7 Equilibria

7.2 Ionic equilibria ☐

7.3 Partition coefficients ☐

IONIC EQUILIBRIA

7 Equilibria

This topic illustrates that many chemical reactions are reversible and involve an equilibrium process. The consideration of the many factors that can affect an equilibrium is an important aspect of physical chemistry.

	Learning outcomes Candidates should be able to:
7.2 Ionic equilibria	a) show understanding of, and use, the Brønsted-Lowry theory of acids and bases, including the use of the acid-I base-I, acid-II base-II concept b) explain qualitatively the differences in behaviour between strong and weak acids and bases and the pH values of their aqueous solutions in terms of the extent of dissociation **c) explain the terms pH, K_a, pK_a and K_w and use them in calculations** **d) calculate [H^+(aq)] and pH values for strong and weak acids and strong bases** **e) explain the choice of suitable indicators for acid-base titrations, given appropriate data** **f) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases** **g) (i) explain how buffer solutions control pH** **(ii) describe and explain the uses of buffer solutions, including the role of HCO_3^- in controlling pH in blood** **h) calculate the pH of buffer solutions, given appropriate data** **i) show understanding of, and use, the concept of solubility product, K_{sp}** **j) calculate K_{sp} from concentrations and vice versa** **k) show understanding of the common ion effect**
7.3 Partition coefficients	**a) state what is meant by partition coefficient; calculate and use a partition coefficient for a system in which the solute is in the same molecular state in the two solvents**

DEFINITIONS

This chapter deals with reversible reactions and their dynamic equilibria in a system.

Reversible reactions can be defined as those that can go in either direction, meaning they can progress forwards or backwards. Reversible reactions are denoted as such:

$$AB(l) \rightleftharpoons A^{+}(aq) + B^{-}(aq)$$

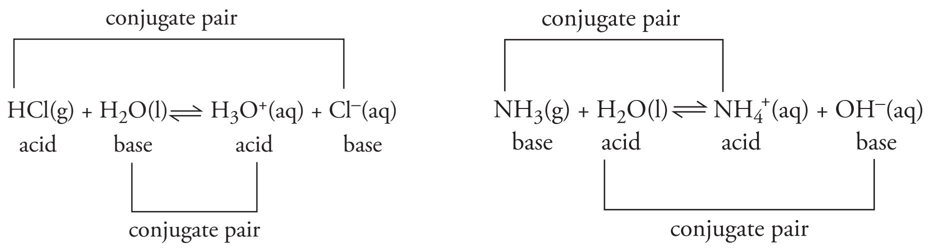
Dynamic equilibrium is a state when the rate of forward reaction equals the rate of backward reaction. Both reactions continue to take place at the same time, and neither the concentration of the products nor the reactants changes, hence the name ‘dynamic.’

ACIDS AND BASES

The Bronsted-Lowry Theory of acids and bases states that:

An acid is a proton (hydrogen ion) donor.

A base is a proton (hydrogen ion) acceptor.



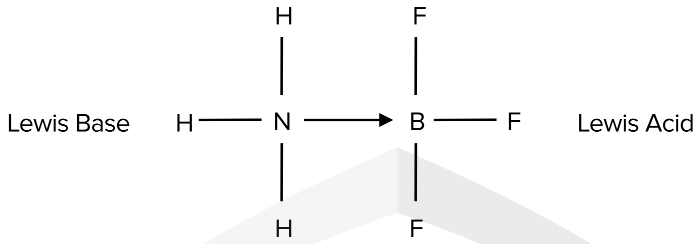
ACIDS AND BASES

The Lewis Theory of acids and bases states that:

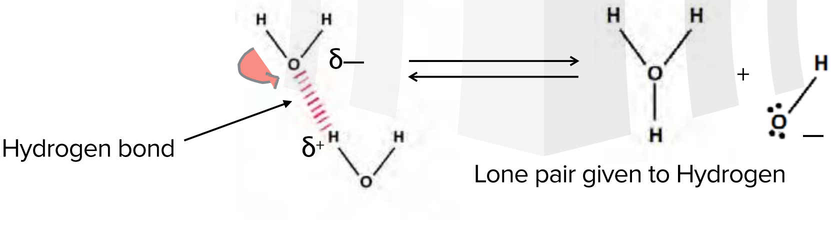
An acid is an electron pair acceptor.

A base is an electron pair donor.

The two theories are entirely consistent.



AUTO-IONISATION OF WATER



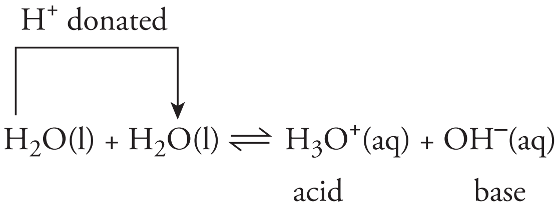
Water molecules can function as both acids and bases.

One water molecule (acting as a base) can accept a hydrogen ion from a second one (acting as an acid).

However, the hydroxonium ion is a very strong acid, and the hydroxide ion is a very strong base. As fast as they are formed, they react to produce water again.

IONIC PRODUCT OF WATER

The net effect is that in pure water, the following equilibrium exists:



$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This is known as self-ionisation or auto ionisation.

Pure water conducts current slightly showing that it contains ions.

IONIC PRODUCT OF WATER

The equation:

$$H_2O \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ (aq) \quad + \quad OH^- (aq)$$

Can be simplified to:

$$H_2O(l) \quad \rightleftharpoons \quad H^+ (aq) \quad + \quad OH^- (aq)$$

Applying the equilibrium law $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$

IONIC PRODUCT OF WATER

The extent of ionisation of water is very low.

The concentration of hydrogen ions and hydroxide ions in pure water (and hence the value of K_c) is extremely small.

Therefore we can regard the concentration of water as being constant.

We can therefore incorporate this into the value of K_c:

$$K_c[H_2O] \text{ is taken as } K_w$$

Thus $K_w = [H^+][OH^–]$ mol²dm⁻⁶

This constant K_w is referred to as ionic product of water.

IONIC PRODUCT OF WATER

At 298 K , $[H^+]$ in water = 1×10^{-7} mol dm^{-3}

In pure water $[H^+] = [OH^-]$

$= [H^+] \times [OH^-]$

$= [H^+] \times [H^+]$

$= (1 \times 10^{-7} \text{ mol dm}^{-3})^2$

$= 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Hence at 298 K **$K_w = 1 \times 10^{-14}$ mol^2 dm^{-6}**

IONIC PRODUCT OF WATER

The dissociation of water is an endothermic process. Hence increase of temperature will increase the extent of ionisation and hence K_w would increase with increase of temperature

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \Delta H = \text{endothermic}$$

K_w increases at high temperature: At 100°C $K_w = 5.13 \times 10^{-13}$ mol^2 dm^{-6}

K_w decreases at low temperature: At 0°C $K_w = 1.1 \times 10^{-15}$ mol^2 dm^{-6}

ACIDITY, ALKALINITY AND pH

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

In aqueous solutions if $[H^+]$ increases then $[OH^-]$ would decrease in order to keep the value of K_w constant

If $[H^+] > [OH^-]$ then the solution is acidic

If $[H^+] < [OH^-]$ then the solution is basic

If $[H^+] = [OH^-]$ then the solution is neutral

ACIDITY, ALKALINITY AND pH

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

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

STRONGLY ACIDIC

WEAKLY ACIDIC

NEUTRAL

WEAKLY ALKALINE

STRONGLY ALKALINE

pH OF WATER

$K_w = [H^+][OH^-] = 1.0\times10^{-14}$

Both ions must be equal in concentration since they were produced in equal molar quantities by the autoionisation reaction.

Let the concentration of each be equal to x.

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

$x^2 = 1.0\times10^{-14}$

$x = 1.0\times10^{-7}$

$pH = -\log_{10}(1.0\times10^{-7}) = 7.00$

ACIDITY AND ALKALINITY

Thus all aqueous solutions will have a definite $[H^+]$ which expresses the acidity or alkalinity of the solution.

In 0.1 mol dm^{-3} solution of HCl, the $[H^+]$ = 0.1 mol dm^{-3}

pH $= -\log_{10}[H^+] = -\log(0.1) = 1$

In 0.02 mol dm^{-3} NaOH solution at 25°C. $[OH^-]$ = 0.02 mol dm^{-3}

Since $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ mol^{2}dm^{-6}

$[H^+] = 5.0 \times 10^{-13}$ mol dm^{-3}

pH $= -\log_{10}[H^+] = -\log_{10}(5.0 \times 10^{-13})$

WORKED EXAMPLES

(a) Calculate the pH of a solution where $[H^+] = 2.34 \times 10^{-3}$ mol dm^{-3}

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

$= -\log_{10} (2.34 \times 10^{-3})$

= 2.63 (solution is acidic)

(b) Calculate the pH of a solution where $[H^+] = 2.34 \times 10^{-10}$ mol dm^{-3}

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

$= -\log_{10} (2.34 \times 10^{-10})$

= 9.63 (solution is alkaline)

SKILL CHECK

Q.Calculate the pH of water at 60°C. K_w at 60°C = 2.6×10^{-14} mol^2 dm^{-6}

SKILL CHECK

Q. (a) Calculate the pH that corresponds to a neutral solution at 0°C. (K_w at 0°C = 1.1×10^{-15} mol^2 dm^{-6})

(b) What does an increase in temperature do to the pH of water?

SKILL CHECK

Q. Calculate the pH of pure water at each of the following temperatures:

(a) at 5°C, K_w is 1.86×10^{-15} mol^2dm^{-6}

(b) at 35 °C, K_w is 2.09×10^{-14} mol^2dm^{-6}

(c) at 100 °C, K_w is 5.13×10^{-13} mol^2dm^{-6}

RELATIONSHIP BETWEEN pH & pOH

$pH = -\log[H^+]$ $pOH = -\log[OH^-]$ $pK_w = -\log K_w$

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

Take logs of both sides $\log[H^+] + \log[OH^-] = \log K_w$

Multiply by the minus sign $-\log[H^+] - \log[OH^-] = -\log K_w$

Change to pH and pOH $pH + pOH = pK_w$

$pH + pOH = 14$ (at 25°C)

STRONG & WEAK ACIDS

Do not confuse the words **strong** and **weak** with the terms **concentrated** and **dilute**.

The **strength** of an acid is related to the proportion of it which has reacted with water to produce ions.

The **concentration** tells you about how much of the original acid is dissolved in the solution.

It is perfectly possible to have a concentrated solution of a weak acid, or a dilute solution of a strong acid.

pH OF STRONG ACIDS

In the general case: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

These reactions are all reversible, but in some cases, the acid is so good at giving away H^+ that we can think of the reaction as being one-way. The acid is virtually 100% ionised.

For example, when HCl dissolves in water, so little of the reverse reaction happens that we can write:

$$HCl \quad + \quad H_2O \qquad\qquad\qquad H_3O^+ \quad + \quad Cl^-$$

At any one time, 100% of the hydrogen chloride will have reacted to produce H_3O^+ ions and chloride ions. Hydrogen chloride is described as a strong acid.

pH OF STRONG ACIDS

Strong acids are those, which are completely ionised in at moderate dilutions. (e.g 0.1M to 0.01M)

For calculations they are assumed to be completely dissociated unless stated otherwise.

$[H^+]$ = molarity of the acid x basicity

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

In normal calculations the $[H^+]$ given by water is neglected.

WORKED EXAMPLES

1. Calculate the pH of a solution of HCl of concentration 0.135 mol dm^{-3}

$[H^+]$ = 0.135 mol dm^{-3}

pH = $-\log [H^+] = -\log(0.135) = 0.87$

2. Calculate the pH of a solution of H_2SO_4 of concentration of 0.20 mol dm^{-3}

$$\underset{0.20}{H_2SO_4} \xrightarrow{\quad} \underset{0.40}{2H^+} + SO_4^{2-}$$

$[H^+]$ = 0.40 mol dm^{-3}

pH = log $[H^+]$

= $-\log(0.40)$

SKILL CHECK

Calculate the pH of the following solutions.

(a) 0.01 mol dm^{-3} hydrochloric acid

(b) 0.025 mol dm^{-3} sulphuric acid

(c) 1.0 mol dm^{-3} hydrochloric acid

(d) 1.0 mol dm^{-3} sulphuric acid

SKILL CHECK

Q. Work out pH values for the following :

(a) a solution containing 0.001 moldm^{-3} H^+ (aq)

(b) a solution containing 1.00 x 10^{-12} moldm^{-3} H^+ (aq)

(c) a solution of 1.00 moldm^{-3} HCl (aq)

(d) a solution of 2.00 x 10^{-4} HNO_3 (aq)

(e) a solution of CH_3COOH of concentration 0.100 moldm^{-3} assuming 5% dissociation of the acid.

pH OF STRONG BASES

A strong base is something like sodium hydroxide or potassium hydroxide which is fully ionic. You can think of the compound as being 100% split up into metal ions and hydroxide ions in solution.

$$NaOH \longrightarrow Na^{+} + OH^{-}$$

Some strong bases like calcium hydroxide aren't very soluble in water. That doesn't matter. What does dissolve is still 100% ionised into calcium ions and hydroxide ions. Calcium hydroxide still counts as a strong base because of that 100% ionisation.

pH OF STRONG BASES

The pH can be worked out in either of the two ways:

1. Calculate $[OH^{-}]$, then $[H^{+}]$ using the expression:

$[H^{+}] \times [OH^{-}] = 1\times10^{-14}$

Then $pH = -\log[H^{+}]$

2. Calculate $[OH^{-}]$ then pOH (where $pOH = -\log[OH^{-}]$)

Then $pH = 14 - pOH$

The $[OH^{-}]$ from water is neglected unless it is comparable to the $[OH^{-}]$ provided by the base.

SKILL CHECK

Q. Calculate the pH of a 0.123 mol dm^{-3} solution of sodium hydroxide.

Q. Calculate the pH of a 0.136 mol dm^{-3} solution of barium hydroxide,

$Ba(OH)_2$

Q. Calculate the pH of a saturated solution of calcium hydroxide which contains 2.78 gdm^{-3} of the base.

SKILL CHECK

Q. Calculate the pOH of the following solutions:

(a) 0.030 moldm^{-3} KOH

(b) 0.500 moldm^{-3} NaOH

(c) 0.020 moldm^{-3} HCl

WEAK ACIDS

A weak acid is one which doesn't ionise fully when it is dissolved in water.

Ethanoic acid is a typical weak acid.

It reacts with water to produce hydroxonium ions and ethanoate ions, but the back reaction is more successful than the forward one.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

The ions react very easily to reform the acid and the water:

WEAK ACIDS

The ions react very easily to reform the acid and the water:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

At any one time, only about 1% of the ethanoic acid molecules have converted into ions. The rest remain as simple ethanoic acid molecules.

Most organic acids are weak.The position of equilibrium of the reaction between the acid and water varies from one weak acid to another. The further it lies to the left, the weaker the acid is.

WEAK ACIDS

Let HA represent a weak acid :

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

But water being in large amount, its concentration may be taken as a constant. $K_c \times [H_2O]$ will be another constant and is represented as K_a as

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

ACID DISSOCIATION CONSTANT

The equation is often simplified as: $HA \rightleftharpoons H^+ + A^-$, so: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$

The weak acid, HA, $[HA] = 0.1 mol/dm^3$, and it ionises about 1%.

	HA	$\rightleftharpoons$	H^+	+	A^-
[Initial]:	**0.1**		**0.0**		**0.0**
[Reacted]:	0.001		0.001		0.001
[Equilibrium]:	0.099		0.001		0.001

Now, $[HA]_{Equilibrium} = 0.099 mol/dm^3 \backsimeq 0.1 mol/dm^3$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.001)(0.001)}{(0.1)} = 1x10^{-5} mol/dm^3$$

SKILL CHECK

Q. Calculate the K_a of 0.20 mol dm^{-3} of ethanoic acid, assuming it ionises about 2%.

	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
[Initial]:					
[Reacted]:					
[Equilibrium]:					

ACID DISSOCIATION CONSTANT

When a weak acid ionises, it produces H^+ and A^- ions in equal quantities.

As weak acids are only very slightly ionised, almost all of the acid molecules remain undissociated, and so it assumed that [HA] = original concentration of unionised weak acid.

This means that the expression for the acid dissociation constant, K_a, simplifies to:

$$K_a = \frac{x^2}{[HA]}$$

The pH of a solution of a weak acid of known concentration can be calculated from the value of K_a.

pKa

The value of K_a indicates the extent of dissociation of the acid:

A high value for K_a (for example, 40 mol dm^{-3}) indicates that the position of equilibrium lies to the right. The acid is almost completely ionised. The greater the concentration of H^+ and OH^-, the greater the value of the numerator.

A low value for K_a (for example, 1.0×10^{-4} mol dm^{-3}) indicates that the position of equilibrium lies to the left. The acid is only slightly ionised and exists mainly as HA molecules and comparatively few H^+ and A^- ions.

pKa

$$pKa = -\log_{10} Ka$$

pK_a bears exactly the same relationship to K_a as pH does to the hydrogen ion concentration. Unlike K_a, pK_a doesn't have any units.

The weaker the acid, the larger the value of pK_a. It is now easy to see the trend towards weaker acids as you go down the table.

pH OF WEAK ACIDS

The pH of a solution of a weak acid of known concentration can be calculated from the value of K_a.

$$HA \rightleftharpoons H^+ + A^-$$

$$[H^+] = [A^-] = x$$

$$K_a = \frac{x^2}{[HA]}$$

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

$$= -\log x$$

pH OF WEAK ACIDS

Calculate the pH of a 0.123 mol dm^{-3} solution of ethanoic acid.
Ka for ethanoic acid = 1.70×10^{-5} mol dm^{-3}.

$$Ka = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = 1.70 \times 10^{-5}$$

$$[H+] = [CH_3COO^-] \quad \& \quad [CH_3COOH] = 0.123 \text{ mol dm}^{-3}$$

$$Ka = \frac{x^2}{0.123} = 1.70 \times 10^{-5}$$

$$x = \sqrt{(1.70 \times 10^{-5} \times 0.123)} = 0.00145 \text{ mol dm}^{-3}$$

$$pH = -\log (0.00145) = 2.84$$

SKILL CHECK

Q. Calculate the pH of a solution of 0.1 mol dm^{-3} ethanoic acid at 25^{o}C. The acid dissociation constant of ethanoic acid at 25^{o}C is 1.8 x10^{-5} mol dm^{-3}.

SKILL CHECK

Q. A solution of propanoic acid, C_2H_5COOH, of concentration 0.222 mol dm^{-3} has a pH of 2.77. **Calculate the K_a of propanoic acid.**

SKILL CHECK

Q. The p.H of 0.1 mol dm^{-3} methanoic acid is 2.4 at 25°C. What is the dissociation constant of methanoic acid at this temperature?

SKILL CHECK

Q. Calculate the pH of 0.1 mol dm^{-3} solution of a weak monobasic acid which is 1% dissociated. Also calculate the pK_a of the acid.

SKILL CHECK

Q. For each of the following reactions:

(i) Identify the two acids and the two bases

(ii) Suggest with reasons, which ion or molecule is the stronger acid, and which the stronger base.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $\quad K_c = 1.8 \times 10^{-5}$ mol^{-3}

$C_6H_5O^- + CH_3CO_2H \rightleftharpoons C_6H_5OH + CH_3CO_2^-$ $\quad K_c = 1.3 \times 10^4$ mol dm^{-3}

SKILL CHECK

Q. The pH of a 0.1 mol dm^{-3} solution of CH_3CO_2H is 2.4, and the pH of 0.1 mol dm^{-3} HCl is 1.0.

(i) Calculate the ratio of hydrogen ions concentrations in these two solutions.

(ii) However, when 100 cm^3 of 0.1 mol dm^{-3} CH_3CO_2H is reacted with an excess of zinc powder, the same volume of hydrogen (120 cm^3) is evolved as when 100 cm^3 of 0.1 mol dm^{-3} HCl is used. Explain why this is so.

SKILL CHECK

Q. The pH of 0.100 in mol dm^{-3} sulphuric acid is 0.98.

(a) Calculate the concentration of hydrogen ions, H^+, in this solution.

(b) Write equations to show the two successive ionisations of sulphuric acid, H_2SO_4, in water.

(c) Suggest why the concentration of hydrogen ions is not 0.20 in mol dm^{-3} in 0.100 in mol dm^{-3} sulphuric acid.

EFFECT OF COMMON IONS

Consider a solution of a weak acid HA to which a salt containing the common ion A^-, for example KA, is added. In aqueous solutions weak acids are only slightly ionised:

$$HA \rightleftharpoons H^+ + A^-$$

But the salt will completely ionise:

$$KA \rightarrow K^+ + A^-$$

When the salt containing the common ion is added, the equilibrium will shift still more to the left and the $[H^+]$ will be further reduced.

$$\overset{\longleftarrow}{HA \rightleftharpoons H^+ + A^-} \quad \textbf{(shifts left)}$$

EFFECT OF COMMON IONS

The concentration of $[H^+]$ in the presence of the common ion will be very small and correspondingly the concentration of A^- provided by the weak acid would also be equally small.

$$HA \rightleftharpoons H^+ + A^-$$

Hence the $[A^-]$ provided by the acid will be negligible in comparison to the $[A^-]$ provided by the salt and the $[A^-]$ in the system may be regarded as only derived from the salt.

$$KA \rightarrow K^+ + A^-$$

$$[A^-]_{total} = [A^-]_{acid} + [A^-]_{salt}$$

but $[A^-]$acid is very low, $\therefore [A^-]_{total} \approx [A^-]_{salt}$

EFFECT OF COMMON IONS

Since the dissociation of the weak acid is very little and has been further suppressed by the presence of the common ion the concentration of the acid at equilibrium may be considered to be equal to the initial concentration of the acid.

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \textit{but} \quad [A^-]_{total} \approx [A^-]_{salt}$$

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

or $$K_a = \frac{[H^+][salt]}{[acid]}$$

Conjugate base

Unionised acid

EXAMPLE

Take 0.1 mol of CH_3COOH in 1dm^3 & then add 0.1 mol of $CH_3COO^-Na^+$

($K_a = 1.8\text{x}10^{-5}$)

Before adding $CH_3COO^-Na^+$:

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & H^+ & + & CH_3COO^- \\ 0.1 & & x & & x \end{array}$$

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.1} = 1.8\text{x}10^{-5}$$

$x = 1.3\text{x}10^{-3}$ mol dm^{-3}

pH = —log x =2.87

EXAMPLE

After adding $CH_3COO^-Na^+$:

$$\begin{array}{ccccc} CH_3COO^-Na^+ & \longrightarrow & CH_3COO^- & + & Na^+ \\ 0.1\text{mol} & & 0.1\text{mol} & & 0.1\text{mol} \end{array}$$

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & H^+ & + & CH_3COO^- \\ 0.1 & & a & & a \end{array}$$

a = small value

$$[CH_3COOH]_{\text{equilibrium}} = 0.1 - a \approx 0.1$$

$$[H^+]_{\text{equilibrium}} = a$$

$$[CH_3COO^-]_{\text{equilibrium}} = 0.1 + a \approx 0.1$$

EXAMPLE CONTINUED

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{a(0.1)}{0.1} = 1.8\text{x}10^{-5}$$

$$a = 1.8\text{x}10^{-5}$$

$$pH = -\log(1.8\text{x}10^{-5})$$
$$= 4.74$$

Note: There has been a change in pH, as the concentration of H^+ decreases, the solution becomes less acidic.

SKILL CHECK

Wherever needed assume the K_a to be 1.8 $\text{x}10^{-5}$ mol dm^{-3}

Q. Evaluate the pH of a 0.10 mol dm^{-3} solution of ethanoic acid, which has been made 0.15 mol dm^{-3} with respect to sodium ethanoate.

SKILL CHECK

Q. Calculate the pH of a solution obtained by dissolving 4.1 g of sodium ethanoate in 500 cm^3 of 0.10 mol dm^{-3} ethanoic acid.

SKILL CHECK

Q. Calculate the pH of a solution obtained by mixing 50 cm^3 of 1.0 mol dm^{-3} ethanoic acid with 25 cm^3 of 1.0 mol dm^{-3} sodium hydroxide solution.

SKILL CHECK

Q. Calculate the pH of a solution made by adding 55 cm^3 of a 0.15 mol dm^{-3} solution of ethanoic acid to 40 cm^3 of 0.20 mol dm^{-3} solution of sodium ethanoate.

55

SKILL CHECK

Q. Calculate the mass of sodium ethanoate that is needed to be added to 100cm^3 of a 0.50 mol dm^{-3} solution of ethanoic acid to make a buffer solution of pH 4.75.

56

SKILL CHECK

Q. Calculate the pH of a solution made by mixing 100 cm^3 of 0.10 $moldm^{-3}$ ethanoic acid, Ka = 1.76×10^{-5} $moldm^{-3}$, with 100 cm^3 of 0.20 $moldm^{-3}$ sodium ethanoate.

ADDING ACID TO WATER

Water does not ionise much. Therefore its concentration of [H^+] and [OH^-] is very low.

in H_2O: $H_2O(l) \rightleftharpoons H^+(aq)\uparrow + OH^-(aq)$

⇠

On addition of a small amount of H^+ ions, the equilibrium will shift backwards but not completely since the amount of OH^- ions aren't enough to completely convert the H^+ to water.

add H^+ ions: pH = ↓

ADDING ACID TO ETHANOIC ACID

Ethanoic acid does not ionise much. Therefore its concentration of [H^+] and [CH_3COO^-] is very low and the concentration of [CH_3COOH].

$$\text{in } CH_3CO_2H: \quad \underleftarrow{CH_3COOH \rightleftharpoons CH_3COO^-} + H^+ \uparrow$$

On addition of a small amount of H^+ ions, the equilibrium will shift backwards but not completely since the amount of CH_3COO^- ions aren't enough to completely convert the H^+ to CH_3COOH.

add H^+ ions: pH = ↓

BUFFER SOLUTIONS

Buffer solution is one whose pH value changes negligibly when small quantities of acids or alkalis are added to it.

Common ion solutions are buffer solutions.

There are three types of buffer solutions:

A solution of a weak acid and its conjugate base, e.g. ethanoic acid and sodium ethanoate

A solution of a weak base and its conjugate acid, e.g aqueous ammonia and ammonium chloride

An aqueous solution of a salt of a weak acid and a weak base, e.g ammonium ethanoate

ACID BUFFER SOLUTIONS

A weak acid and a salt of that weak acid. e.g a solution of ethanoic acid containing its salt sodium ethanoate (conjugate base).

The salt would be fully dissociated while the acid only slightly dissociated due to the common ion suppressing the ionization of the acid.

$$CH_3COONa \rightarrow \underset{\text{high}}{CH_3COO^-} + Na^+$$

$$\underset{\text{high}}{CH_3COOH} \rightleftharpoons \underset{\text{low}}{CH_3COO^-} + \underset{\text{low}}{H^+}$$

Thus the mixture will contain relatively **high concentration of unionized ethanoic acid** and a relatively **high concentration of ethanoate ion**, its conjugate base.

ACID BUFFER SOLUTIONS

When a small quantity of an acid is added, the H^+ ions introduced will combine with the base, ethanoate ions to form more of the unionised ethanoic acid.

$$\underset{\text{low}}{H^+} + \underset{\text{high}}{CH_3COO^-} \rightarrow \underset{\text{high}}{CH_3COOH}$$

- Because the amount of CH_3COO^- ions was large and only small amount of H^+ ions were added, $[CH_3COO^-]$ remains approximately constant.
- Because the original amount of $[CH_3COOH]$ was large and only small amount was produced by the reaction above, $[CH_3COOH]$ remains approximately constant.
- As both are approximately unchanged, $[H^+]$ and hence the pH are also approximately unchanged.

ACID BUFFER SOLUTIONS

When a small quantity of a base is added, the OH^- introduced will combine with the H^+ ions to form water. (H^+ ions are reduced):

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The removal of the H^+ ions will shift the equilibrium of the acid forwards.

$$\underset{\text{high}}{CH_3COOH} \rightleftharpoons \underset{\text{high}}{CH_3COO^-} + H^+$$

Overall equation: $OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$

The acid will further ionise and the concentration of the H^+ ions will be almost restored to the initial value because of the relatively high concentration of the unionised acid molecules in the system. Thus the pH will remain almost the same.

ACID BUFFER SOLUTIONS EQUATIONS

CH_3COOH (acid) & CH_3COO^- (conjugate base):

on adding H^+ ions: $H^+ + \underset{\text{base}}{CH_3COO^-} \rightarrow \underset{\text{acid}}{CH_3COOH}$

on adding OH^- ions: $OH^- + \underset{\text{acid}}{CH_3COOH} \rightarrow \underset{\text{base}}{CH_3COO^-} + H_2O$

$H_2PO_4^-$ (acid) & HPO_4^{2-} (conjugate base):

on adding H^+ ions: $H^+ + \underset{\text{base}}{HPO_4^{2-}} \rightarrow \underset{\text{acid}}{H_2PO_4^-}$

on adding OH^- ions: $OH^- + \underset{\text{acid}}{H_2PO_4^-} \rightarrow \underset{\text{base}}{HPO_4^{2-}} + H_2O$

ALKALINE BUFFER: NH_3 & $NH_4^+Cl^-$

A solution of a weak base with one its salts e.g. a solution of aqueous ammonia containing one of its salts e.g. ammonium chloride.

The salt would be fully dissociated while the base only slightly dissociated due to the common ion suppressing the ionization of the base.

$$NH_4Cl \rightarrow \underset{\text{high}}{NH_4^+} + Cl^-$$

$$\underset{\text{high}}{NH_3} + H_2O \rightleftharpoons \underset{\text{low}}{NH_4^+} + \underset{\text{low}}{OH^-}$$

Thus the mixture will contain relatively **high concentration of unionised ammonia** and a relatively **high concentration of ammonium ion**, its conjugate acid.

ALKALINE BUFFER: NH_3 & $NH_4^+Cl^-$

When a small quantity of a base is added, the OH^- ions introduced will combine with the acid, ammonium ions to form water and more of the unionised ammonia molecules.

$$OH^- + NH_4^+ \rightarrow NH_3 + H_2O$$

As the NH_4^+ ions are found in large excess (from the salt), the small amount of OH^- ions added will be removed almost completely.

The pH will be almost constant. (The pH will increase but not significantly).

ALKALINE BUFFER: NH_3 & $NH_4^+Cl^-$

When a small amount of H^+ ions are added, they react with the large reservoir of NH_3 molecules (conjugate base):

$$H^+ + \underset{\text{base}}{NH_3} \rightarrow NH_4^+$$

The relatively large values of $[NH_3]$ and $[NH_4^+]$ do not alter significantly, and almost all the added H^+ ions are converted from NH_3 to NH_4^+ , so overall $[H^+]$ and hence pH do not alter significantly.

ALKALINE BUFFER: NH_3 & $NH_4^+Cl^-$ SUMMARY

A mixture of NH_3 and NH_4Cl contains high amounts (concentrations) of NH_4^+ (acid) and NH_3 (base) and low concentration of OH^-:

$$NH_4Cl \rightarrow \underset{\text{high}}{NH_4^+} + Cl^-$$

$$\underset{\text{high}}{NH_3} + H_2O \rightleftharpoons \underset{\text{low}}{NH_4^+} + \underset{\text{low}}{OH^-}$$

NH_3 (base) and NH_4^+ (conjugate acid):

on adding H^+ ions: $H^+ + \underset{\text{base}}{NH_3} \rightarrow \underset{\text{acid}}{NH_4^+}$

on adding OH^- ions: $OH^- + \underset{\text{acid}}{NH_4^+} \rightarrow \underset{\text{base}}{NH_3} + H_2O$

BUFFER SOLUTIONS

Every buffer solution has a definite pH value and the addition of a small quantity of either an acid or a base will not cause any appreciable change in the pH of the solution.

Dilution has no effect on the pH of the buffer solution.
This is because the pH of the buffer solution depends on the ratio of the concentration of the acid and the salt and not on the actual values.

The ratio is unaffected by dilution.

Every buffer solution has a pH range within which it acts as a buffer.

USES

Buffer solutions play an important part in the field of biochemistry, medicine, agriculture and industry.

In industry it is employed in electroplating and in the manufacture of leather, photographic material and dyes.

It is also used in the lab to check the readings on a pH meter. For accurate work, you would make up a buffer solution with a pH of, say, 4.0, and then adjust your pH meter so that it was reading exactly that value.

CONTROLLING pH IN BLOOD

The pH of blood is kept constant pH between 7.35 and 7.45. There are several things which buffer the pH of the blood, one of which is the following equilibrium involving HCO_3^- ions:

$$H_2CO_3 \longrightarrow CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

If the $[H^+]$ in the blood decreases (if the pH rises), then this equilibrium will move to the right to replace the missing H^+.

If the $[H^+]$ in the blood increases (if the pH falls), then this equilibrium will move to the left to remove the extra H^+.

The carbon dioxide in the blood comes from, for example, the break-down of carbohydrates in the body.

SKILL CHECK

Q.Calculate the pH of these buffer mixtures.

(a) A solution containing equal amounts in moles of $H_2PO_4^-$(aq) and HPO_4^{2-}(aq). pK_a for the dihydrogenphosphate(v) ion is 7.2.

(b) A solution containing 12.2 g benzenecarboxylic acid ($C_6H_5CO_2H$) and 7.2 g of sodium benzenecarboxylate in 250 cm^3 solution. pK_a for benzenecarboxylic acid is 4.2.

SKILL CHECK

Q. Benzoic acid, C_6H_5COOH, is a weak monobasic acid ($K_a = 6.4 \times 10^{-5}$ mole dm^{-3}).

(a) Explain with equations how a mixture of benzoic acid and sodium benzoate can act as a buffer on the addition of small amounts of either HCl(aq) or NaOH(aq).

(b) What is the $[H^+]$ in 0.02M benzoic acid?

SKILL CHECK

(c) What is the pH of 0.02M benzoic acid?

(d) What is the pH of a solution containing 7.2 g of sodium benzoate in 1 dm^3 of 0.02M benzoic acid?

SKILL CHECK

Q. Assuming that the pH of blood is maintained at 7.4 by the acid, $H_2PO_4^-$, and its salt, HPO_4^{2-}, calculate the ratio of concentration of $H_2PO_4^-$ to that of HPO_4^{2-} in blood. [$K_a(H_2PO_4^-) = 6.4 \times 10^{-8}$ mol dm^{-3}]

75

SKILL CHECK

Q. Using the pK_a value of 4.76 for ethanoic acid, calculate the value for K_a for ethanoic acid. What mass of sodium ethanoate needs to be present in 1.00 dm^3 of a solution of 0.500 mol dm^{-3} ethanoic acid to give a buffer solution with a pH of 5.0?

76

SKILL CHECK

Q. Some 0.10 mol dm^{-3} sodium hydroxide is added to 25.0cm^3 of 0.10 mol dm^{-3} hydrochloric acid.

(a) Calculate the initial pH of the acid.

(b) Calculate the pH of the resulting solution after the addition of:

i. 20.0 cm^3 of NaOH

ii. 24.0 cm^3 of NaOH

iii. 26.0 cm^3 of NaOH

ACID BASE INDICATORS

Acid-base indicators are substances, which change colour according to the pH of the solution to which they are added.

They are either complex organic weak acids or bases whose unionised molecule or the ion or both are coloured.

Their dissociation is so weak that they do not affect the pH of the solution to which they are added. Most indicators being weak acids may be represented by HIn.

$$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$$

The unionised form (HIn) is a different colour to the anionic form (In^-).

ACID BASE INDICATORS

When the indicator is added to an acid solution the equilibrium will shift backwards increasing the concentration of HIn, and revealing the

Litmus: $\overleftarrow{HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)}$

red

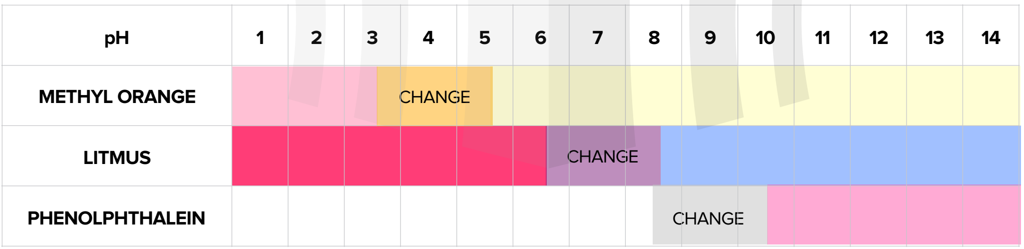
When added to an alkaline solution the equilibrium will shift forwards, increasing the concentration of In⁻ and thus reveal the colour of In⁻.

When the concentration of HIn and In⁻ are equal an intermediate colour will be seen.

Litmus: $\overrightarrow{HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)}$

blue

COLOUR CHANGES OF SOME INDICATORS



pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
METHYL ORANGE	🟥	🟥	🟥	CHANGE		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
LITMUS	🟥	🟥	🟥	🟥	🟥	🟥	CHANGE		🟦	🟦	🟦	🟦	🟦	🟦
PHENOLPHTHALEIN									CHANGE		🟥	🟥	🟥	🟥

Methyl Orange: pink ⟵ 3 – 5 ⟶ yellow

Litmus: red ⟵ 6 – 8 ⟶ blue

Phenolphthalein: colourless ⟵ 8 – 10 ⟶ pink

pH CURVES

The equivalence point in a titration occurs when chemical equivalent amounts of the acid and alkali are added together (The ‘vertical’ line on the pH curve).

The solution obtained however need not be neutral.

The indicator that we use to detect the equivalence point should be the one, which can change colour around the pH of the neutralised solution.

End-point in a titration is when the indicator changes its colour.

ph curves follow the pH changes in the conical flask. Before adding any solution from the burette, the initial pH will be due to the solution in the flask.

pH CURVES

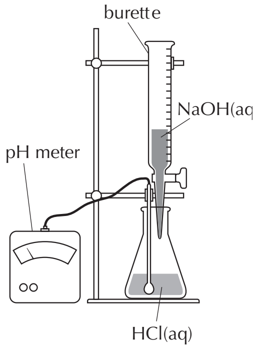
While titrating acids against alkalis a drop of indicator added near the equivalence point must produce a large change in pH (at least by 2) so that the indicator can change its color.

Only then there will be a sharp end point.

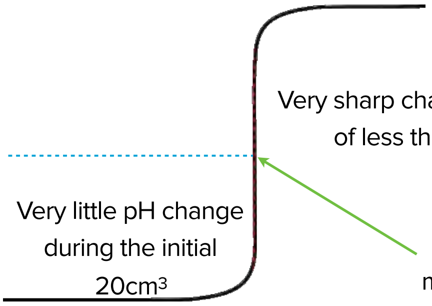
End point: The point during a titration when a colour change shows that enough of the solution in the burette has been added to react exactly with the amount of the chemical n the flask.

End point corresponds with equivalence point.

STRONG ACID (HCl) VS. STRONG BASE (NaOH)



pH 1 at the start due to
0.1M HCl (strong acid)



Curve levels off at pH 13 due to
excess 0.1M NaOH (a strong alkali)

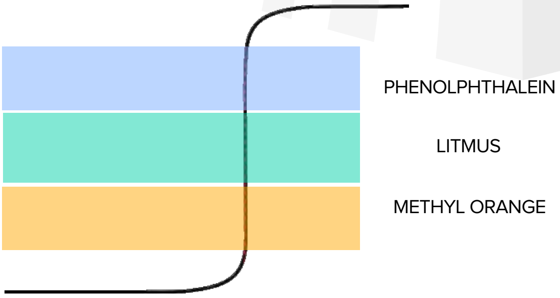
Very sharp change in pH over the addition
of less than half a drop of NaOH

Very little pH change
during the initial
20cm^3

Equivalence point Is
midpoint of vertical line
pH = 7

volume of alkali added / cm^3
(Burette)

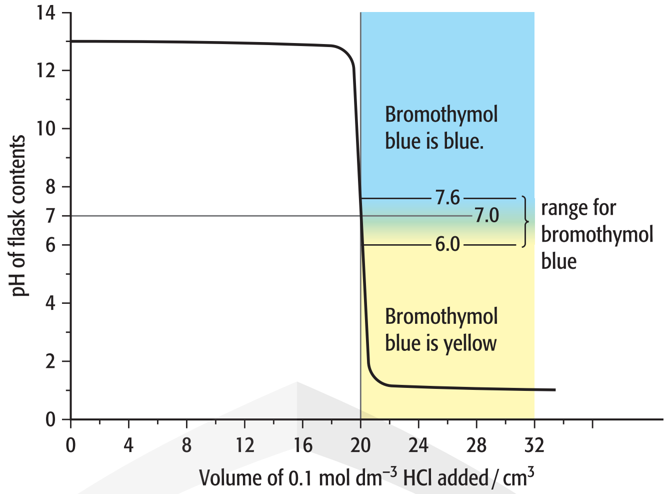
STRONG ACID (HCl) VS. STRONG BASE (NaOH)



Any of the indicators listed
will be suitable — they all
change in the 'vertical'
portion

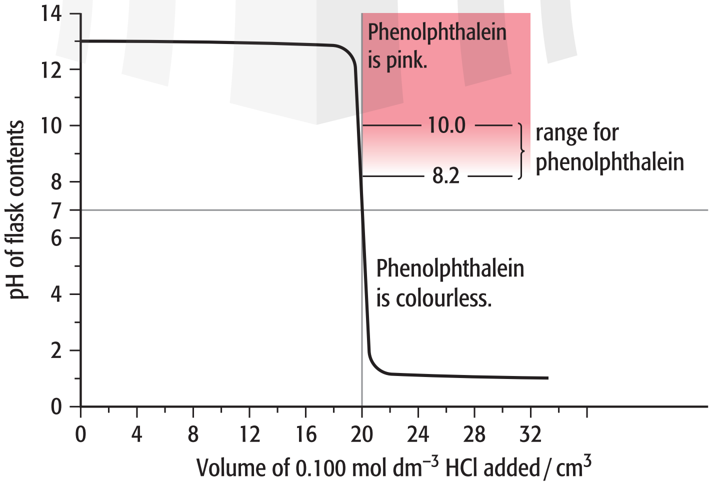
STRONG ACID (HCl) VS. STRONG BASE (NaOH)

20 cm³ of 0.1 mol dm⁻³ NaOH (strong base) vs 0.1 mol dm⁻³ HCl (strong acid)



STRONG ACID (HCl) VS. STRONG BASE (NaOH)

20 cm³ of 0.1 mol dm⁻³ NaOH (strong base) vs 0.1 mol dm⁻³ HCl (strong acid)



STRONG ACID (HCl) VS. WEAK BASE (NH_3)

steady pH

Curve levels off at pH 10 due to excess 0.1M NH_3 (a weak alkali)

Equivalence Point below pH 7 due to NH_4Cl, which is slightly acidic salt.

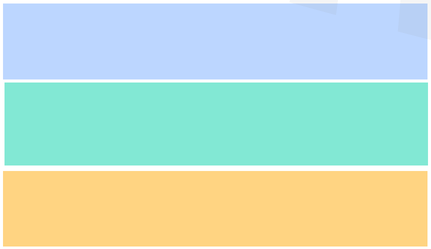
Very sharp change in pH over the addition of less than half a drop of NH_3

Very little pH change

pH 1 at the start due to 0.1M HCl (strong acid)

volume of alkali added / cm^3

STRONG ACID (HCl) VS. WEAK BASE (NH_3)



PHENOLPHTHALEIN

LITMUS

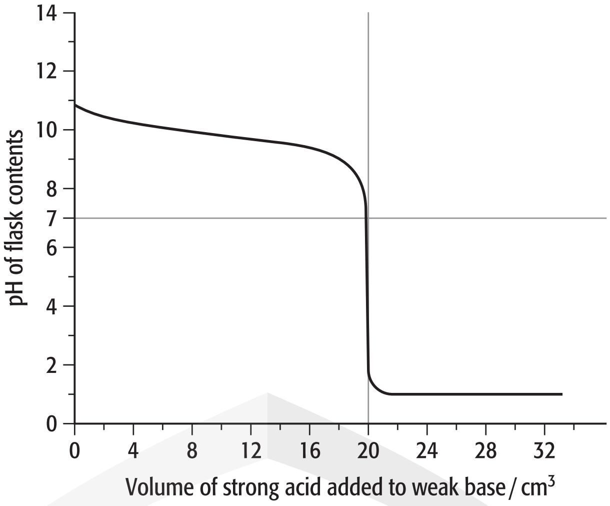
METHYL ORANGE

Only methyl orange is suitable — it is the only one to change in the ‘vertical’ portion

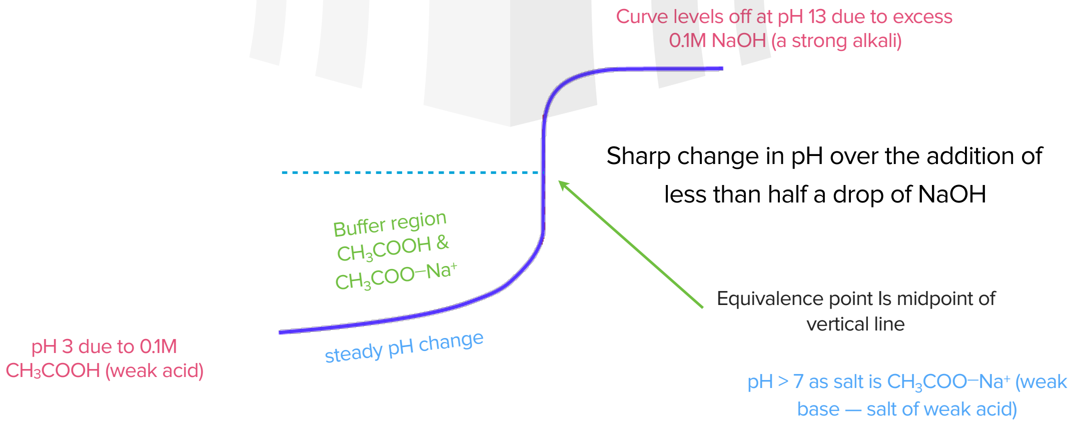
volume of alkali added / cm^3

STRONG ACID (HCl) VS. WEAK BASE (NH_3)

20 cm^3 of 0.1 mol dm^{-3} NH_3 (weak base) vs 0.1 mol dm^{-3} HCl (strong acid)



WEAK ACID (CH_3COOH) VS. STRONG BASE (NaOH)



Curve levels off at pH 13 due to excess 0.1M NaOH (a strong alkali)

Sharp change in pH over the addition of less than half a drop of NaOH

Buffer region CH_3COOH & $CH_3COO^-Na^+$

Equivalence point Is midpoint of vertical line

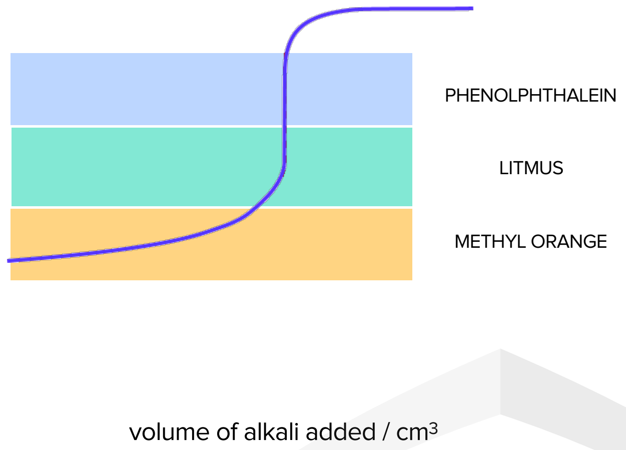
pH 3 due to 0.1M CH_3COOH (weak acid)

steady pH change

pH > 7 as salt is $CH_3COO^-Na^+$ (weak base — salt of weak acid)

volume of alkali added / cm^3

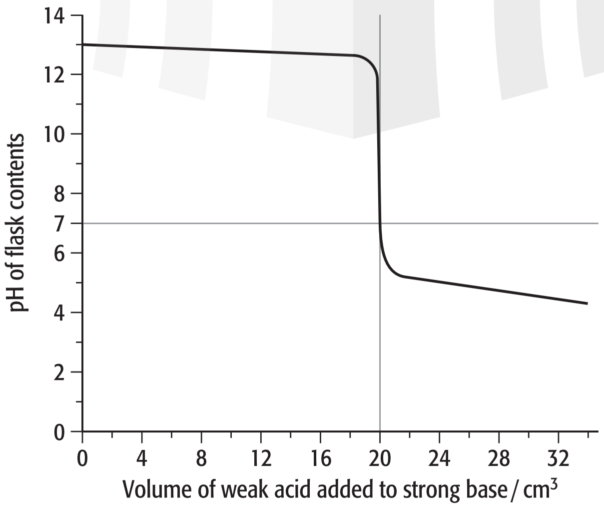
WEAK ACID (CH_3COOH) VS. STRONG BASE (NaOH)



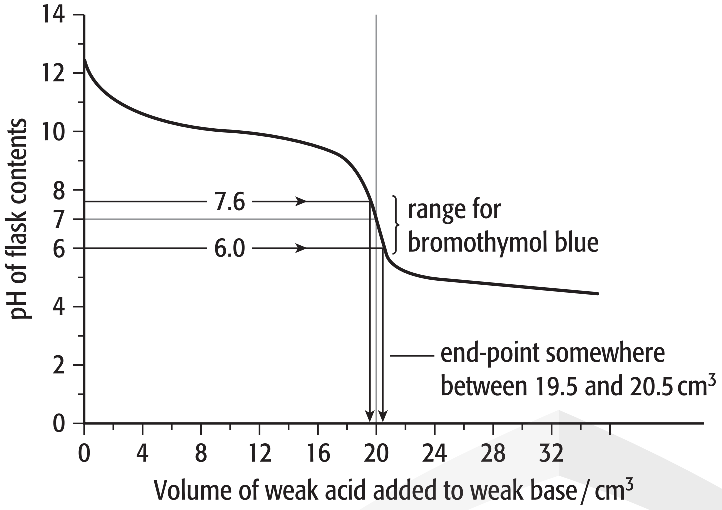
Only phenolphthalein is suitable — it is the only one to change in the ‘vertical’ portion

WEAK ACID VS STRONG BASE

20 cm^3 of 0.1 mol dm^{-3} NaOH (strong base) vs 0.1 mol dm^{-3} CH_3CO_2H (weak acid)



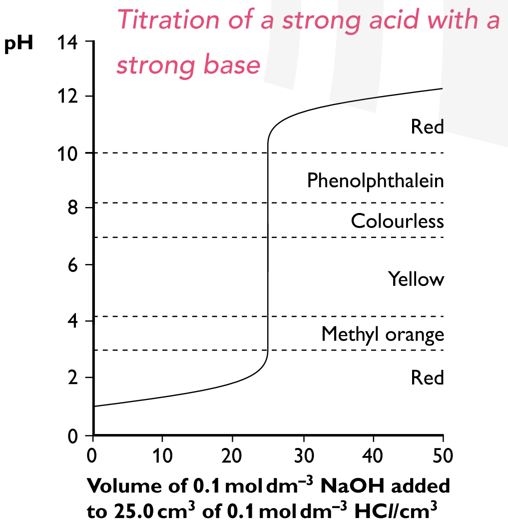
WEAK ACID VS WEAK BASE

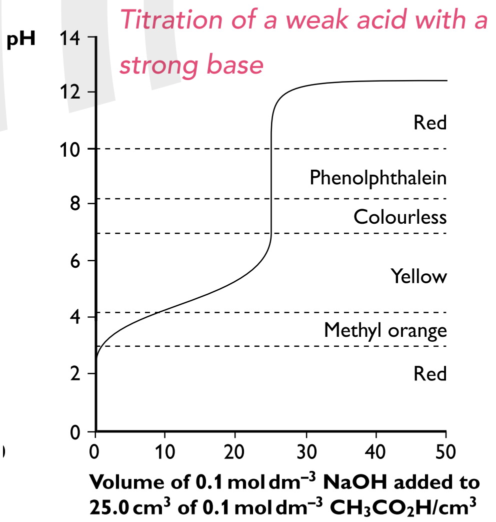


There is no sharp fall in the graph line.

No acid–base indicator is suitable to determine the end-point of this reaction.

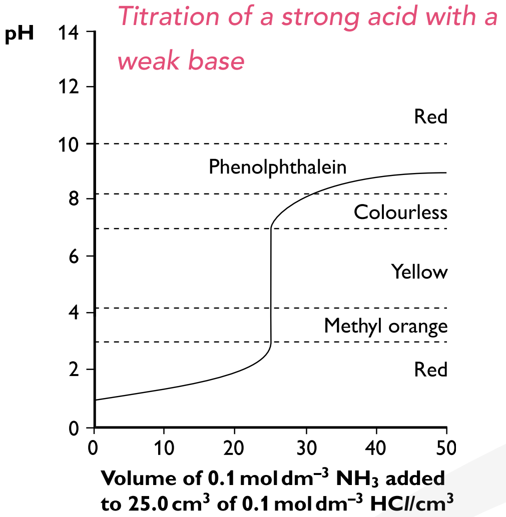
TITRATION CURVES SUMMARY


Titration of a strong acid with a strong base

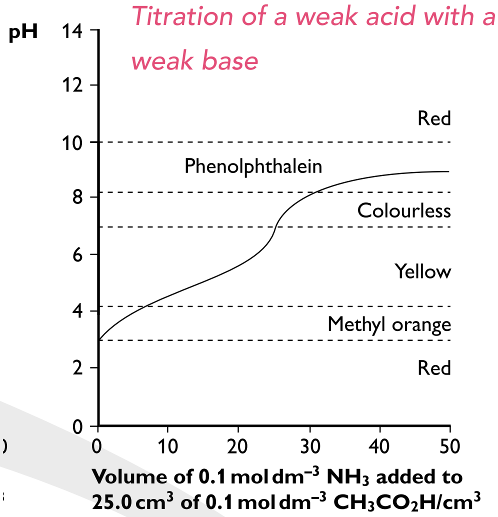

Titration of a weak acid with a strong base

TITRATION CURVES SUMMARY

Titration of a strong acid with a weak base



Titration of a weak acid with a weak base



SKILL CHECK

Q. A 20cm^3 sample of 0.200M NH_3(aq) was titrated with 0.10 M H_2SO_4.

(a) Calculate the mol of NH_3.

(b) Calculate the mol of H_2SO_4.

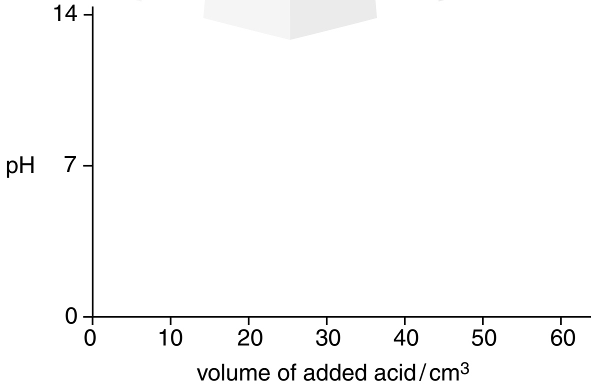
SKILL CHECK

(c) Calculate the volume of H_2SO_4 required for complete neutralization.

(d) Given that the pH of 0.20 M NH_3 is 11.3, deduce the final pH at the equivalence point.

SKILL CHECK

(e) On the following axes, sketch how the pH changes during titration. Mark clearly where the end point occurs.



SKILL CHECK

Q. (a) Propanoic acid is weak acid with a K_a of 1.22 x 10^{-5} $moldm^{-3}$

i. Write an equation for the ionisation of propanoic acid.

(b) Calculate pK_a, for propanoic acid.

SKILL CHECK

Q. Sodium propanoate is made by the reaction of sodium hydroxide with propanoic acid.

(a) Write an equation for the reaction.

(b) If the reaction were carried out by titration using 0.1M solutions of the hydroxide and the acid, state the name of suitable indicator.

SKILL CHECK

Q. A mixture of sodium propanoate and propanoic acid act as a buffer solution.

(a) What is mean by the term buffer solution?

(b) Explain how the mixture of sodium propanoate and propanoic acid act as a buffer solution.

(c) Calculate the pH of the solution formed by adding 15.0cm^3 of 0.1M sodium hydroxide to 30.0cm^3 of 0.1M propanoic acid.

SKILL CHECK

Q. Lactic acid and sodium lactate are both used as food additives.

A solution of 0.100 moldm^{-3} lactic acid is titrated against 25.0 cm^3 0.100 moldm^{-3} sodium hydroxide.

(a) Sketch the labeled pH titration curve

(b) Suggest an indicator that is suitable to be used for this titration

(c) An equimolar mixture of the lactic acid and sodium lactate is present in a food. These compounds are described as acid regulators. Explain how this mixture can act as a buffer solution.

INSOLUBLE SALTS

Salts which are considered to be insoluble in water, e.g. AgCl, $BaSO_4$, $PbCl_2$, are soluble at least to some extent.

If you take solid AgCl and add it to water and let it sit there for a while, a very small amount of solid AgCl will in fact dissolve in water. And it would form a small concentration of Ag^+ and a small concentration of Cl^- ions.

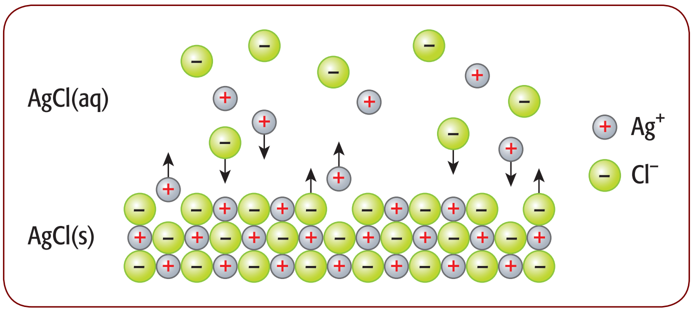
Very quickly an equilibrium is set up between where the solid AgCl is still dissolving and ions, Ag^+ and Cl^-, are re-precipitating at equal rates.

$$\mathbf{AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}}$$

EQUILIBRIUM AND SOLUBILITY

An equilibrium is established when an undissolved ionic compound is in contact with a saturated solution of its ions.

The ions move from the solid to the saturated solution at the same rate as they move from the solution to the solid.



SOLUBILITY PRODUCT

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

And since this is an equilibrium, we can write the equilibrium constant expression for the above reaction.

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since AgCl is a solid, we do not include that in our equilibrium expression.

$$K_c = [Ag^+][Cl^-] = K_{sp}$$

SOLUBILITY PRODUCT

There is an equilibrium between an ionic solid and its saturated solution.

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq) \quad K_{sp} = [M^+][X^-]$$

Even the most insoluble ionic compounds dissolve to a small extent.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Unsaturated solutions can still have more solid dissolved and hence have not reached equilibrium. Hence, there is no K_{sp}. Solubility equilibria only exists when the solution is saturated.

SKILL CHECK

Q.Write the K_{sp} expression, along with its units, for the following equations:

(a) $PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$

(b) $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^{-}(aq)$

(c) $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^{-}(aq)$

SOLUBILITY PRODUCT

Thus solubility product of a sparingly soluble electrolyte is the product of the concentration of the ions in a saturated solution with each concentration term raised to its own stoichiometric coefficient.

Solubility is affected by temperature and hence the value of Ksp depends on temperature.

K_{sp} has always units and it depends on the number of ions involved.

$AgCl_{(s)} \rightleftharpoons Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$ **K_{sp} for AgCl = 1.8×10^{-10} $mol^2\ dm^{-6}$**

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$ **$K_{sp} = [Pb^{2+}][Cl^{-}]^2\ mol^3\ dm^{-9}$**

EXAMPLE

Question: The solubility of ionic compound MY_2 at 25°C is 5×10^{-10} gdm^{-3}. The relative mass of MY_2 is 200. Calculate the solubility product of the salt MY_2 at 25°C.

1. Find the solubility of MY_2 in mol dm^{-3} :

$$\text{solubility in g} = \frac{5 \times 10^{-10}\text{ g dm}^{-3}}{\text{molar mass}} = \frac{2.5 \times 10^{-12}\text{ mol dm}^{-3}}{200}$$

EXAMPLE

2. Find the concentration of ions at equilibrium

$$MY_{2(s)} \rightleftharpoons M^{2+}{}_{(aq)} + 2Y^{-}{}_{(aq)}$$

	MY_2	M^{2+}	Y^-
[Initial]:	a	0	0
[Reacted]:	2.5×10^{-12}	2.5×10^{-12}	5.0×10^{-12}
[Equilibrium]:	$a - 2.5 \times 10^{-12}$	2.5×10^{-12}	5.0×10^{-12}

3. Plug in the values of the concentration of ions @ equilibrium into the Ksp expression

$$K_{sp} = [M^{2+}][Y^-]^2 = (2.5 \times 10^{-12})(5.0 \times 10^{-12})^2 =$$

SKILL CHECK

Q. The solubility of silver chloride is 1.45 mg dm^{-3} at 18°C. Hence calculate the solubility product of silver chloride at 18°C.

SKILL CHECK

Q. At 25°C the solubility of calcium hydroxide is 2.78 g dm^{-3}. Hence calculate the solubility product of calcium hydroxide at this temperature.

EXAMPLE

Solubility products can be used to calculate the solubility of compounds:

Question: At 25°C the solubility product of AgCl is 1.8×10^{-10} mol^2dm^{-6}. Calculate the solubility of AgCl.

Lets say “x” is the amount of AgCl that dissolves per dm^3 of water to make it a saturated solution

	$AgCl(s)$ $\rightleftharpoons$	$Ag^+ (aq)$ +	$Cl^-(aq)$
[Initial]:	a	0	0
[Reacted]:	x	x	x
[Equilibrium]:	a — x	x	x

EXAMPLE

$$K_{sp} = [Ag^+][Cl^-] = x^2$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.34 \times 10^{-5}$$

EXAMPLE

In a saturated solution of $Ca(OH)_2$, the $[Ca^{2+}]$ is 0.0135 $moldm^{-3}$. Calculate the K_{sp}.

$$\overset{0.0135}{Ca(OH)_2} \rightarrow \overset{0.0135}{Ca^{2+}(aq)} + \overset{0.027}{2OH^{-}(aq)}$$

$$Ksp= (0.0135)\,(0.027)^2\ mol^3dm^{-9}$$

SKILL CHECK

Q. At 25°C the K_{sp} of PbS is 4×10^{-28} $mol^2\ dm^{-6}$. **Calculate the solubility of PbS.**

SKILL CHECK

Q. Calculate the solubility of $CaCl_2$ given that its K_{sp} is 3.9×10^{-11} mol^3 dm^{-9}.

SKILL CHECK

Q. Calculate the solubility of Li_3PO_4, given its $K_{sp} = 3.2 \times 10^{-9}$ mol^4dm^{-12}.

EXAMPLE

Q. 10cm^3 of a 0.1 moldm^{-3} solution of HCl was required to completely neutralize 25cm^3 of a saturated solution of Ca(OH)$_2$. Calculate:

a) [OH–] in the saturated solution

$$\text{mol of HCl} = cv = 0.1 \times 10/1000 = 10^{-3}\text{ mol}$$

$$\text{Since } H^+ + OH^- \rightarrow H_2O$$

$$\text{mol of } OH^- = 10^{-3}\text{ mol}$$

$$[OH^-] = c = n/v = 10^3/ 0.025 = 0.04\text{ moldm}^{-3}$$

EXAMPLE

b) K_{sp} of the Ca(OH)$_2$ saturated solution

$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

$$0.02 \qquad 0.04$$

$$K_{sp} = 0.02 \times (0.04)^2$$

$$= 3.2 \times 10^{-5}$$

PREDICTING PRECIPITATION

The solubility product can be used to predict whether precipitation will occur when two solutions are mixed.

Both barium chloride and sodium carbonate are soluble salts, but barium carbonate is relatively insoluble. We must consider the equilibrium for the insoluble salt dissolving in water:

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

PREDICTING PRECIPITATION

The solubility product is given by:

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.5 \times 10^{-10}\ mol^2\ dm^{-6}$$

If $[Ba^{2+}][CO_3^{2-}]$ is greater than $5.5 \times 10^{-10}\ mol^2\ dm^{-6}$ a precipitate will form.

If $[Ba^{2+}][CO_3^{2-}]$ is less than $5.5\times10^{-10}\ mol^2\ dm^{-6}$ no precipitate will form.

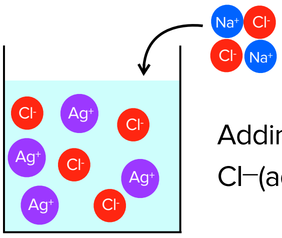
THE COMMON ION EFFECT

Adding a common ion, (one which is already present in the solution), will result in the precipitation of a sparingly soluble ionic compound.

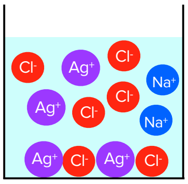
Definition: The common ion effect is the reduction in the solubility of a dissolved salt achieved by adding a solution of a compound which has an ion in common with the dissolved salt. This often results in precipitation.

Adding NaCl to a saturated solution of AgCl will result in the precipitation of AgCl.

THE COMMON ION EFFECT



Adding NaCl to a solution of AgCl increases the concentration of $Cl^-(aq)$. $Cl^-(aq)$ is a common ion as it is already in solution.



The extra Cl^- ions means that the solubility product is exceeded. To reduce the value of $[Ag^+(aq)][Cl^-(aq)]$ below the K_{sp}, some ions are removed from solution by precipitating.

THE COMMON ION EFFECT

The effect of increasing or decreasing the concentration of one of the ions in equilibrium with the sparingly soluble salt may be predicted qualitatively using Le Chatelier's principle.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

The addition of either of $Ag^+(aq)$ or $Cl^-(aq)$ into the above system in equilibrium would displace the equilibrium to the left causing the precipitation of AgCl.

In other words when either $M^+(aq)$ or $X^-(aq)$ is added the ion product will exceed the solubility product and MX will be precipitated until the value of the K_{sp} is restored.

THE COMMON ION EFFECT

Since the K_{sp} $[Ag^+][Cl^-] = 1x10^{-10}$ mol^2dm^{-6}

$$[Ag^+] = [Cl^-] = 1x10^{-5}\ moldm^{-3}$$

When $[Cl^-]$ is raised to 0.01 mol dm^{-3} by adding either NaCl or HCl

the $[Ag^+]$ must decrease to $1x10^{-8}$ mol dm^{-3}

$$\text{as } K_{sp} = [Ag^+][Cl^-]$$

$$= 1x10^{-8} \times 0.01 = 1x10^{-10}$$

In calculations of solubility in solutions containing common ion, the concentration of the ion from the sparingly soluble salt is usually negligible in comparison to the concentration of the common ion.

CALCULATION EXAMPLE

To 1 dm^3 of a saturated solution of $PbCl_2$ (aq) and 0.1 mol of NaCl and find the concentration of Pb^{2+} after precipitation. K_{sp} of $PbCl_2 = 1 \times 10^{-4}$ mol/dm^3.

$$\underset{x}{PbCl_2} \rightleftharpoons \underset{x}{Pb^{2+}} + \underset{2x}{2Cl^-}$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = (x)(0.1)^2 = 1 \times 10^{-4}$$

$$x = 0.01 \text{mol dm}^{-3}$$

CALCULATION EXAMPLE

$[Pb^{2+}]$ is only from $PbCl_2$, ∴ **$[Pb^{2+}] = x$**

$[Cl^-]$ is from $PbCl_2$ AND NaCl,

And since ‘x’ is very small, ∴ **$[Cl^-] = 0.1 + 2x \approx 0.1$**

Note: K_{sp} is the same because it only changes with changes in temperature.

The solubility of $PbCl_2$ in pure water is greater than its solubility in NaCl

SKILL CHECK

Q.Calculate the mass of calcium hydroxide that will dissolve in 100 cm^3 of 0.1 $moldm^{-3}$ sodium hydroxide solution at 25°C. The K_{sp} of calcium hydroxide at 25°C is 2.12 $x10^{-4}$ mol^3 dm^{-9}.

EXAMPLE

Q.K_{sp} of $PbBr_2$ is 6.6 x 10^{-6} mol^3dm^{-9}. Calculate:

a) [Pb^{2+}] in the saturated solution of $PbBr_2$

$$\underset{y}{PbBr_2} \rightleftharpoons \underset{y}{Pb^{2+}} + \underset{2y}{2Br^-}$$

$$y \times (2y)^2 = 6.6\ 10^{-6}$$

$$y = 0.0118 \text{ mol dm}^{-3}$$

EXAMPLE

(b) An excess of $PbBr_2$ is stirred with 0.4 $moldm^{-3}$ KBr solution, and excess $PbBr_2$ filtered off. Calculate the $[Pb^{2+}]$ in the remaining solution.

$$Ksp = [Pb^{2+}]\,[Br^-]^2 = 6.6\times 10^{-6}$$

$$y \times (0.4)^2 = 6.6\times 10^{-6}$$

$$y = 4.13\times 10^{-5}$$

Note that $[Br^-]$ is only from KBr

SKILL CHECK

Q. The solubility of lead chloride is 4.75 gdm^{-3} at 25°C. What mass of lead chloride will be precipitated if 5.85 g of sodium chloride is added to 1 dm^3 of saturated solution of lead chloride?

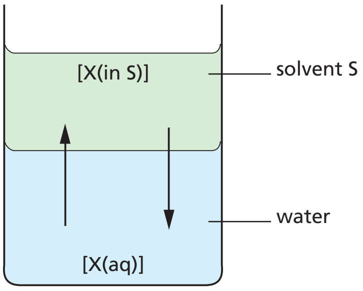
SKILL CHECK

Q. (a) The K_{sp} for $Ca(OH)_2$ at 298K is 4.78×10^{-5}. Calculate the $[Ca^{2+}]$ in the saturated solution.

(b) 5 dm^3 of a saturated solution of was made. To this was added 0.1 $moldm^{-3}$ of NaOH. What mass of $Ca(OH)_2$ will precipitate?

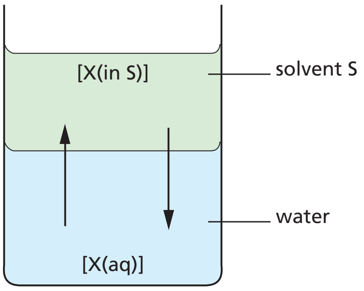
PARTITION COEFFICIENT

Partition: the distribution of a dissolved substance between two solvents which do not mix (they are immiscible). Partition is the basis for solvent and paper chromatography.



PARTITION COEFFICIENT

Shaking a solid with two immiscible solvent produces an equilibrium system to which the *equilibrium law* applies at equilibrium. The ratio of the concentrations in the two layers is constant, at a given temperature:



$$K_{pc} = \frac{[x]_{\text{organic solvent S}}}{[x]_{\text{aqueous}}}$$

PARTITION COEFFICIENT

Partition coefficient is the ratio of concentration of a solute in two immiscible layers at a particular temperature at equilibrium.

The partition obeys the equilibrium law only so long as the dissolved chemical has the same molecular structure on both solvents.

Partition can also be defined as the separation of components dus to their different solubilities in the two solvents.

Each component has a specific partition coefficient and thus, the solubility in the mobile and stationary phase are different. Thus, the rate of movement of each component differs.

PARTITION COEFFICIENT

When some iodine crystals are shaken with a mixture of hexane and water until no further change takes place, and the two layers allowed to separate, we find that the ratio of the concentrations of iodine in each layer is a constant, no matter how much iodine we start with. This constant is the equilibrium constant for the change:

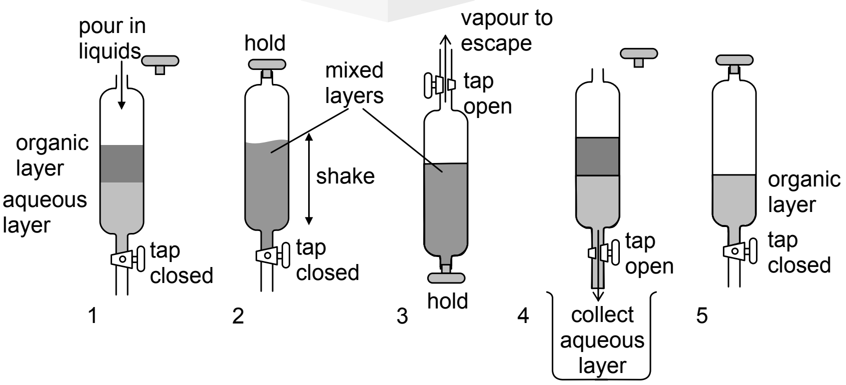
$$\mathrm{I_2(aq)} \rightleftharpoons \mathrm{I_2(hexane)}$$

$$K_c = [\mathrm{I_2(hexane)}]/(\mathrm{I_2(aq)}]$$

K_c is called the partition coefficient of iodine between hexane and water. The usual symbol for a partition coefficient is K_{pc}.

PARTITION COEFFICIENT

Note: The partition coefficient is a simple ratio of two concentrations. It does not matter what concentration units you use, as long as you use the same on top and bottom.



SKILL CHECK

Q. A solution of 5.00 g of an organic compound X in 50 cm^3 of water was shaken with 100 cm^3 of ether. After separation, the aqueous solution was found to contain 0.80 g of X. Determine the partition coefficient of x between ether and water.

SKILL CHECK

Q. When 100 cm^3 of an aqueous solution containing 2.0 g of organic dye X was shaken with 20 cm^3 of hexane, it was found that 1.6 g of the dye had been extracted into the hexane.

(a) Calculate the partition coefficient of X between hexane and water.

(b) Calculate the minimum volume of hexane needed to reduce the amount of X in the aqueous layer to less than 0.1 g.

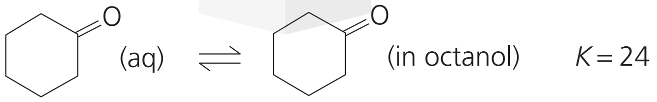
SUCCESSIVE EXTRACTIONS

Solvents are often expensive and flammable, and can also be polluting to the environment. It is sensible, therefore, to use the minimum amount of solvent that is needed to achieve the intended goal. Thus in the example above, the use of 20 cm^3 of hexane allowed 1.6 g of the dye X to be extracted from its aqueous solution, i.e. (1.6/2.0) x 100 = 80%.

We can extract more (89%) than this if we use two separate 10 cm^3 portions of hexane, rather than one 20 cm^3 portion.

SUCCESSIVE EXTRACTIONS

The partition coefficient for the distribution of cyclohexanone between water and octanol is 24. Calculate the mass of cyclohexanone that would be extracted if 20cm^3 of octanol was shaken with 100cm^3 of an aqueous solution containing 2.5g of cyclohexanone.



Let [X] be the concentration of cyclohexanone expressed in g cm^{-3}; let the mass of cyclohexanone extracted be x g; the mass remaining in the aqueous layer will therefore be (2.5 − x) g.

$$K = \frac{[X(octanol)]}{[X(aq)]}$$

$$[X(octanol)] = [X(aq)] \times K$$

$$\frac{x}{20} = \left(\frac{2.5 - x}{100}\right) \times 24$$

$$5x = (2.5 - x) \times 24$$

$$5x = 60 - 24x$$

$$\boldsymbol{x = 2.07\,g}$$

SUCCESSIVE EXTRACTIONS

This process has extracted about 83% of the 2.5 g of cyclohexanone that was in the water.

If we wanted to extract more cyclohexanone, we could repeat the process. But this would require another 20 cm^3 of octanol.

However, if we were to split the original 20 cm^3 of octanol into two 10 cm^3 portions, and use these for successive extractions, our yield of extracted material would increase. The following calculations will make this clear.

SUCCESSIVE EXTRACTIONS

Let the mass of cyclohexanone extracted by the first 10 cm^3 portion of octanol be y g. The mass remaining in the water will therefore be (2.5 – y) g.

$$\frac{y}{10} = \left(\frac{2.5 - y}{100}\right) \times 24$$

$$10y = (2.5 - y) \times 24$$

$$10y = 60 - 24y$$

$$\mathbf{y = 1.765\,g}$$

This first extraction results in 2.5 − 1.765 = 0.735 g of cyclohexanone remaining in the aqueous layer.

SUCCESSIVE EXTRACTIONS

We can now calculate how much of this remaining cyclohexanone can be extracted by using the second 10 cm^3 portion of octanol.

Let the mass of cyclohexanone extracted by the second 10 cm^3 portion of octanol be z g. The mass remaining in the water will be (0.735 – z) g.

$$\frac{z}{10} = \left(\frac{0.735 - z}{100}\right) \times 24$$

$$10z = 17.64 - 24z$$

$$\boldsymbol{z = 0.519\,\mathrm{g}}$$

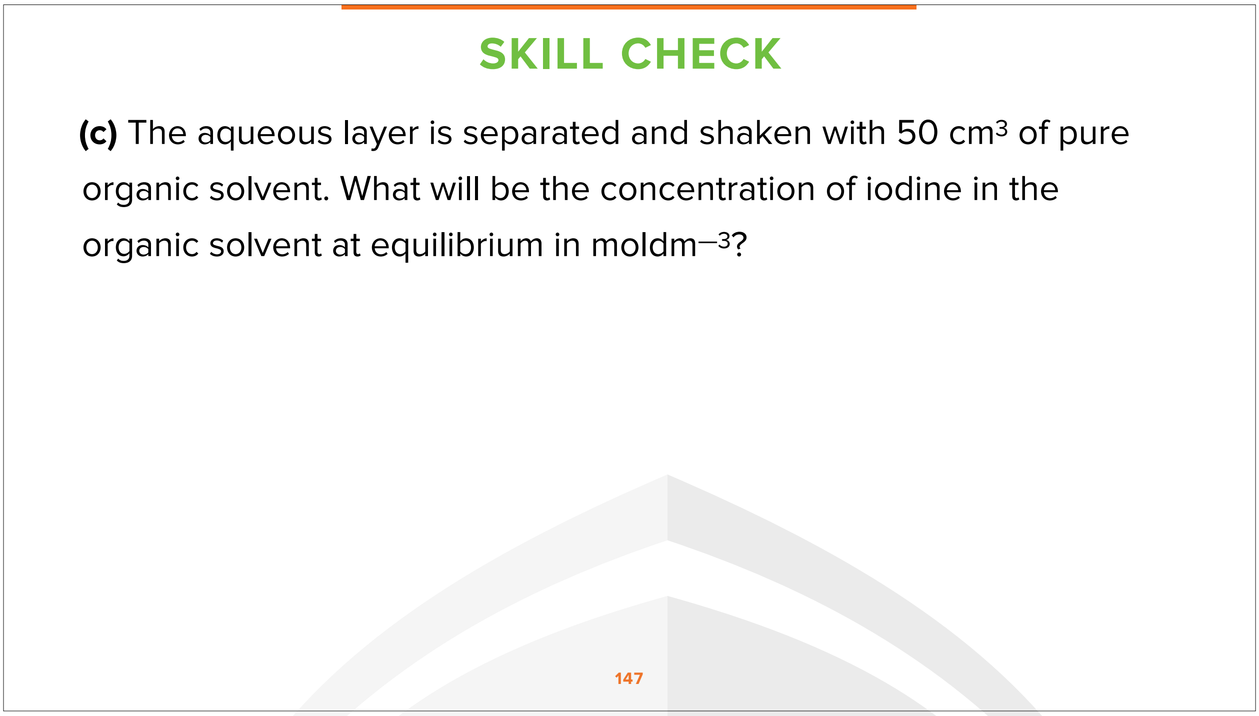
The total mass of cyclohexanone extracted is y + z = 1.765 + 0.519 = 2.28 g

The use of two successive extractions has now raised the percentage extracted from 83% to 91%

SKILL CHECK

Q. (a) What is meant by partition coefficient.

(b) If iodine is shaken with 100 cm^3 of water and 100 cm^3 of an organic solvent, the concentration of iodine in the water layer is 4.0 x 10^{-3} moldm^{-3} and in the organic solvent is 1.0 x 10^{-3} moldm^{-3}. Calculate the partition coefficient for iodine between the organic solvent and water.



SKILL CHECK

(c) The aqueous layer is separated and shaken with 50 cm^3 of pure organic solvent. What will be the concentration of iodine in the organic solvent at equilibrium in $mol dm^{-3}$?