

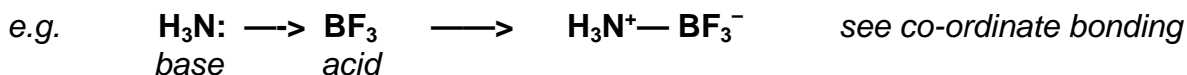
ACIDS & BASES - IONIC EQUILIBRIA

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

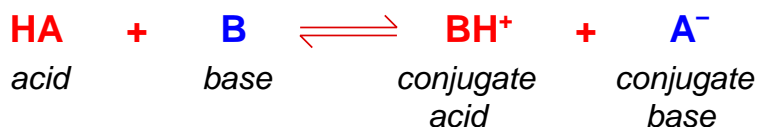
Lewis

Conjugate systems

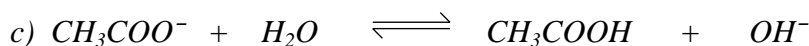
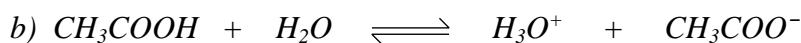
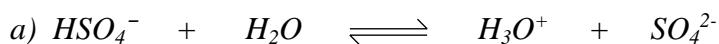
Acids are related to bases $ACID \rightleftharpoons PROTON + CONJUGATE\ BASE$

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...

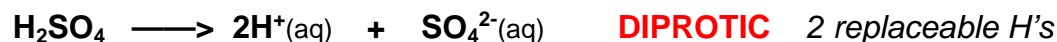
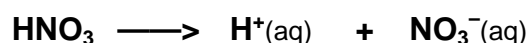
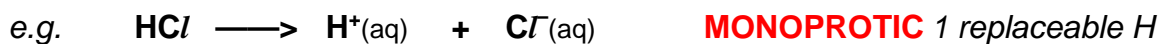


Q.2 *Classify all the species in the following equations as acids or bases.*



THE STRENGTH OF ACIDS

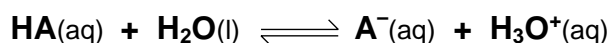
Strong acids **completely dissociate** (split up) into ions in aqueous solution



Weak acids **partially dissociate** into ions in aqueous solution eg 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 $\text{p}K_a$ values (see later).

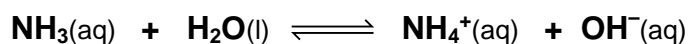
The **dissociation constant** for weak acid HA is $K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$ mol dm⁻³
(see later for a fuller discussion)

THE STRENGTH OF BASES

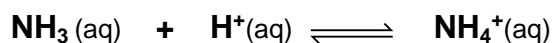
Strong **completely** dissociate into ions in aqueous solution $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$

Weak **partially** react to give ions in aqueous solution

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

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

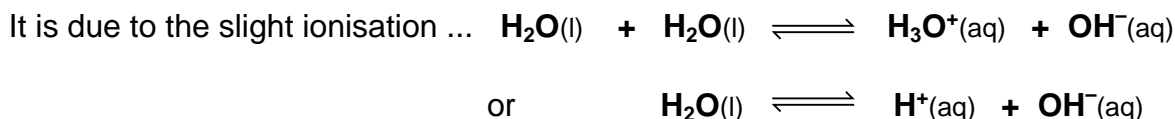
to convert pH into hydrogen ion concentration $[\text{H}^+(\text{aq})] = \text{antilog}(-\text{pH})$

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

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.



Applying the Equilibrium Law
$$K_c = \frac{[\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

[] 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 (K_c) to get a new constant (K_w).

$$\begin{aligned} K_w &= [\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})] \text{ mol}^2 \text{ dm}^{-6} \\ &= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad (\text{at } 25^\circ\text{C}) \end{aligned}$$

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?

The relationship between pH and pOH

Because H^+ and OH^- ions are produced in equal amounts when water dissociates their concentrations will be the same.

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

- take the equation for K_w

$$[H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

- take logs of both sides

$$\log[H^+] + \log[OH^-] = -14$$

- multiply by minus

$$-\log[H^+] - \log[OH^-] = 14$$

- change to pH and pOH

$$\text{pH} + \text{pOH} = 14 \quad (\text{at } 25^\circ\text{C})$$

N.B. As they are based on the position of equilibrium and that varies with temperature, the above values are only true if the temperature is 25°C (298K)

Neutral solutions are best described as those where $[H^+] = [OH^-]$

Therefore a neutral solution is pH 7 only at a temperature of 25°C (298K)

The value of K_w is constant for any aqueous solution at the stated temperature

$[H^+]$	1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12} 10^{-13} 10^{-14}
$[OH^-]$	10^{-14} 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1
pH	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Q.3 Convert the following pH values to $[H^+]$; 13 7.5 3.21 -0.6993

Convert the following $[H^+]$ values to pH; 0.01 2.5×10^{-4} 1.1×10^{-13}

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

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

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

Example 2 Calculate the pH of 0.001M sodium hydroxide.

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

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

$$\begin{aligned} \text{pOH} &= -\log_{10} [\text{OH}^-] = -\log_{10} (10^{-3}) = 3 \\ \text{and } \text{pH} &= 14 - \text{pOH} = 14 - 3 = 11 \quad \text{ANS. 11} \end{aligned}$$

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

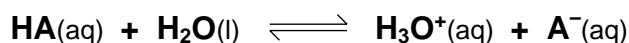
- HCl; 0.1M, 0.5M*
- H₂SO₄; 0.1M, 0.5M*
- KOH; 0.1M*
- NaOH; 2M, 0.0005M*
- The solution remaining when 30 cm³ of 0.100M NaOH has been added to 20 cm³ of 0.200M HCl*
- The solution remaining when 24.9 cm³ of 0.100M NaOH has been added to 25 cm³ of 0.100M HCl*

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

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

[] 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'.

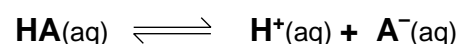
$[\text{H}_2\text{O(l)}]$ is 'constant'

Combine this 'constant' with (K_c) to get a new one (K_a).

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

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

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



The dissociation constant K_a is then

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

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 pKa values

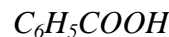
The conversion is carried out thus...

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

To convert pKa into K_a

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

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



Calculating the pH of a weak acid

Theory Weak monobasic acid (HA) dissociates in water $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

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

Assumptions The equation shows that, on dissociation, ions are formed in equimolar amounts.

$$[H^+(aq)] = [A^-(aq)]$$

$$\therefore K_a = \frac{[H^+(aq)] [H^+(aq)]}{[HA(aq)]}$$

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 ...

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

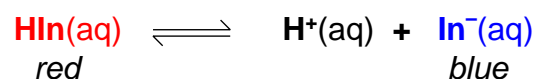
Q.6 Calculate the pH of the following solutions of weak acids . . .

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⁻).

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

Apply Le Chatelier's Principle to predict any colour change

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

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

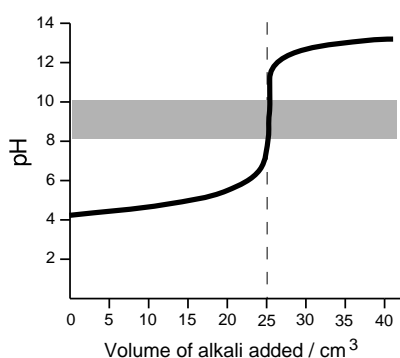
Choice

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

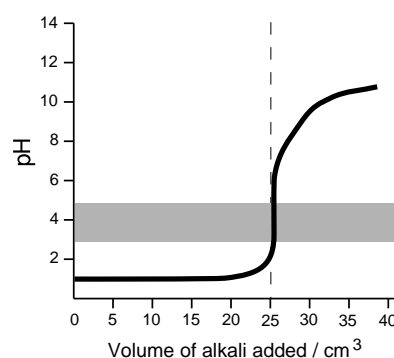
	pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>examples</i>	Methyl Orange		pink			change						yellow				
	Litmus				red			change					blue			
	Phenolphthalein				colourless						change			red		

A suitable 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



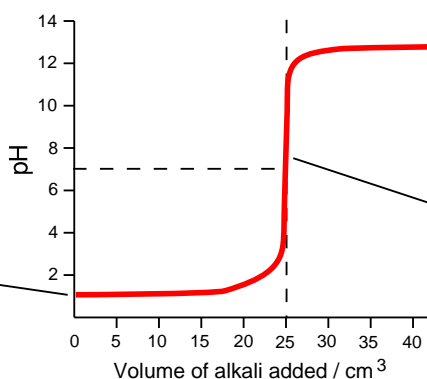
methyl orange

pH Curves

All solutions are 0.1 mol dm^{-3}

1 Strong acid (HCl) v strong base (NaOH)

HCl is a strong acid so is **fully dissociated**. $[\text{H}^+]$ is 0.1 mol dm^{-3} so $\text{pH} = 1$.

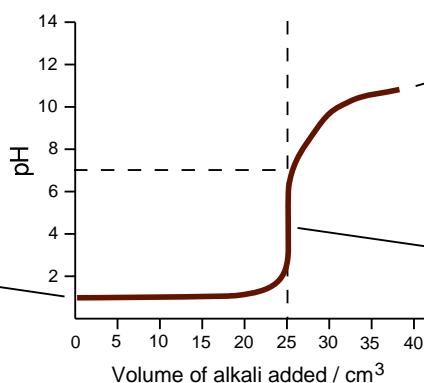


Excess 0.1 mol dm^{-3} NaOH (a strong alkali) is being added so the pH will tend towards 13.

Large pH change (4-10) at the end point.

2 Strong acid (HCl) v weak base (NH_3)

HCl is a strong acid so is **fully dissociated**. $[\text{H}^+]$ is 0.1 mol dm^{-3} so $\text{pH} = 1$.

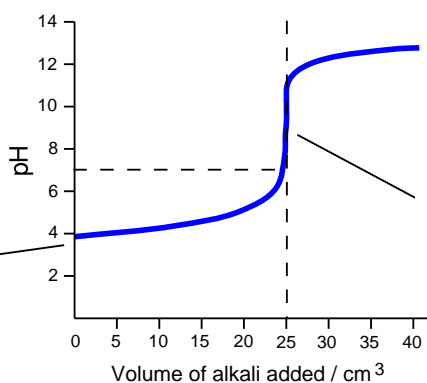


Excess 0.1 mol dm^{-3} NH_3 (a weak alkali) is being added so the pH will rise slowly.

pH change (4-6) at the end point.

3 Weak acid (CH_3COOH) v strong base (NaOH)

CH_3COOH is a weak acid so is **not fully dissociated**. The pH will be around 3-4.

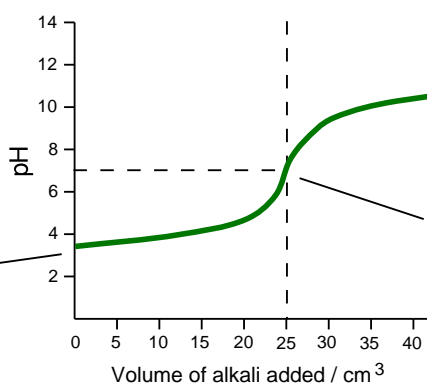


Excess 0.1 mol dm^{-3} NaOH (a strong alkali) is being added so the pH will tend towards 13.

pH change (8-10) at the end point.

4 Weak acid (CH_3COOH) v weak base (NH_3)

CH_3COOH is a weak acid so is **not fully dissociated**. The pH will be around 3-4.



Excess 0.1 mol dm^{-3} NH_3 (a weak alkali) is being added so the pH will rise slowly.

No 'vertical' pH change at the end point.

NO SUITABLE INDICATOR

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

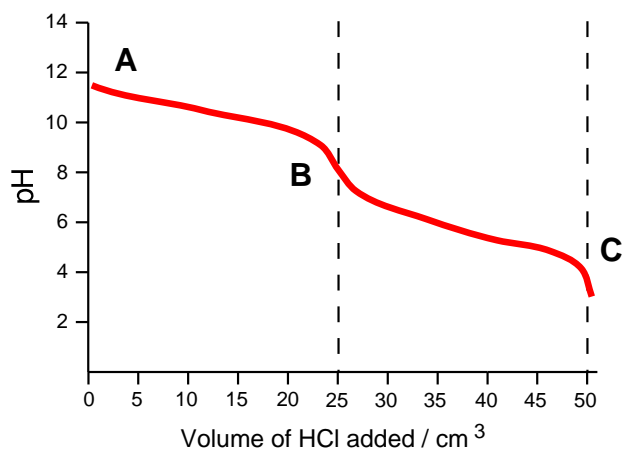
- What alternative methods can be used?

Other pH curves

Some titrations have more than one 'vertical' portion

- acid v. carbonate
- NaOH v. diprotic acids

Q.8 Explain the pH curve obtained when 0.1M HCl is added to 0.1M Na₂CO₃



Sketch the pH curve obtained when 0.1M NaOH is added to 0.1M ethanedioic acid

