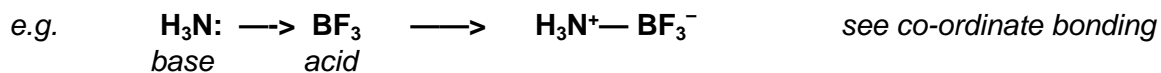


ACIDS & BASES - IONIC EQUILIBRIA

Acid-base theories

LEWIS

acid **electron pair acceptor** H^+ , $AlCl_3$
 base **electron pair donor** NH_3 , H_2O , C_2H_5OH , OH^-



BRØNSTED - LOWRY

acid **proton donor** $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$
 base **proton acceptor** $NH_3(aq) + H^+_{(aq)} \longrightarrow NH_4^+_{(aq)}$

Q.1 Classify the following according to Lewis theory and Brønsted-Lowry theory.



B-L

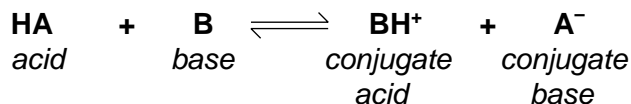
Lewis

Conjugate systems

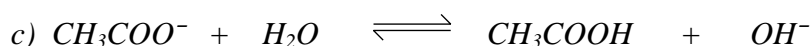
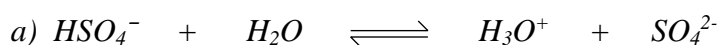
Acids are related to bases $ACID \rightleftharpoons PROTON + CONJUGATE\ BASE$

Bases are related to acids $BASE + PROTON \rightleftharpoons CONJUGATE\ ACID$

For an acid to behave as an acid, it must have a base present to accept a proton...

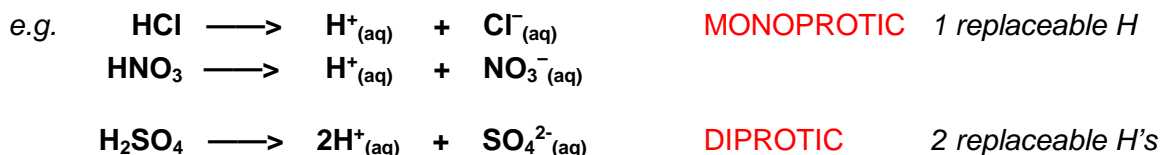


Q.2 Classify all the species in the following equations as acids or bases.



THE STRENGTH OF ACIDS

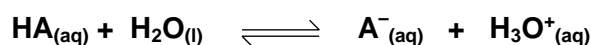
Strong acids completely dissociate (split up) into ions in aqueous solution



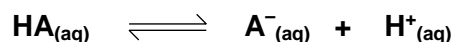
Weak acids partially dissociate into ions in aqueous solution e.g. ethanoic acid



Theory When a weak acid dissolves in water an **equilibrium** is set up



The **water** is essential as it **stabilises the resulting ions**. However to make calculations easier the dissociation is usually written in a shorter way



The weaker the acid

- the less it dissociates
- the more the equilibrium lies to the left.

The relative strengths of acids can be expressed as K_a or pK_a values (see later).

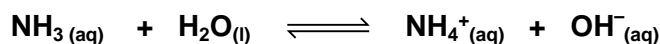
The **dissociation constant** for the weak acid HA is $K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]}$ mol dm⁻³
(see later for a fuller discussion)

THE STRENGTH OF BASES

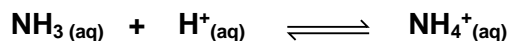
Strong bases completely dissociate into ions in aqueous solution e.g. $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$

Weak bases partially react to give ions in aqueous solution e.g. ammonia (see below)

When a weak base dissolves in water an equilibrium is set up



as in the case of acids it is more simply written



The **weaker the base**

- the **less it dissociates**
- the **more the equilibrium lies to the left**

The relative strengths of bases can be expressed as K_b or pK_b values.

HYDROGEN ION CONCENTRATION

- Introduction*
- hydrogen ion concentration determines the acidity of a solution
 - hydroxide ion concentration determines the alkalinity
 - for strong acids and bases the concentration of ions is very much larger than their weaker counterparts which only partially dissociate.

pH hydrogen ion concentration can be converted to pH **pH = $-\log_{10} [H^+_{(aq)}]$**

to convert pH into hydrogen ion concentration **$[H^+_{(aq)}] = \text{antilog}(-\text{pH})$**

pOH An equivalent calculation for bases converts the hydroxide ion concentration to pOH **pOH = $-\log_{10} [OH^-_{(aq)}]$**

in the above, [] represents the concentration in mol dm⁻³

Ionic Product of Water. . . K_w

Formula Despite being covalent, water conducts electricity to a very small extent.

This is due to the slight ionisation ... $H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

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

Applying the equilibrium law to the second we get $K_c = \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O_{(l)})}$

[] is the equilibrium concentration in mol dm⁻³

As the **dissociation is small**, the water concentration is very large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as constant.

This "constant" is combined with the dissociation constant (K_c) to get a new constant (K_w).

$$K_w = [H^+_{(aq)}][OH^-_{(aq)}] \text{ mol}^2 \text{ dm}^{-6}$$

$$= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad (\text{at } 25^\circ\text{C})$$

Variation The value of K_w **varies with temperature** because it is based on an equilibrium.

Temperature / °C	0	20	25	30	60
$K_w / 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$	0.11	0.68	1.0	1.47	5.6

What does the trend tell you about the sign of ΔH for the dissociation of water?

CALCULATING THE pH AND pOH OF STRONG ACIDS AND BASES

- This is relatively easy because the species have completely dissociated
- Only needs to **know the original concentration** of the acid or base

Example 1 Calculate the pH of 0.1M hydrochloric acid.

HCl (a strong monoprotic acid) is fully dissociated. $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

The $[H^+]$ is therefore the same as the original concentration of HCl i.e. 0.1M.

$$pH = -\log_{10} [H^+] = -\log_{10} (10^{-1}) = 1 \qquad \text{ANS. 1}$$

Example 2 Calculate the pH of 0.001M sodium hydroxide.

Sodium hydroxide (a strong base) is fully dissociated. $Na^+OH^- \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$

The $[OH^-]$ is therefore the same as the original concentration of NaOH i.e. 0.001M.

$$pOH = -\log_{10} [OH^-] = -\log_{10} (10^{-3}) = 3$$

and $pH = 14 - pOH = 14 - 3 = 11 \qquad \text{ANS. 11}$

Q.4 Calculate the pH and pOH of the following solutions.

a) HCl; 0.1M, 0.5M

b) H₂SO₄; 0.1M, 0.5M

c) KOH; 0.1M

d) NaOH; 2M, 0.0005M

e) The solution remaining when 30 cm³ of 0.100M NaOH has been added to 20 cm³ of 0.200M HCl

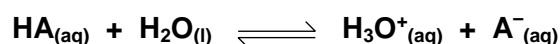
f) The solution remaining when 24.9 cm³ of 0.100M NaOH has been added to 25 cm³ of 0.100M HCl

CALCULATING THE pH AND pOH OF WEAK ACIDS AND BASES

- can't be calculated by just knowing the concentration
- need to know the extent of the ionisation (from K_a) and the original concentration.

The dissociation constant for a weak acid (K_a)

A weak monobasic acid (HA) dissociates in water thus.



Applying the equilibrium law we get

$$K_c = \frac{[\text{H}_3\text{O}^+_{(\text{aq})}] [\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}] [\text{H}_2\text{O}_{(\text{l})}]}$$

[] is the equilibrium concentration in mol dm⁻³

For a weak acid (little dissociation) in dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant so its concentration can be regarded as constant.

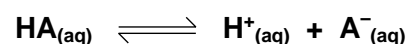
$[\text{H}_2\text{O}_{(\text{l})}]$ is "constant"

Combine this "constant" with the dissociation constant (K_c) to get a new one (K_a).

$$\text{where } K_a = K_c [\text{H}_2\text{O}_{(\text{l})}]$$

$$K_a = \frac{[\text{H}_3\text{O}^+_{(\text{aq})}] [\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]} \text{ mol dm}^{-3}$$

A **simpler way** to write it all out is



The dissociation constant K_a is then

$$K_a = \frac{[\text{H}^+_{(\text{aq})}] [\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]} \text{ mol dm}^{-3}$$

The weaker the acid

- the less it dissociates
- the fewer ions you get
- the smaller K_a

The stronger the acid

- the more the equilibrium lies to the right
- the larger K_a

pKa

- very weak acids have very small K_a values
- it is easier to compare the strength as p K_a values

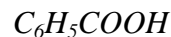
The conversion is carried out thus...
- the units of K_a are mol dm⁻³

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

to convert pH into hydrogen ion concentration

$$K_a = \text{antilog} (-\text{p}K_a)$$

Q.5 Write out expressions for K_a for the following weak acids . . .



Calculating the pH of a weak acid

Theory A weak monobasic acid (HA) dissociates in water $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$
 the dissociation constant (K_a) is $K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} \text{ mol dm}^{-3}$

Assumptions The equation shows that, on dissociation, ions are formed in equimolar amounts. $[H^+_{(aq)}] = [A^-_{(aq)}]$

The **acid is weak**, so **dissociation is small**.

The **equilibrium concentration of HA** can be **approximated to be its original** value.

the equation can be re-written ...

$$[H^+_{(aq)}]^2 = K_a [HA_{(aq)}]$$

and

$$[H^+_{(aq)}] = \sqrt{K_a [HA_{(aq)}]}$$

The pH can then be calculated ...

$$\text{pH} = -\log_{10} [H^+_{(aq)}]$$

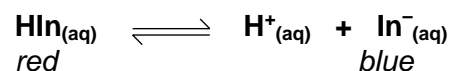
Q.6 Calculate the pH of the following solutions of weak acids . . .

a) 0.1M monobasic (monoprotic) acid ($K_a = 2 \times 10^{-4} \text{ mol dm}^{-3}$)

b) 0.01M monobasic (monoprotic) acid ($K_a = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$)

ACID - BASE INDICATORS

General Many indicators are weak acids and partially dissociate in aqueous solution



The un-ionised form (HIn) is a **different colour** to the anionic form (In⁻).

$$\text{and } K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{In}^-_{(\text{aq})}]}{[\text{HIn}_{(\text{aq})}]}$$

Apply Le Chatelier's Principle to predict any colour change

[] is the equilibrium conc. in mol dm⁻³

Example **In acid** - increases [H⁺] - equilibrium moves to the left to give red undissociated form

In alkali - increases [OH⁻] - although OH⁻ ions don't appear in the equation they remove H⁺ ions to form water.
- equilibrium will move to the right to produce a blue colour

- Choice*
- Must have an easily observed colour change.
 - Must change quickly in the required pH range over the addition of 'half' a drop of reagent

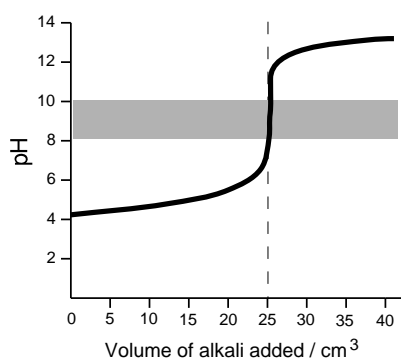
examples

	pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methyl Orange		pink			change						yellow					
Litmus				red				change				blue				
Phenolphthalein				colourless						change			red			

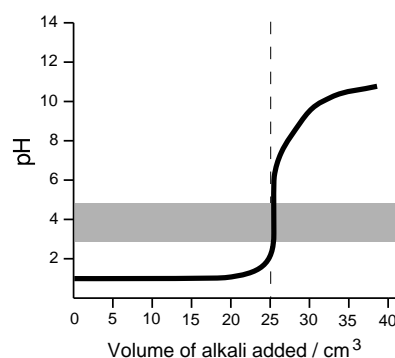
To be useful, an indicator must...

change over the "vertical" section of the curve where there is a **large change in pH** for the **addition of a very small volume**.

The indicator used depends on the pH changes around the end point
- the indicator must change during the 'vertical' portion of the curve -



phenolphthalein



methyl orange

pH Curves

Types

There are **four possible types of acid-base titration**; each has a characteristic curve.

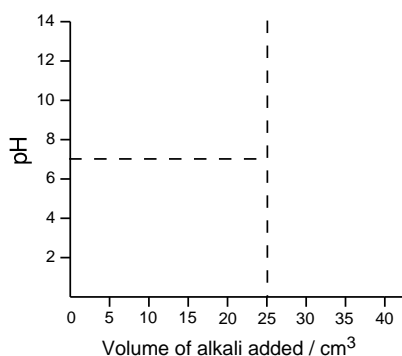
- strong acid (HCl) v strong base (NaOH)
- weak acid (CH₃COOH) v strong alkali (NaOH)
- strong acid (HCl) v weak base (NH₃)
- weak acid (CH₃COOH) v weak base (NH₃)

In the examples below, alkali (0.1M) is added to 25cm³ of acid (0.1M).

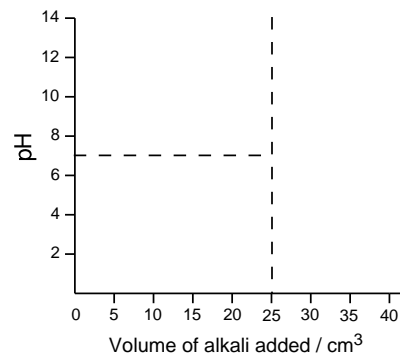
The end points need not be "neutral" due to the phenomenon of salt hydrolysis

Draw the shape of each pH curve on the grids

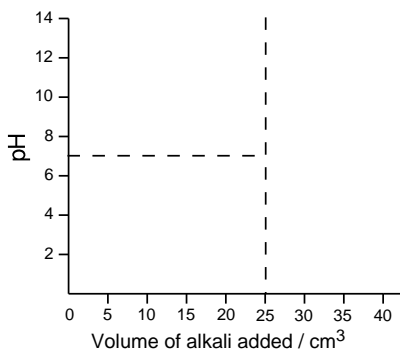
You may want to draw the graphs to a larger scale on a separate sheet



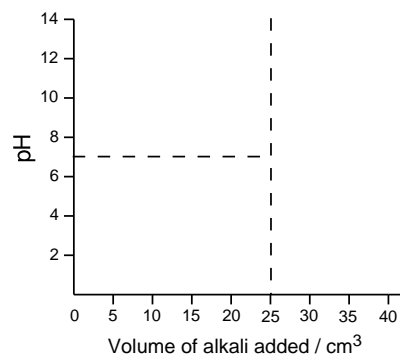
STRONG ACID - STRONG BASE



STRONG ACID - WEAK BASE



WEAK ACID - STRONG BASE



WEAK ACID - WEAK BASE

Q.7 • Why can't indicators be used for a weak acid - weak base titration?

- What alternative methods can be used?

Other curves

Some titrations have more than one 'vertical' portion

- acid v. carbonate
- NaOH v. diprotic acids

Q.8 Sketch and explain the pH curves you get when ...

- 0.1M hydrochloric acid is added to 0.1M sodium carbonate
- 0.1M sodium hydroxide is added to 0.1M ethanedioic acid

CALCULATING THE pH OF ACID/ALKALI MIXTURES

The method depends on whether there are weak or strong acids and alkalis and which is in excess

STRONG ACID STRONG BASE

- 1 Calculate initial moles of H^+ and OH^-
- 2 Calculate which one is in excess
- 3 Calculate its concentration in the combined solution
- 4 Convert concentration to pH

Example Calculate the pH after 20cm^3 of 0.1M HCl is added to 25cm^3 of 0.1M NaOH

1	original moles of H^+	= $0.1 \times 20/1000$	= 2×10^{-3} moles
2	original moles of OH^-	= $0.1 \times 25/1000$	= 2.5×10^{-3} moles
	moles of excess OH^-	= 5×10^{-4}	
3	final volume ($20 + 25$)	= 45cm^3	= 0.045dm^3
4	$[OH^-]$	= $5 \times 10^{-4} / 0.045$	= $0.0111 \text{ mol dm}^{-3}$
	pOH	= 1.95	
	pH	= $14 - 1.95$	= 12.05

WEAK ACID EXCESS STRONG BASE

- 1 Calculate initial moles of acid and alkali
- 2 Calculate the excess moles of OH^-
- 3 Calculate the OH^- concentration in the combined solution
- 4 Convert concentration to pH

Example Calculate the pH after 22cm^3 of $0.1\text{M CH}_3\text{COOH}$ is added to 25cm^3 of 0.1M NaOH

1	original moles of H^+	= $0.1 \times 22/1000$	= 2.2×10^{-3} moles
2	original moles of OH^-	= $0.1 \times 25/1000$	= 2.5×10^{-3} moles
	moles of excess OH^-	= 3×10^{-4}	
3	final volume ($22 + 25$)	= 47cm^3	= 0.047dm^3
4	$[OH^-]$	= $3 \times 10^{-4} / 0.047$	= $6.38 \times 10^{-3} \text{ mol dm}^{-3}$
	pOH	= 2.20	
	pH	= $14 - 2.20$	= 11.80

EXCESS WEAK ACID STRONG BASE

- 1 Calculate initial moles of acid and alkali
- 2 Calculate the excess moles of acid
- 3 Calculate the moles of anion formed (same as the alkali used up)
- 4 Use the value of K_a for the weak acid to calculate the value of $[H^+]$
- 5 Convert concentration to pH

Example Calculate the pH after 20cm^3 of 0.1M KOH is added to 25cm^3 of $0.1\text{M CH}_3\text{COOH}$

1	original moles of CH_3COOH	= $0.1 \times 25/1000$	= 2.5×10^{-3} moles
	original moles of KOH	= $0.1 \times 20/1000$	= 2.0×10^{-3} moles
2	excess moles CH_3COOH	= 5.0×10^{-4}	
3	moles of CH_3COO^- formed	= moles of H^+ used	= 2.0×10^{-3}
4	K_a for CH_3COOH	= $\frac{[H^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$	= 1.7×10^{-5} at 25°C

YOU ONLY NEED TO PUT IN THE MOLAR RATIO
(NOT THE CONCENTRATIONS) BECAUSE THE
VOLUME IS THE SAME FOR BOTH SPECIES

$$[H^+] = \frac{1.7 \times 10^{-5} \times 5 \times 10^{-4}}{2.0 \times 10^{-3}} = 4.25 \times 10^{-6} \text{ mol dm}^{-3}$$

$$5 \quad \text{pH} = -\log [H^+] = \mathbf{5.37}$$

Calculating the pK_a of a weak acid by titration

Method

- titrate a weak acid with sodium hydroxide solution
- record the pH after every addition - 1cm^3 at first; smaller amounts near the end point
- carry on beyond the end point until the pH evens out
- plot a graph of pH (*y axis*) against volume of alkali added (*x axis*)
- calculate the pH and volume added at the end point
- calculate the pH at '**half neutralisation**'

Calculation

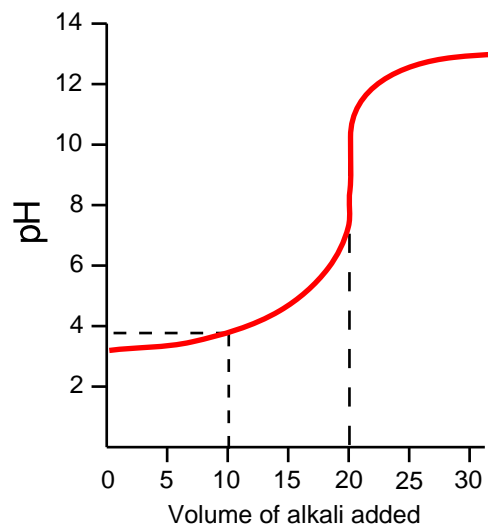
$$K_a = \frac{[\text{H}^+_{(\text{aq})}] [\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]} \quad \text{mol dm}^{-3}$$

At '**half neutralisation**', half the acid has been converted to its anion and their concentrations are equal

$$[\text{HA}_{(\text{aq})}] = [\text{A}^-_{(\text{aq})}]$$

Substituting in the equation gives

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



BUFFER SOLUTIONS - INTRODUCTION AND USES

Definition

"Solutions which **resist** changes in pH when **small quantities** of acid or alkali are added."

Biological

Uses

In biological systems (saliva, stomach, and blood) it is essential that the pH stays 'constant' in order for any processes to work properly. Most enzymes work best at particular pH values.

Blood

If the pH of blood varies by 0.5 it can lead to unconsciousness and coma

Other

Uses

Many household and cosmetic products need to control their pH values.

Shampoo

Buffer solutions counteract the alkalinity of the soap and prevent irritation

Baby lotion

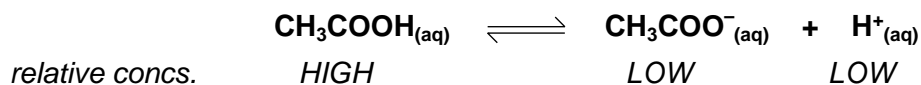
Buffer solutions maintain a pH of about 6 to prevent bacteria multiplying

Others

Washing powder, eye drops, fizzy lemonade

BUFFER SOLUTIONS - ACTION

Acid buffer It is **essential to have a weak acid** for an equilibrium to be present so that ions can be removed and produced. The dissociation is small and there are few ions.



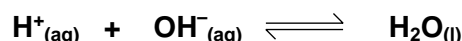
NB A strong acid can't be used as **it is fully dissociated and cannot remove $\text{H}^+_{(\text{aq})}$**



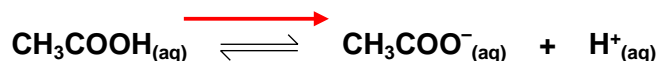
Adding acid Any H^+ is removed by reacting with CH_3COO^- ions to form CH_3COOH via the equilibrium. Unfortunately, the concentration of CH_3COO^- is small and only a few H^+ can be "mopped up". A much larger concentration of CH_3COO^- is required.

To build up the concentration of CH_3COO^- ions, sodium ethanoate is added.

Adding alkali This adds OH^- ions. Although they do not appear in the equation, they react with H^+ ions



Removal of H^+ from the weak acid equilibrium means that, according to Le Chatelier's Principle, more CH_3COOH will dissociate to form ions to replace those being removed.



As the added OH^- ions remove the H^+ from the weak acid system, the equilibrium moves to the right to produce more H^+ ions. Obviously, there must be a large concentration of undissociated acid molecules to be available.

Other The concentration of a buffer solution is also important

If the concentration is too low, there won't be enough CH_3COOH and CH_3COO^- to cope with the ions added.

Summary For an acidic buffer solution one needs ...

large $[\text{CH}_3\text{COOH}_{(\text{aq})}]$ - for dissociating into $\text{H}^+_{(\text{aq})}$ when alkali is added

large $[\text{CH}_3\text{COO}^-_{(\text{aq})}]$ - for removing $\text{H}^+_{(\text{aq})}$ as it is added

This situation can't exist if only acid is present so a mixture of the acid and salt is used.

The weak acid provides the equilibrium and the large $\text{CH}_3\text{COOH}_{(\text{aq})}$ concentration. The sodium salt provides the large $\text{CH}_3\text{COO}^-_{(\text{aq})}$ concentration.

∴ One uses a WEAK ACID + its SODIUM OR POTASSIUM SALT

CALCULATING THE pH OF AN ACIDIC BUFFER SOLUTION

Example 1 Calculate the pH of a buffer solution whose $[HA]$ is 0.1 mol dm^{-3} and $[A^-]$ of 0.1 mol dm^{-3} . Assume the K_a of the weak acid HA is $2 \times 10^{-4} \text{ mol dm}^{-3}$.

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

$$\text{re-arranging} \quad [H^+_{(aq)}] = \frac{[HA_{(aq)}] K_a}{[A^-_{(aq)}]} = \frac{0.1 \times 2 \times 10^{-4}}{0.1} = 2 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log_{10} [H^+_{(aq)}] = 3.699$$

Example 2 Calculate the pH of the solution formed when 500cm^3 of 0.1 mol dm^{-3} of weak acid HX is mixed with 500cm^3 of a 0.2 mol dm^{-3} solution of its salt NaX . $K_a = 4 \times 10^{-5} \text{ mol dm}^{-3}$.

$$K_a = \frac{[H^+_{(aq)}][X^-_{(aq)}]}{[HX_{(aq)}]}$$

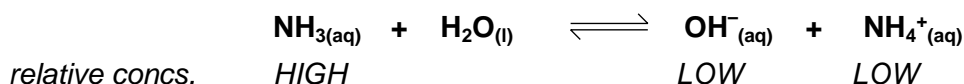
$$\text{re-arranging} \quad [H^+_{(aq)}] = \frac{[HX_{(aq)}] K_a}{[X^-_{(aq)}]}$$

The solutions have been mixed; volume is now 1 dm^3 $[HX] = 0.05 \text{ mol dm}^{-3}$
 $[X^-] = 0.10 \text{ mol dm}^{-3}$

$$\therefore [H^+_{(aq)}] = \frac{0.05 \times 4 \times 10^{-5}}{0.1} = 2 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log_{10} [H^+_{(aq)}] = 4.699$$

Alkaline buffer Very similar but is based on the equilibrium surrounding a weak base e.g. ammonia



but one needs ; a large conc. of $\text{OH}^-_{(aq)}$ to react with any $\text{H}^+_{(aq)}$ added
a large conc of $\text{NH}_4^+_{(aq)}$ to react with any $\text{OH}^-_{(aq)}$ added

There is enough NH_3 to act as a source of OH^- but one needs to increase the concentration of ammonium ions by adding an ammonium salt.

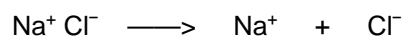
One uses AMMONIA (a weak base) + AMMONIUM CHLORIDE (one of its salts)

SALT HYDROLYSIS

Introduction Many salts dissolve in water to produce solutions which are not neutral. This is because the ions formed react with the hydroxide and hydrogen ions formed when water dissociates. There are four distinct systems. All dissociated ions are aqueous ions. **When mixed, the ions of strong acids and bases remain apart. Ions of weak acids and bases associate.**

Salts of strong acids and strong bases

Sodium chloride completely dissociates



Water partially dissociates

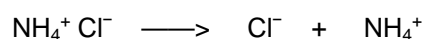


Pairs of ions stay apart as they are from strong acids and bases.

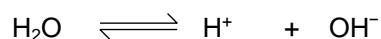


Salts of strong acids and weak bases

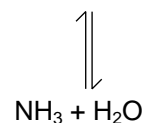
Ammonium chloride completely dissociates



Water partially dissociates

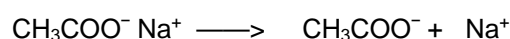


Some ammonium and hydroxide ions associate to form ammonia (a weak base) and water.



Salts of weak acids and strong bases

Sodium ethanoate completely dissociates



Water partially dissociates

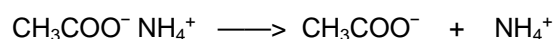


Some ethanoate and hydrogen ions associate to form ethanoic acid (a weak acid).



Salts of weak acids and weak bases

Ammonium ethanoate completely dissociates



Water partially dissociates



Some ethanoate and some hydrogen ions associate to form ethanoic acid and some ammonium ions combine with some hydroxide ions to produce ammonia. The pH depends on the relative values of the two dissociation constants but the solution will be . . .

