strong base	$\text{CH}_3\text{COOH(aq)} + \text{NaOH(aq)}$	$\text{NaCH}_3\text{COO(aq)}$	anion hydrolyses	basic	> 7
strong acid and weak base	$\text{HCl(aq)} + \text{NH}_3(\text{aq})$	$\text{NH}_4\text{Cl(aq)}$	cation hydrolyses	acidic	< 7
weak acid and weak base	$\text{CH}_3\text{COOH(aq)} + \text{NH}_3(\text{aq})$	$\text{NH}_4\text{CH}_3\text{COO(aq)}$	anion and cation hydrolyse	depends on relative strengths of conjugates	cannot generalize

Exercises

40 Predict for each salt in aqueous solution whether the pH will be greater than, less than, or equal to 7.

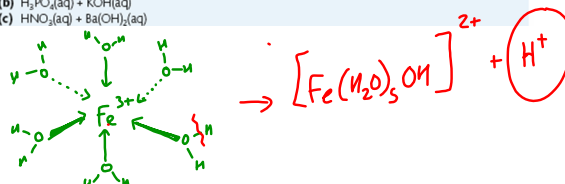
- (a) NaCl Equal
 (b) FeCl_3 Less

41 Which compound will dissolve in water to give a solution with a pH greater than 7?

- A sodium chloride C ammonium nitrate
 B potassium carbonate D lithium sulfate

42 Deduce whether the pH of the resulting salt solution will be greater than, less than, or equal to 7 when the following solutions exactly neutralize each other.

- (a) $\text{H}_2\text{SO}_4(\text{aq}) + \text{NH}_3(\text{aq})$
 (b) $\text{H}_3\text{PO}_4(\text{aq}) + \text{KOH}(\text{aq})$
 (c) $\text{HNO}_3(\text{aq}) + \text{Ba(OH)}_2(\text{aq})$



18.3 pH curves

When carrying out acid-base titrations, we might expect that plotting a graph of pH would give a linear relationship. This, however, is not the case mostly due to the logarithmic nature of the pH scale.

It is found that in most titrations a big jump in pH occurs at equivalence, and this is known as the **point of inflection**. The equivalence point is determined as being half-way up this jump.

The **equivalence point** is when the acid and base perfectly neutralise each other.

In the graphs that you must be able to sketch and explain, we assume the following:

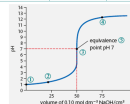
- 0.10 mol dm⁻³ solutions of all acids and bases;
- an initial volume of 50.0 cm³ of acid in the conical flask with base added from the burette;
- acids and bases which all react in a 1:1 ratio, so that equivalence is achieved at equal volumes for these equimolar solutions (i.e. when 50 cm³ of base has been added to the 50 cm³ of acid).

1 Strong acid and strong base

For example: $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

• pH at equivalence = 7 as neither ion hydrolyses appreciably.

0.00 cm ³ Blank contains acid only	25.00 cm ³ Blank contains excess acid	50.00 cm ³ Blank contains excess acid at equivalence	50.00 cm ³ Excess of base at equivalence	75.00 cm ³ Blank contains excess base
NaOH added = 0.10 mol dm ⁻³ × 0.050 l = 0.0050 mol	NaOH added = 0.10 mol dm ⁻³ × 0.050 l = 0.0050 mol	NaOH added = 0.10 mol dm ⁻³ × 0.050 l = 0.0050 mol	NaOH added = 0.10 mol dm ⁻³ × 0.050 l = 0.0050 mol	NaOH added = 0.10 mol dm ⁻³ × 0.050 l = 0.0050 mol
acid remaining = 0.0050 - 0.0050 = 0.0000 mol	acid remaining = 0.0050 - 0.0050 = 0.0000 mol	acid remaining = 0.0050 - 0.0050 = 0.0000 mol	acid remaining = 0.0050 - 0.0050 = 0.0000 mol	acid remaining = 0.0050 - 0.0050 = 0.0000 mol
base remaining = 0.0000 - 0.0000 = 0.0000 mol	base remaining = 0.0000 - 0.0000 = 0.0000 mol	base remaining = 0.0000 - 0.0000 = 0.0000 mol	base remaining = 0.0050 - 0.0000 = 0.0050 mol	base remaining = 0.0050 - 0.0000 = 0.0050 mol
new volume = 0.0500 + 0.0500 = 0.1000 l	new volume = 0.0500 + 0.0500 = 0.1000 l	new volume = 0.0500 + 0.0500 = 0.1000 l	new volume = 0.0500 + 0.0500 = 0.1000 l	new volume = 0.0500 + 0.0500 = 0.1000 l
pH = 1.0	pH = 1.0	pH = 7.0	pH = 7.0	pH = 11.0



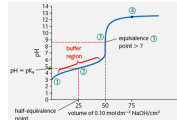
The following points can be deduced from the graph:

- 1 initial pH ≈ 1.0 of strong acid;
- 2 pH changes only gradually until equivalence;
- 3 very sharp jump in pH at equivalence: from pH 3 to pH 11;
- 4 after equivalence the curve flattens out at a high value (pH of strong base);
- 5 pH at equivalence = 7.

2 Weak acid and strong base

For example: $\text{CH}_3\text{COOH(aq)} + \text{NaOH(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-\text{(aq)} + \text{H}_2\text{O(l)}$

• pH at equivalence > 7 as the anion hydrolysis releases OH⁻.



The following points can be deduced from the graph:

- 1 initial pH fairly high (pH of weak acid);
- 2 pH stays relatively constant until equivalence - labelled as buffer region;
- 3 jump in pH at equivalence from about pH 7 to pH 11, which is not as much of a jump as for a strong acid-strong base titration;
- 4 after equivalence the curve flattens out at a high value (pH of strong base);
- 5 pH at equivalence is > 7.

The **half-equivalence point** is when exactly half of the acid has been neutralised. Around this point in the graph we have a buffer solution formed as there are approximately equal amounts of the weak acid and its conjugate base.

Calculating pK_a from the pH at the half-equivalence point

The pH at the half-equivalence point gives us an easy way to calculate pK_a because at this point $[\text{acid}] = [\text{salt}]$, we can substitute these values into the equilibrium expression of the acid:



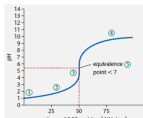
so if we assume that $[\text{acid}] = [\text{HA}]$ and $[\text{salt}] = [\text{A}^-]$, then $[\text{HA}] = [\text{A}^-]$ and so we can cancel these terms in the equilibrium expression:

$$\therefore K_a = [\text{H}^+] \text{ and } pK_a = \text{pH}$$

3 Strong acid and weak base

For example: $\text{HCl(aq)} + \text{NH}_3\text{(aq)} \rightleftharpoons \text{NH}_4\text{Cl(aq)}$

• pH at equivalence < 7 as cation hydrolysis releases H⁺.



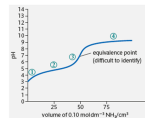
The following points can be deduced from the graph:

- 1 initial pH ≈ 11.0 of strong acid;
- 2 pH stays relatively constant through the buffer region to equivalence;
- 3 jump in pH at equivalence from about pH 11 to pH 3;
- 4 after equivalence the curve flattens out at a fairly low pH (pH of weak base);
- 5 pH at equivalence is < 7.

4 Weak acid and weak base

For example: $\text{CH}_3\text{COOH(aq)} + \text{NH}_3\text{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-\text{(aq)} + \text{NH}_4^+\text{(aq)}$

• pH at equivalence is difficult to define.



- 1 initial pH is fairly high (pH of weak acid);
- 2 addition of base causes the pH to rise slowly;
- 3 change in pH at the equivalence point is much less sharp than in the other titrations;
- 4 after equivalence the curve flattens out at a fairly low pH (pH of weak base).

This titration does not give a clearly defined equivalence point as there is no significant jump in pH to identify, due to several equilibria being involved. For this combination of acid and base, it is better to use other techniques, such as conductometric measurements, to determine the equivalence point.

Exercises

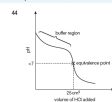
43 Separate 20.0 cm³ solutions of a weak acid and a strong acid of the same concentration are titrated with NaOH solution. Which will be the same for these two titrations?

- 1 initial pH
- 2 pH at equivalence point
- 3 volume of NaOH required to reach the equivalence point

A 1 only B 2 only C 1 and 2 only D 1 and 3

44 Sketch a graph for the pH change as 1.0 mol dm⁻³ NaOH is added to 25.0 cm³ of 0.1 mol dm⁻³ HCl(aq). Mark on your graph the pH at equivalence and the buffer region.

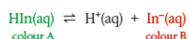
45 Titration experiments can be used to deduce the pK_a of a weak acid. Using the neutralisation reaction between CH_3COOH and NaOH as an example, show how the pK_a for this acid can be deduced from two different points on the titration curve.



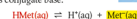
46 Initial pH of acid = pK_a of acid = pK_a of salt. At half equivalence, pH = pK_a , so this can be read directly off the curve.

Indicators signal change in pH

These indicators are themselves weak acids or weak bases in which the undissociated and dissociated forms have different colours. If we consider an indicator HIn that is a weak acid, it exists in equilibrium in solution as follows:



For example, methyl orange is an indicator that is red when placed in a solution of acid such as HCl. As an alkali is added and the pH increases, the indicator changes to yellow. We can show this in an equation using HMet to represent the weak acid and Met⁻ to represent its conjugate base.



By applying Le Chatelier's principle, we can predict how this equilibrium will respond to a change in the pH of the medium.

- Increasing [H⁺]: the equilibrium will shift to the left in favour of HIn.
- Decreasing [H⁺]: the equilibrium will shift to the right in favour of In⁻.

In other words, at low pH colour A will dominate and at higher pH colour B will dominate.



* Indicators change colour when the pH is equal to their pK_a

The change in colour of methyl orange, known as its **change point** or **end-point**, happens in the range pH 3.1–4.4. What determines the pH at which this occurs for an indicator?

We can answer this by considering the equilibrium expression for the above reaction.

The acid dissociation constant is defined as follows:

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

At the point where the equilibrium is balanced between the acid and its conjugate base, that is where [In⁻] = [HIn], the indicator is exactly in the middle of its colour change. As these values cancel in the equation

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

the expression becomes simplified as K_a = [H⁺] or pK_a = pH.

A small amount of added acid or alkali will disrupt this equilibrium and therefore cause a colour change.

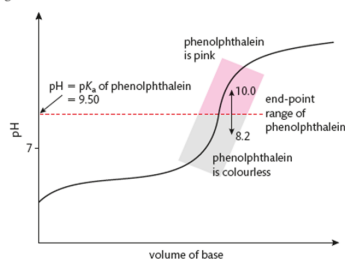
If the pH at which an indicator changes happens to be in the equivalence point of an acid-base titration then we can use it to indicate the end-point.

Choosing a suitable indicator for a titration

If the pH at which an indicator changes happens to be in the equivalence point of an acid-base titration then we can use it to indicate the end-point.

- 1 Determine what combination of weak and strong acid and base are reacting together.
- 2 Deduce the pH of the salt solution at equivalence from the nature of the parent acid and base (page 384).
- 3 Choose an indicator with an end-point in the range of the equivalence point by consulting data tables.

For example, in the titration of a weak acid with a strong base the equivalence point occurs in the range pH 7–11. An appropriate indicator would therefore be one whose end-point lies in this range, such as phenolphthalein (end-point range 8.2–10.0) as shown in Figure 8.15.



Phenolphthalein
range
pH 8-10

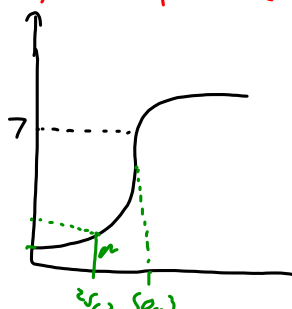
Reactants in titration	pH range at equivalence	Example of suitable indicators	pK _a	End-point range of indicator and colour change
strong acid + strong base	3–11	phenolphthalein methyl orange	9.50 3.46	8.2–10.0; colourless to pink 3.2–4.4; red to yellow
weak acid + strong base	7–11	phenolphthalein phenol red	9.50 8.00	8.2–10.0; colourless to pink 6.6–8.0; yellow to red
strong acid + weak base	3–7	methyl orange bromophenol blue	3.46 4.10	3.2–4.4; red to yellow 3.0–4.6; yellow to blue
weak acid + weak base	this combination of acid and base does not give a significant change in pH at equivalence, so there is no suitable indicator to use here			

22. Acid-base indicators

Indicator	pK _a	pH range	Colour change	
			Acid	Alkali
methyl orange	3.7	3.1–4.4	red	yellow
bromophenol blue	4.2	3.0–4.6	yellow	blue
bromocresol green	4.7	3.8–5.4	yellow	blue
methyl red	5.1	4.4–6.2	red	yellow
bromothymol blue	7.0	6.0–7.6	yellow	blue
phenol red	7.9	6.8–8.4	yellow	red
phenolphthalein	9.6	8.3–10.0	colourless	pink

1. Brønsted-Lowry acid
2. Conjugate base for CH_3COOH ? CH_3COO^-
3. $\text{Mg} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2$
4. $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
5. $\Delta H^\circ_{\text{neutralisation}}$ is always $+/-$?
6. $\text{pH} = -\log_{10} [\text{H}^+]$
7. One pH unit = a $\times 10$ increase/decrease in H^+ concentration?
8. Symbol for dissociation constant of H_2O ? K_w
9. $K_w = [\text{H}^+][\text{OH}^-]$
10. $\text{pH} + \text{pOH} = 14$
11. 2 Strong acids + 2 weak bases. HCl H_2SO_4
12. 2 methods of distinguishing weak/strong acids + bases? NH_3 CH_3NH_2
13. Lewis base? Donate e^- indicator conductivity meter
14. a. $\text{pOH} = -\log_{10} [\text{OH}^-]$ b. $[\text{OH}^-] = ?$ 10^{pOH}
15. Acid $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$ write expression for $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
Base $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$ $K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]}$
16. $K_a \times K_b = ? K_w$
17. Low $\text{pK}_a = \text{stronger}$ or weaker acid
18. Sketch a graph adding a W base to a S acid.
19. " " " a S acid to a S base.
20. How can we work out the pK_a of a weak acid or base from a pH curve?

W base
+ S acid



Practice questions

- The K_b value for a base is $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ at 298 K. What is the K_a value for its conjugate acid at this temperature?
 A 5.0×10^{-2} B 2.0×10^{-6} C 2.0×10^{-12} D 2.0×10^{-13}
- Which combination will form a buffer solution?
 A 100 cm³ of 0.10 mol dm⁻³ hydrochloric acid with 50 cm³ of 0.10 mol dm⁻³ sodium hydroxide
 B 100 cm³ of 0.10 mol dm⁻³ ethanoic acid with 50 cm³ of 0.10 mol dm⁻³ sodium hydroxide
 C 50 cm³ of 0.10 mol dm⁻³ hydrochloric acid with 100 cm³ of 0.10 mol dm⁻³ sodium hydroxide
 D 50 cm³ of 0.10 mol dm⁻³ ethanoic acid with 100 cm³ of 0.10 mol dm⁻³ sodium hydroxide
- Equal volumes and concentrations of hydrochloric acid and ethanoic acid are titrated with sodium hydroxide solutions of the same concentration. Which statement is correct?
 A The initial pH values of both acids are equal.
 B At the equivalence points, the solutions of both titrations have pH values of 7.
 C The same volume of sodium hydroxide is needed to reach the equivalence point.
 D The pH values of both acids increase equally until the equivalence points are reached.
- Bromophenol blue changes from yellow to blue over the pH range of 3.0 to 4.6. Which statement is correct?
 A Molecules of bromophenol blue, HIn, are blue.
 B At pH < 3.0, a solution of bromophenol blue contains more ions, In⁻, than molecules, HIn.
 C The pK_a of bromophenol blue is between 3.0 and 4.6.
 D Bromophenol blue is a suitable indicator to titrate ethanoic acid with potassium hydroxide solution.
- What is the K_b expression for the reaction of ethylamine with water?
 A $K_b = \frac{[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$
 B $K_b = \frac{[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$
 C $K_b = \frac{[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$
 D $K_b = [\text{CH}_3\text{CH}_2\text{NH}_2][\text{H}_2\text{O}]$

- If 20 cm³ samples of 0.1 mol dm⁻³ solutions of the acids below are taken, which acid would require a different volume of 0.1 mol dm⁻³ sodium hydroxide for complete neutralization?
 A nitric acid B sulfuric acid C ethanoic acid D hydrochloric acid
- Which mixture of acid and alkali would produce a buffer solution?

	Acid	Alkali
A	40 cm ³ 0.1 mol dm ⁻³ HCl	60 cm ³ 0.1 mol dm ⁻³ NaOH
B	60 cm ³ 0.1 mol dm ⁻³ HCl	40 cm ³ 0.1 mol dm ⁻³ NaOH
C	40 cm ³ 0.1 mol dm ⁻³ HCl	60 cm ³ 0.1 mol dm ⁻³ NH ₃
D	60 cm ³ 0.1 mol dm ⁻³ HCl	40 cm ³ 0.1 mol dm ⁻³ NH ₃

- Ammonia acts as a weak base when it reacts with water. What is the K_b expression for this reaction?
 A $\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$ B $\frac{[\text{NH}_3][\text{H}_2\text{O}]}{[\text{NH}_4^+][\text{OH}^-]}$ C $\frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]}$ D $\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$
- The indicator HIn is used in a titration between an acid and base. Which statement about the dissociation of the indicator, HIn, is correct?

$$\text{HIn(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{In}^-(\text{aq})$$

colour A colour B

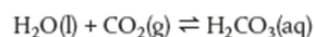
 A In a strongly alkaline solution, colour B would be observed.
 B In a strongly acidic solution, colour B would be observed.
 C [In⁻] is greater than [HIn] at the equivalence point.
 D In a weakly acidic solution colour B would be observed.
- Which salt dissolves in water to form an acidic solution?
 A ammonium nitrate C potassium chloride
 B sodium ethanoate D sodium hydrogencarbonate
- Which of the following mixtures of equimolar solutions produces a buffer with pH < 7 at 298 K?
 A 50 cm³ HCl(aq) and 150 cm³ NH₃(aq)
 B 50 cm³ CH₃COOH(aq) and 50 cm³ HCl(aq)
 C 100 cm³ CH₃COOH(aq) and 50 cm³ NaOH(aq)
 D 50 cm³ CH₃COOH(aq) and 50 cm³ NH₃(aq)

- Ammonia can be converted into nitric acid (HNO₃(aq)) and hydrocyanic acid (HCN(aq)). The pK_a of hydrocyanic acid is 9.21.
 (a) Distinguish between the terms *strong acid* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. (3)
 (b) Deduce the expression for the ionization constant, K_a , of hydrocyanic acid and calculate its value from the pK_a value given. (2)
 (c) Use your answer from part (b) to calculate the [H⁺] and the pH of an aqueous solution of hydrocyanic acid of concentration 0.108 mol dm⁻³. State **one** assumption made in arriving at your answer. (4)
 (Total = 9 marks)

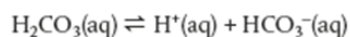
8.5 Acid deposition

Causes of acid deposition

All rain water is naturally acidic owing to the presence of dissolved carbon dioxide, which dissolves in water to form the weak acid carbonic acid, H_2CO_3 .



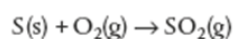
Carbonic acid ionizes to form the following equilibrium:



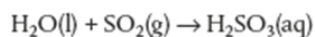
Acid deposition is a broader term than acid rain and includes all processes by which acidic components as precipitates or gases leave the atmosphere. There are two main types of acid deposition:

- wet acid deposition: rain, snow, sleet, hail, fog, mist, dew fall to ground as aqueous precipitates;
- dry acid deposition: acidifying particles, gases fall to ground as dust and smoke, later dissolve in water to form acids.

Sulfur oxides



Sulfur dioxide is a colourless gas with a sharp smell. It dissolves in water to form sulfurous acid, $\text{H}_2\text{SO}_3(\text{aq})$.



Sulfur dioxide can also be oxidized to sulfur trioxide, SO_3 , which then dissolves in water to form sulfuric acid, H_2SO_4 .

