Cambridge A2 Chemistry

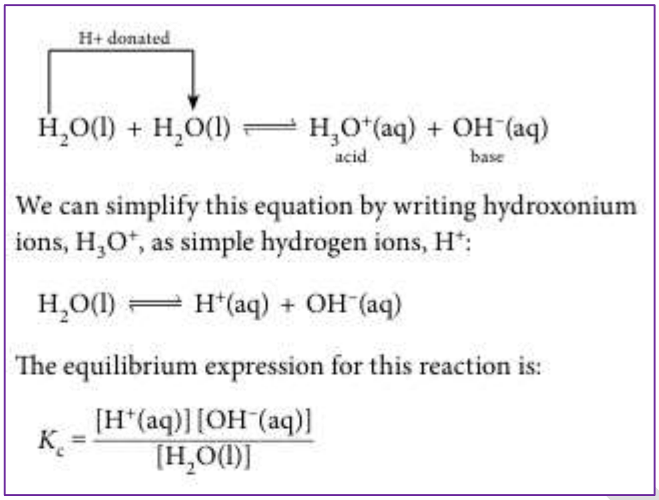
(Code: 9701)

Chapter 21

Further aspects of equilibria

The ionic product of water, K_w

Water is able to act as either an acid (by donating protons, H+) or a base (by accepting protons).



H+ donated

$$\underset{}{H_2O(l)} + H_2O(l) \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

We can simplify this equation by writing hydroxonium ions, H_3O^+, as simple hydrogen ions, H^+:

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

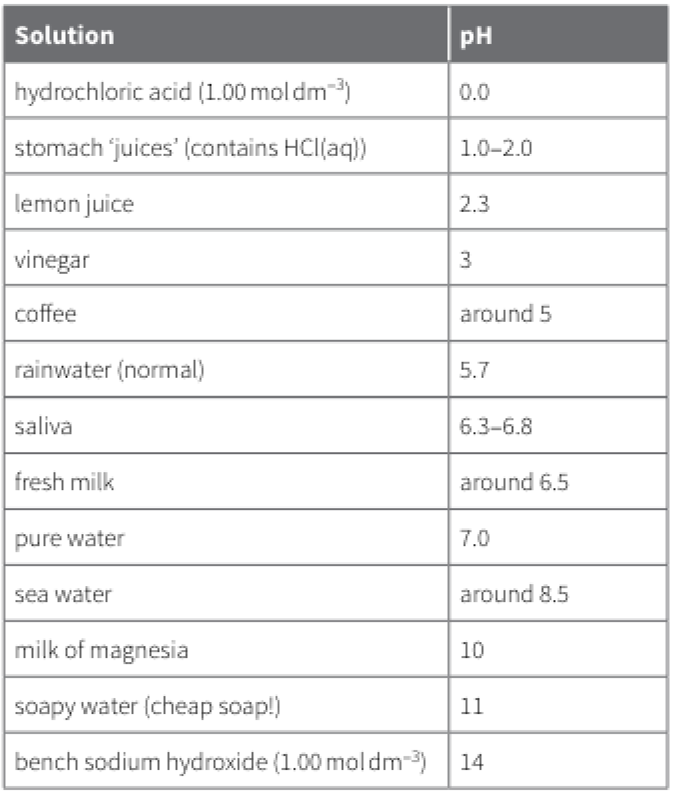
The equilibrium expression for this reaction is:

$$K_c = \frac{[H^+(aq)]\,[OH^-(aq)]}{[H_2O(l)]}$$

K_w is called the ionic product of water. Its value at 298K is $1.00 \times 10^{-14} mol^2 dm^{-6}$.

pH calculations

pH is defined as the negative logarithm to the base 10 of the hydrogen ion concentration. In symbols this is written: $pH = -\log_{10}[H^+]$

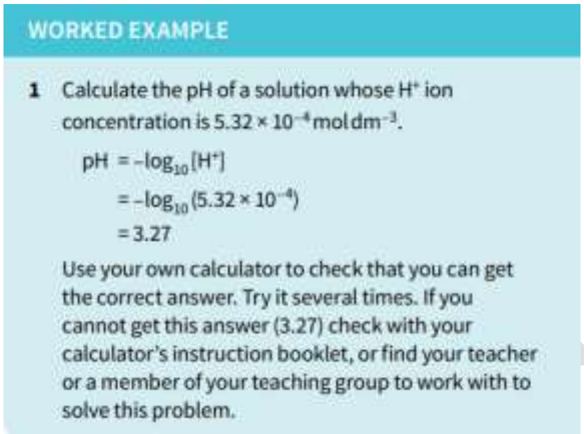


Solution	pH
hydrochloric acid (1.00 mol dm^{-3})	0.0
stomach 'juices' (contains HCl(aq))	1.0–2.0
lemon juice	2.3
vinegar	3
coffee	around 5
rainwater (normal)	5.7
saliva	6.3–6.8
fresh milk	around 6.5
pure water	7.0
sea water	around 8.5
milk of magnesia	10
soapy water (cheap soap!)	11
bench sodium hydroxide (1.00 mol dm^{-3})	14

Note that:

- the negative sign is introduced to make the pH values positive in most cases
- the logarithms used are to the base 10 (not to the base e), so make sure that when doing calculations you press the log or lg button on your calculator (not the ln button)
- we can use this equation to convert [H^+] to pH or pH to [H+].

Calculating pH values from [H^+]



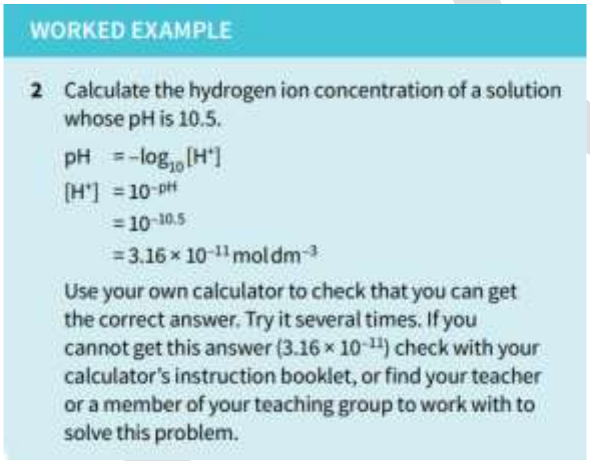
WORKED EXAMPLE

1 Calculate the pH of a solution whose H^+ ion concentration is $5.32 \times 10^{-4}\,mol\,dm^{-3}$.

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ &= -\log_{10}(5.32 \times 10^{-4}) \\ &= 3.27 \end{aligned}$$

Use your own calculator to check that you can get the correct answer. Try it several times. If you cannot get this answer (3.27) check with your calculator's instruction booklet, or find your teacher or a member of your teaching group to work with to solve this problem.

Calculating [H^+] from pH



WORKED EXAMPLE

2 Calculate the hydrogen ion concentration of a solution whose pH is 10.5.

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ [H^+] &= 10^{-pH} \\ &= 10^{-10.5} \\ &= 3.16 \times 10^{-11}\,mol\,dm^{-3} \end{aligned}$$

Use your own calculator to check that you can get the correct answer. Try it several times. If you cannot get this answer (3.16×10^{-11}) check with your calculator's instruction booklet, or find your teacher or a member of your teaching group to work with to solve this problem.

The pH of strong acids

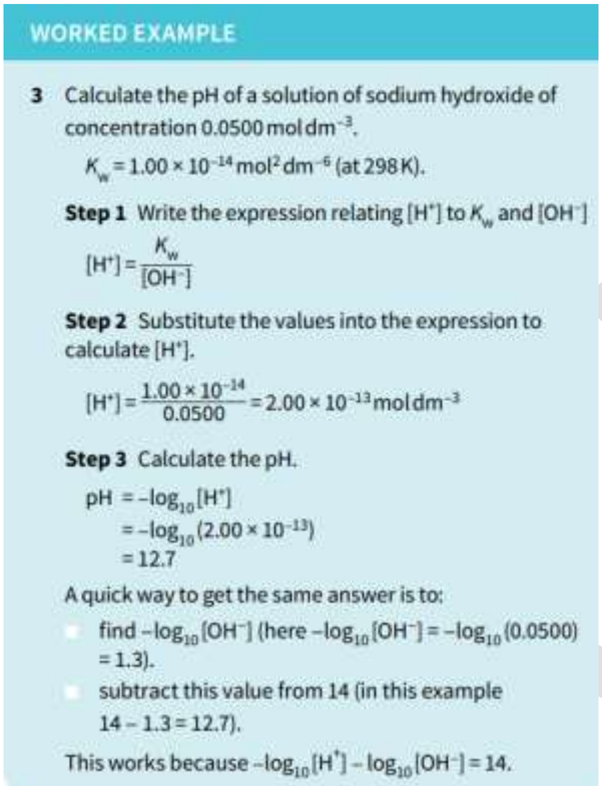
Monobasic acids contain only one replaceable hydrogen atom per molecule. Strong monobasic acids such as hydrochloric acid are completely ionised in solution.

- pH of $0.1 moldm^{-3}$ HCl is $-\log(1 \times 10^{-1} moldm^{-3})$ = pH 1
- pH of $0.01 moldm^{-3}$ HCl is $-\log(1 \times 10^{-2} moldm^{-3})$ = pH 2
- pH of $0.001 moldm^{-3}$ HCl is $-\log(1 \times 10^{-3} moldm^{-3})$ = pH 3

Calculating the pH of strong bases

To calculate the pH of a solution of strong base we need to know:

- the concentration of OH– ions in solution
- the equilibrium expression for the ionisation of water:
  $K_w = [H^+][OH^-]$
- the value of Kw for water



WORKED EXAMPLE

3 Calculate the pH of a solution of sodium hydroxide of concentration 0.0500 mol dm^{-3}.

$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} (at 298 K).

Step 1 Write the expression relating [H$^+$] to K_w and [OH$^-$]

$$[H^+] = \frac{K_w}{[OH^-]}$$

Step 2 Substitute the values into the expression to calculate [H$^+$].

$$[H^+] = \frac{1.00 \times 10^{-14}}{0.0500} = 2.00 \times 10^{-13}\,\text{mol dm}^{-3}$$

Step 3 Calculate the pH.

$$\begin{aligned} \text{pH} &= -\log_{10}[H^+] \\ &= -\log_{10}(2.00 \times 10^{-13}) \\ &= 12.7 \end{aligned}$$

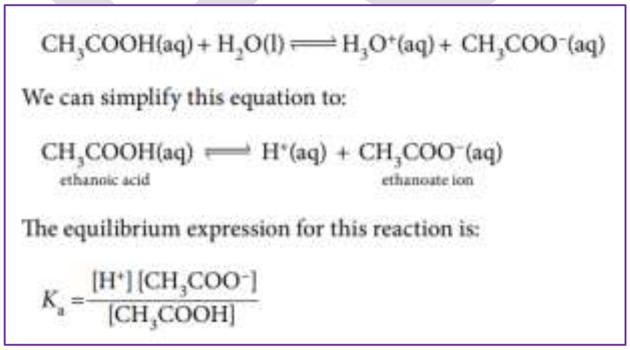
A quick way to get the same answer is to:

- find $-\log_{10}[OH^-]$ (here $-\log_{10}[OH^-] = -\log_{10}(0.0500) = 1.3$).
- subtract this value from 14 (in this example $14 - 1.3 = 12.7$).

This works because $-\log_{10}[H^+] - \log_{10}[OH^-] = 14$.

Weak acids – using the acid dissociation constant, K_a

K_a and pK_a



$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

We can simplify this equation to:

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} \rightleftharpoons H^+(aq) + \underset{\text{ethanoate ion}}{CH_3COO^-(aq)}$$

The equilibrium expression for this reaction is:

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

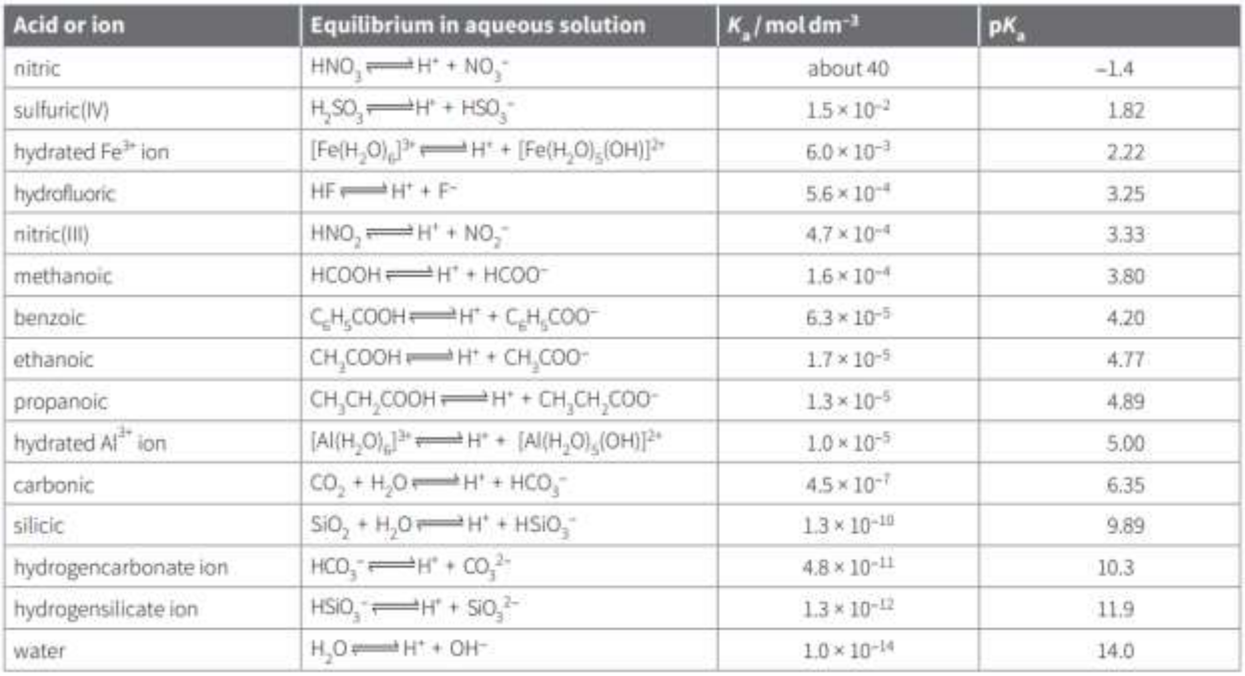
K_a is called the acid dissociation constant. At 298K the value of K_a for the dissociation of ethanoic acid is 1.74×10^{-5}moldm^{-3}. The units of K_a are determined in the same way as for K_c. For the dissociation of a monobasic acid the units are mol dm^{-3}.

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.
- A low value for K_a (for example, $1.0 \times 10^{-4} mol dm^{-3}$) 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.

As K_a values for many acids are very low, we can use pK_a values to compare their strengths.

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

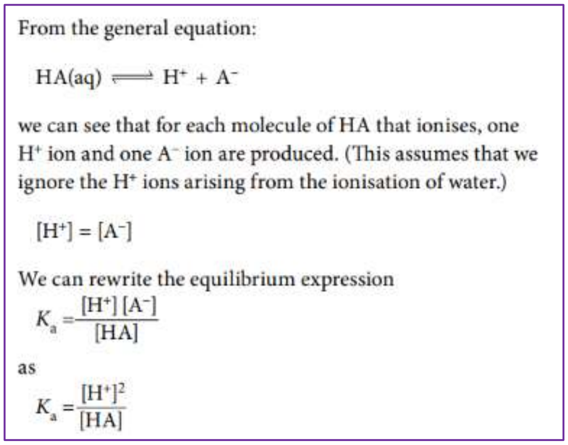


Acid or ion	Equilibrium in aqueous solution	K_a / mol dm^{-3}	pK_a
nitric	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	about 40	–1.4
sulfuric(IV)	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	1.5×10^{-2}	1.82
hydrated Fe^{3+} ion	$[Fe(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Fe(H_2O)_5(OH)]^{2+}$	6.0×10^{-3}	2.22
hydrofluoric	$HF \rightleftharpoons H^+ + F^-$	5.6×10^{-4}	3.25
nitric(III)	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.7×10^{-4}	3.33
methanoic	$HCOOH \rightleftharpoons H^+ + HCOO^-$	1.6×10^{-4}	3.80
benzoic	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.3×10^{-5}	4.20
ethanoic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.7×10^{-5}	4.77
propanoic	$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$	1.3×10^{-5}	4.89
hydrated Al^{3+} ion	$[Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(H_2O)_5(OH)]^{2+}$	1.0×10^{-5}	5.00
carbonic	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$	4.5×10^{-7}	6.35
silicic	$SiO_2 + H_2O \rightleftharpoons H^+ + HSiO_3^-$	1.3×10^{-10}	9.89
hydrogencarbonate ion	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.8×10^{-11}	10.3
hydrogensilicate ion	$HSiO_3^- \rightleftharpoons H^+ + SiO_3^{2-}$	1.3×10^{-12}	11.9
water	$H_2O \rightleftharpoons H^+ + OH^-$	1.0×10^{-14}	14.0

Calculating K_a for a weak acid

We can calculate the value of K_a for a weak acid if we know:

- the concentration of the acid
- the pH of the solution.



From the general equation:

$$HA(aq) \rightleftharpoons H^+ + A^-$$

we can see that for each molecule of HA that ionises, one H^+ ion and one A^- ion are produced. (This assumes that we ignore the H^+ ions arising from the ionisation of water.)

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

We can rewrite the equilibrium expression

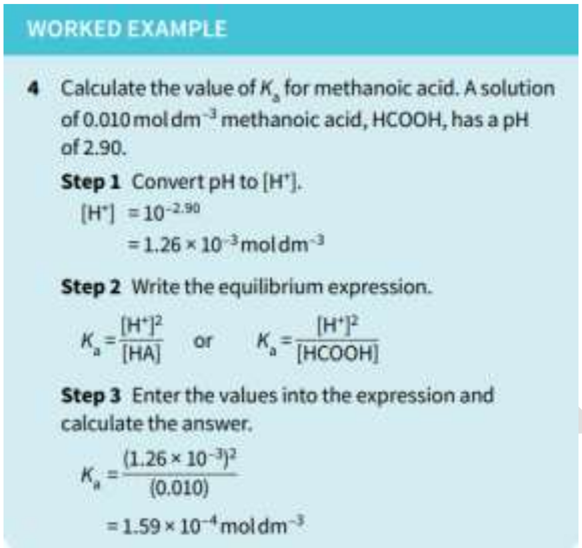
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

as

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

In order to calculate the value of K_a we make two assumptions.

- We ignore the concentration of hydrogen ions produced by the ionisation of the water molecules present in the solution. This is reasonable because the ionic product of water (1.00 × 10^{-14} mol^2dm^{-6}) is negligible compared with the values for most weak acids
- We assume that the ionisation of the weak acid is so small that the concentration of undissociated HA molecules present at equilibrium is approximately the same as that of the original acid.



WORKED EXAMPLE

4 Calculate the value of K_a for methanoic acid. A solution of 0.010 mol dm^{-3} methanoic acid, HCOOH, has a pH of 2.90.

Step 1 Convert pH to [H$^+$].

$$[H^+] = 10^{-2.90}$$
$$= 1.26 \times 10^{-3}\,\text{mol dm}^{-3}$$

Step 2 Write the equilibrium expression.

$$K_a = \frac{[H^+]^2}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+]^2}{[HCOOH]}$$

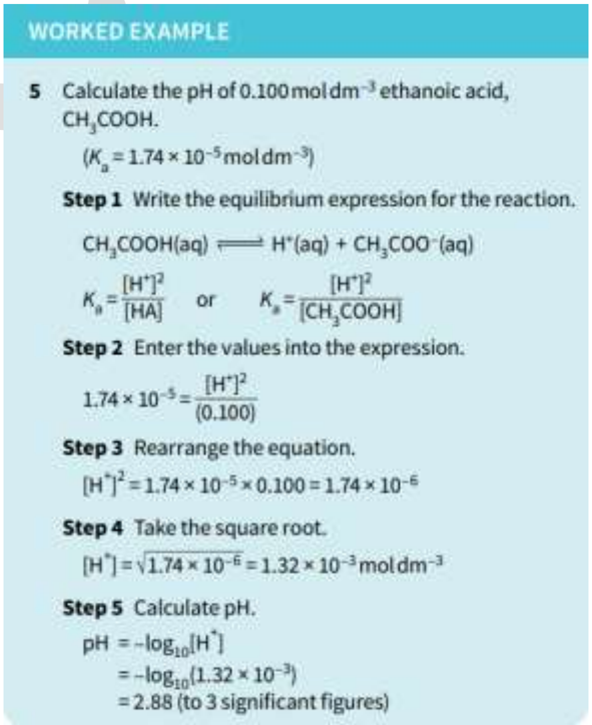
Step 3 Enter the values into the expression and calculate the answer.

$$K_a = \frac{(1.26 \times 10^{-3})^2}{(0.010)}$$
$$= 1.59 \times 10^{-4}\,\text{mol dm}^{-3}$$

Calculating the pH of a weak acid

We can calculate the pH value (or [H$^+$]) of a weak acid if we know:

- the concentration of the acid
- the value of K_a for the acid.



WORKED EXAMPLE

5 Calculate the pH of 0.100 mol dm^{-3} ethanoic acid, CH_3COOH.

(K_a = 1.74 × 10^{-5} mol dm^{-3})

Step 1 Write the equilibrium expression for the reaction.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H^+]^2}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

Step 2 Enter the values into the expression.

$$1.74 \times 10^{-5} = \frac{[H^+]^2}{(0.100)}$$

Step 3 Rearrange the equation.

$$[H^+]^2 = 1.74 \times 10^{-5} \times 0.100 = 1.74 \times 10^{-6}$$

Step 4 Take the square root.

$$[H^+] = \sqrt{1.74 \times 10^{-6}} = 1.32 \times 10^{-3}\,\text{mol dm}^{-3}$$

Step 5 Calculate pH.

$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(1.32 \times 10^{-3})$$
$$= 2.88 \text{ (to 3 significant figures)}$$

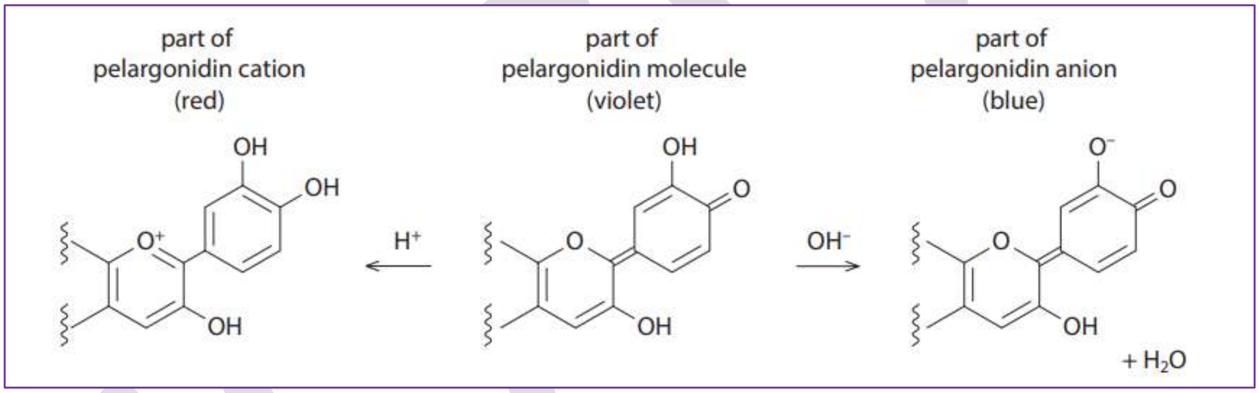
Indicators and acid–base titrations

Introducing indicators

many indicators can be considered as weak acids in which the acid (HIn) and its conjugate base (In^-) have different colours.

$$\underset{\text{un-ionised indicator colour A}}{\mathrm{HIn}} \rightleftharpoons \mathrm{H^+} + \underset{\text{conjugate base colour B}}{\mathrm{In^-}}$$

- Adding an acid to this indicator solution shifts the position of equilibrium to the left. There are now more molecules of colour A.
- Adding an alkali shifts the position of equilibrium to the right. There are now more ions of colour B.
- The colour of the indicator depends on the relative concentrations of HIn and In^-. The colour of the indicator during a titration depends on the concentration of H^+ ions present.

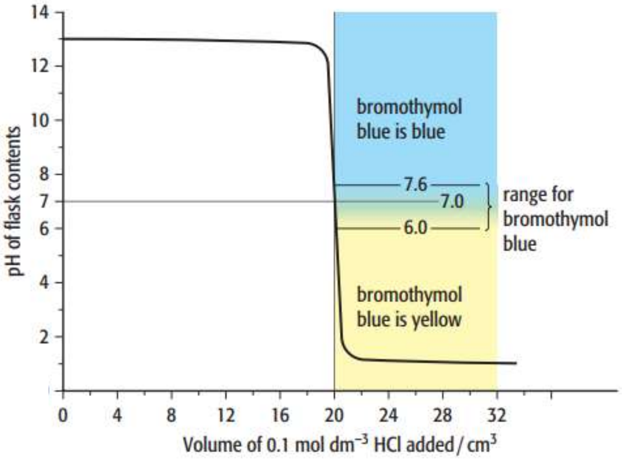


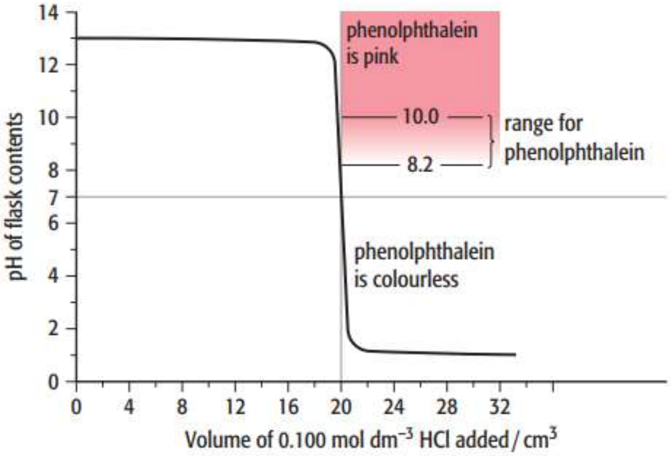
Name of dye	Colour at lower pH	pH range	End-point	Colour at higher pH
methyl violet	yellow	0.0–1.6	0.8	blue
methyl yellow	red	2.9–4.0	3.5	yellow
methyl orange	red	3.2–4.4	3.7	yellow
bromophenol blue	yellow	2.8–4.6	4.0	blue
bromocresol green	yellow	3.8–5.4	4.7	blue
methyl red	red	4.2–6.3	5.1	yellow
bromothymol blue	yellow	6.0–7.6	7.0	blue
phenolphthalein	colourless	8.2–10.0	9.3	pink/violet
alizarin yellow	yellow	10.1–13.0	12.5	orange/red

Strong acids with strong bases

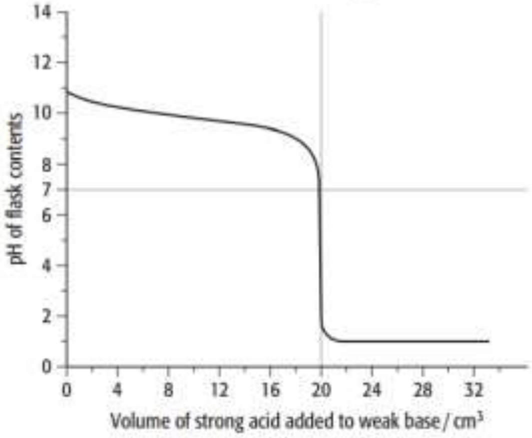
These results show:

- a sharp fall in the graph line between pH 10.5 and pH 3.5; in this region tiny additions of H^+ ions result in a rapid change in pH
- a midpoint of the steep slope at pH 7
- the midpoint of the sharp fall corresponds to the point at which the H^+ ions in the acid have exactly reacted with the OH^- ions in the alkali; this is the end-point of the titration
- that bromothymol blue indicator changed from blue to yellow over the range 7.6 to 6.0 where the slope is steepest.





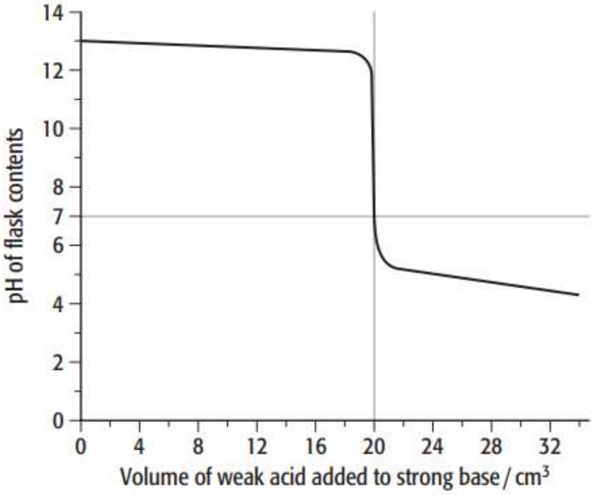
Strong acids with weak bases



These results show:

- a sharp fall in the graph line between pH 7.5 and pH 3.5
- that the midpoint of the steep slope is at about pH 5.

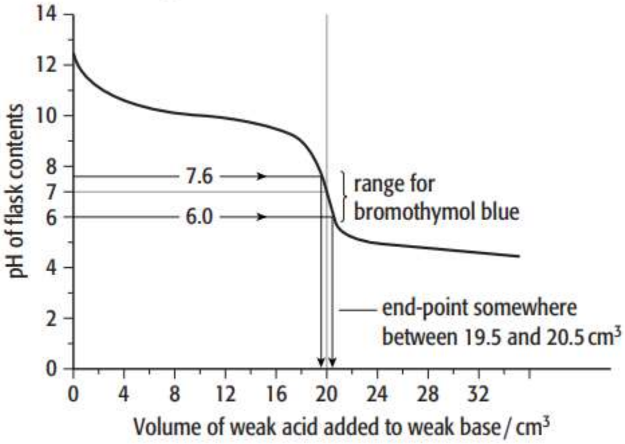
Weak acids with strong bases



These results show:

- a sharp fall in the graph line between pH 11 and pH 7.5
- that the midpoint of the steep slope is at about pH 9.

Weak acids with weak bases



Buffer solutions

What is a buffer solution?

A buffer solution is a solution in which the pH does not change significantly when small amounts of acids or alkalis are added. A buffer solution is used to keep pH (almost) constant.

An increase in hydrogen ion concentration would greatly lower the pH of water, but when H+ ions are added to the buffer solution:

- addition of H+ ions shifts the position of equilibrium to the left because H+ ions combine with CH_3COO^- ions to form more CH_3COOH^- until equilibrium is re-established
- the large reserve supply of CH_3COO^- ensures that the concentration of CH_3COO^- ions in solution does not change significantly
- the large reserve supply of CH_3COOH ensures that the concentration of CH_3COOH molecules in solution does not change significantly
- so the pH does not change significantly

An increase in hydroxide ion concentration would greatly increase the pH of water, but when OH– ions are added to the buffer solution:

- the added OH^- ions combine with H+ ions to form water
- this reduces the H^+ ion concentration
- the position of equilibrium shifts to the right
- so CH_3COOH molecules ionise to form more H^+ and CH_3COO^- ions until equilibrium is re-established
- the large reserve supply of CH_3COOH ensures that the concentration of CH_3COOH molecules in solution does not change significantly
- the large reserve supply of CH_3COO^- ensures that the concentration of CH_3COO^- ions in solution does not change significantly
- so the pH does not change significantly

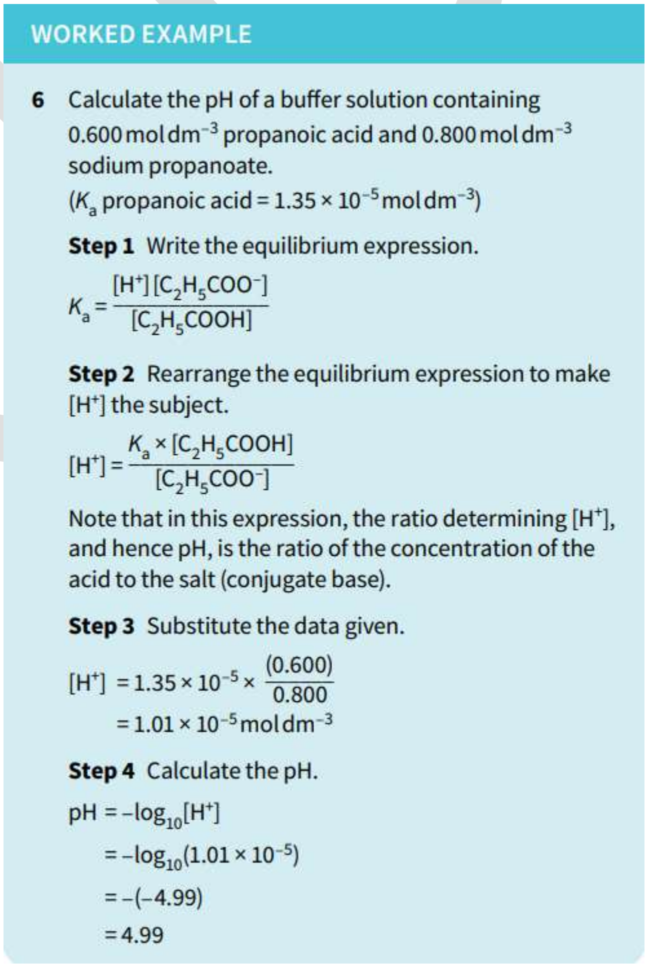
Calculating the pH of a buffer solution

We can calculate the pH of a buffer solution if we know:

- the Ka of the weak acid
- the equilibrium concentration of the weak acid and its conjugate base (salt).

Uses of buffer solutions

Buffer solutions play an important part in many industrial processes, including electroplating, the manufacture of dyes and in the treatment of leather.



WORKED EXAMPLE

6 Calculate the pH of a buffer solution containing 0.600 mol dm^{-3} propanoic acid and 0.800 mol dm^{-3} sodium propanoate.
(K_a propanoic acid = 1.35×10^{-5} mol dm^{-3})

Step 1 Write the equilibrium expression.

$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

Step 2 Rearrange the equilibrium expression to make $[H^+]$ the subject.

$$[H^+] = \frac{K_a \times [C_2H_5COOH]}{[C_2H_5COO^-]}$$

Note that in this expression, the ratio determining $[H^+]$, and hence pH, is the ratio of the concentration of the acid to the salt (conjugate base).

Step 3 Substitute the data given.

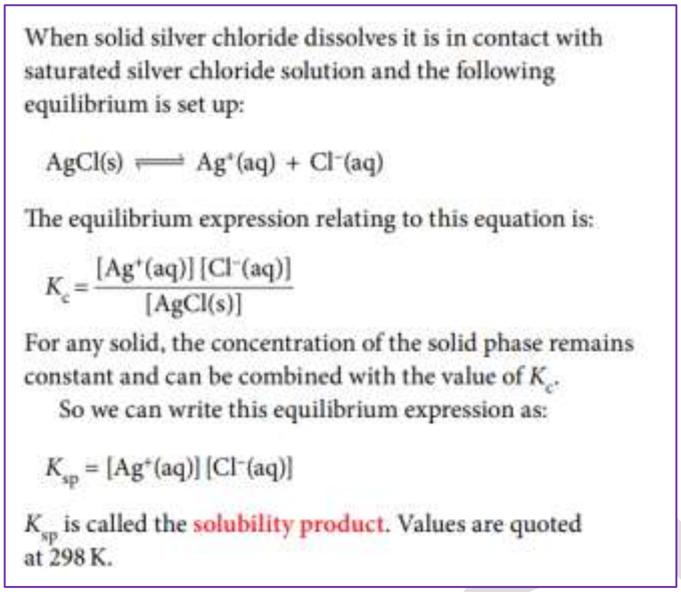
$$\begin{aligned}[H^+] &= 1.35 \times 10^{-5} \times \frac{(0.600)}{0.800} \\ &= 1.01 \times 10^{-5}\ \text{mol dm}^{-3}\end{aligned}$$

Step 4 Calculate the pH.

$$\begin{aligned}\text{pH} &= -\log_{10}[H^+] \\ &= -\log_{10}(1.01 \times 10^{-5}) \\ &= -(-4.99) \\ &= 4.99\end{aligned}$$

Equilibrium and solubility

Solubility product



When solid silver chloride dissolves it is in contact with saturated silver chloride solution and the following equilibrium is set up:

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

The equilibrium expression relating to this equation is:

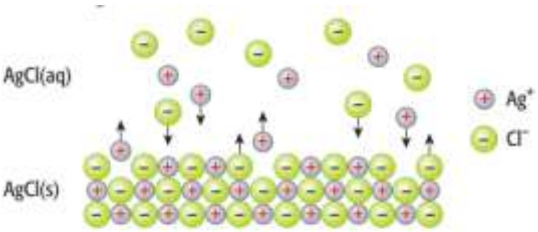
$$K_c = \frac{[Ag^{+}(aq)]\,[Cl^{-}(aq)]}{[AgCl(s)]}$$

For any solid, the concentration of the solid phase remains constant and can be combined with the value of K_c.

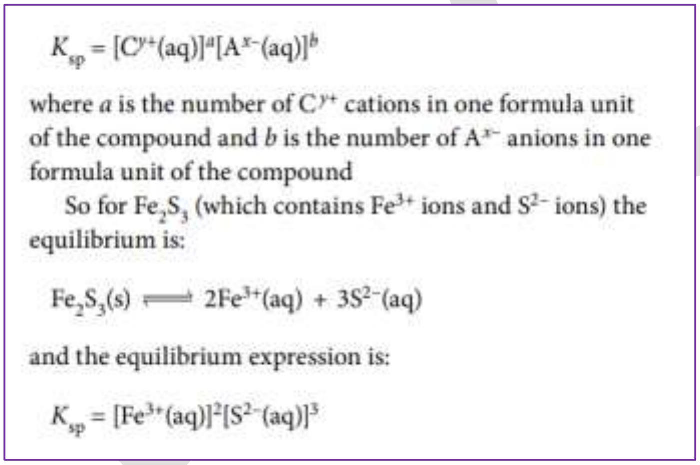
So we can write this equilibrium expression as:

$$K_{sp} = [Ag^{+}(aq)]\,[Cl^{-}(aq)]$$

K_{sp} is called the **solubility product**. Values are quoted at 298 K.



Solubility product is the product of the concentrations of each ion in a saturated solution of a sparingly soluble salt at 298K, raised to the power of their relative concentrations.



$$K_{sp} = [C^{y+}(aq)]^{a}[A^{x-}(aq)]^{b}$$

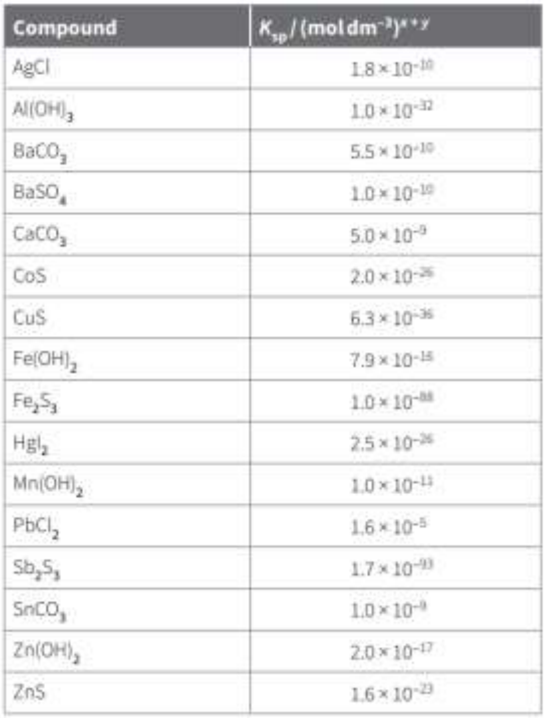
where a is the number of C^{y+} cations in one formula unit of the compound and b is the number of A^{x-} anions in one formula unit of the compound

So for Fe_2S_3 (which contains Fe^{3+} ions and S^{2-} ions) the equilibrium is:

$$Fe_2S_3(s) \rightleftharpoons 2Fe^{3+}(aq) + 3S^{2-}(aq)$$

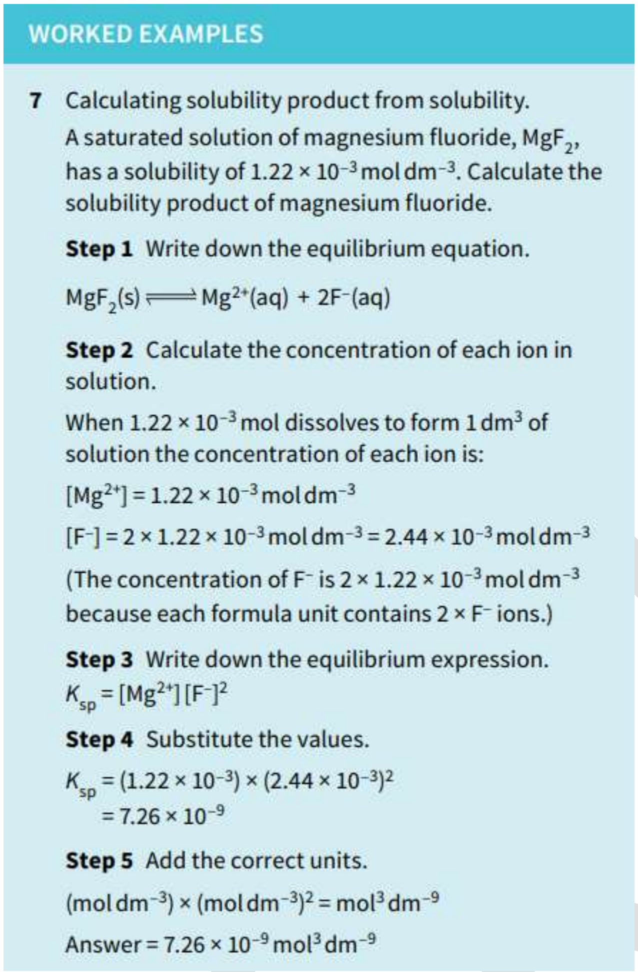
and the equilibrium expression is:

$$K_{sp} = [Fe^{3+}(aq)]^{2}[S^{2-}(aq)]^{3}$$



Compound	K_{sp} / (mol dm^{-3})$^{x+y}$
AgCl	1.8×10^{-10}
$Al(OH)_3$	1.0×10^{-32}
$BaCO_3$	5.5×10^{-10}
$BaSO_4$	1.0×10^{-10}
$CaCO_3$	5.0×10^{-9}
CoS	2.0×10^{-26}
CuS	6.3×10^{-36}
$Fe(OH)_2$	7.9×10^{-16}
Fe_2S_3	1.0×10^{-88}
HgI_2	2.5×10^{-26}
$Mn(OH)_2$	1.0×10^{-11}
$PbCl_2$	1.6×10^{-5}
Sb_2S_3	1.7×10^{-93}
$SnCO_3$	1.0×10^{-9}
$Zn(OH)_2$	2.0×10^{-17}
ZnS	1.6×10^{-23}

Solubility product calculations



WORKED EXAMPLES

7 Calculating solubility product from solubility.

A saturated solution of magnesium fluoride, MgF_2, has a solubility of $1.22 \times 10^{-3}\,mol\,dm^{-3}$. Calculate the solubility product of magnesium fluoride.

Step 1 Write down the equilibrium equation.

$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$

Step 2 Calculate the concentration of each ion in solution.

When 1.22×10^{-3} mol dissolves to form 1 dm^3 of solution the concentration of each ion is:

$[Mg^{2+}] = 1.22 \times 10^{-3}\,mol\,dm^{-3}$

$[F^-] = 2 \times 1.22 \times 10^{-3}\,mol\,dm^{-3} = 2.44 \times 10^{-3}\,mol\,dm^{-3}$

(The concentration of F^- is $2 \times 1.22 \times 10^{-3}\,mol\,dm^{-3}$ because each formula unit contains $2 \times F^-$ ions.)

Step 3 Write down the equilibrium expression.

$K_{sp} = [Mg^{2+}][F^-]^2$

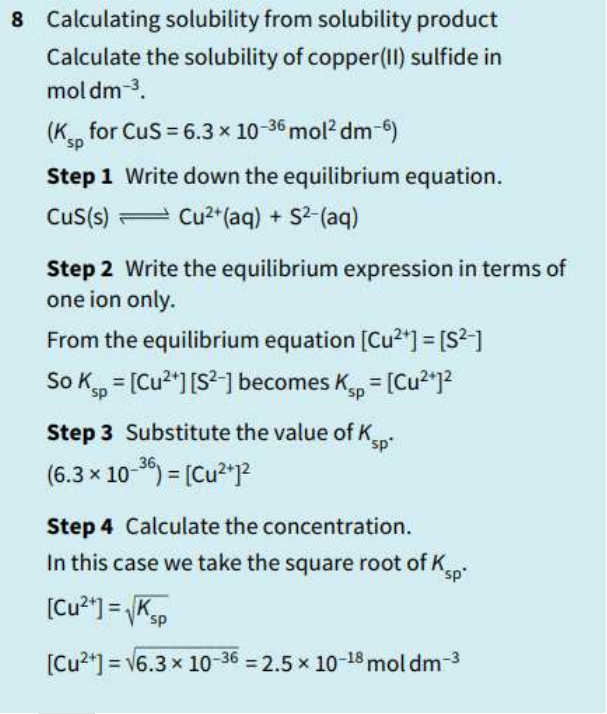
Step 4 Substitute the values.

$$K_{sp} = (1.22 \times 10^{-3}) \times (2.44 \times 10^{-3})^2$$
$$= 7.26 \times 10^{-9}$$

Step 5 Add the correct units.

$(mol\,dm^{-3}) \times (mol\,dm^{-3})^2 = mol^3\,dm^{-9}$

Answer $= 7.26 \times 10^{-9}\,mol^3\,dm^{-9}$



8 Calculating solubility from solubility product

Calculate the solubility of copper(II) sulfide in $mol\,dm^{-3}$.

(K_{sp} for CuS $= 6.3 \times 10^{-36}\,mol^2\,dm^{-6}$)

Step 1 Write down the equilibrium equation.

$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$

Step 2 Write the equilibrium expression in terms of one ion only.

From the equilibrium equation $[Cu^{2+}] = [S^{2-}]$

So $K_{sp} = [Cu^{2+}][S^{2-}]$ becomes $K_{sp} = [Cu^{2+}]^2$

Step 3 Substitute the value of K_{sp}.

$(6.3 \times 10^{-36}) = [Cu^{2+}]^2$

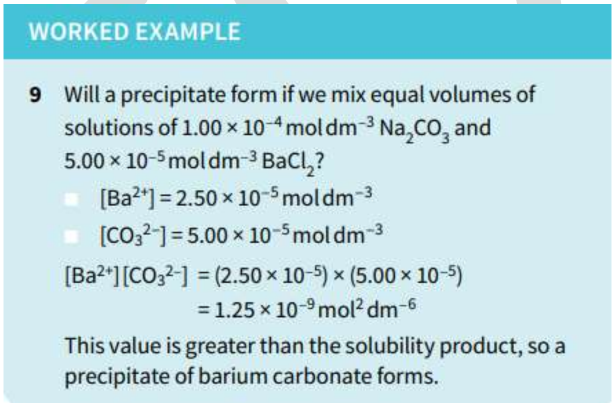
Step 4 Calculate the concentration.

In this case we take the square root of K_{sp}.

$[Cu^{2+}] = \sqrt{K_{sp}}$

$[Cu^{2+}] = \sqrt{6.3 \times 10^{-36}} = 2.5 \times 10^{-18}\,mol\,dm^{-3}$

Predicting precipitation



WORKED EXAMPLE

9 Will a precipitate form if we mix equal volumes of solutions of $1.00 \times 10^{-4}\,mol\,dm^{-3}$ Na_2CO_3 and $5.00 \times 10^{-5}\,mol\,dm^{-3}$ $BaCl_2$?

- $[Ba^{2+}] = 2.50 \times 10^{-5}\,mol\,dm^{-3}$
- $[CO_3^{2-}] = 5.00 \times 10^{-5}\,mol\,dm^{-3}$

$$[Ba^{2+}][CO_3^{2-}] = (2.50 \times 10^{-5}) \times (5.00 \times 10^{-5})$$
$$= 1.25 \times 10^{-9}\,mol^2\,dm^{-6}$$

This value is greater than the solubility product, so a precipitate of barium carbonate forms.

The common ion effect

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.

Partition coefficients

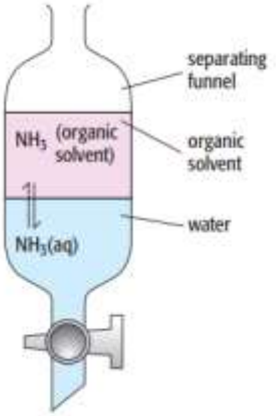


Figure 21.16 Ammonia (the solute) dissolves in both solvents, water and the organic solvent. A state of dynamic equilibrium is established.

WORKED EXAMPLE

10 100 cm^3 of a 0.100 mol dm^{-3} solution of ammonia in water at 20 °C was shaken with 50 cm^3 of an organic solvent and left in a separating funnel for equilibrium to be established.

A 20.0 cm^3 portion of the aqueous layer was run off and titrated against 0.200 mol dm^{-3} dilute hydrochloric acid. The end-point was found to be 9.40 cm^3 of acid.

What is the partition coefficient of ammonia between these two solvents at 20 °C?

The alkaline ammonia solution is neutralised by dilute hydrochloric acid:

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

1 mole of ammonia reacts with 1 mole of the acid.

In the titration we used:

$\frac{9.40}{1000} \times 0.200$ moles of HCl

$= 1.88 \times 10^{-3}$ moles

WORKED EXAMPLE (CONTINUED)

This reacts with ammonia in the ratio 1 : 1 so there must be 1.88×10^{-3} moles of NH_3 in the 20.0 cm^3 portion titrated.

Therefore in the 100 cm^3 aqueous layer there are

$1.88 \times 10^{-3} \times \frac{100}{20.0}$ mol

$= 9.40 \times 10^{-3}$ mol

The number of moles of ammonia in the organic layer must be equal to the initial number of moles of ammonia minus the amount left in the aqueous layer at equilibrium

initial number of moles of ammonia

$= 0.100 \times \frac{100}{1000}$

$= 0.0100$ mol

final number of moles of ammonia in organic layer

$= 0.0100 - 9.40 \times 10^{-3}$ mol

$= 6.00 \times 10^{-4}$ mol

Now we need to change the numbers of moles of ammonia in each layer into concentrations (i.e. the number of moles in 1000 cm^3 or 1 dm^3) to substitute into the equilibrium expression for the partition coefficient, K_{pc}.

The concentration of ammonia in 100 cm^3 of the aqueous layer

$= 9.40 \times 10^{-3} \times \frac{1000}{100}$

$= 0.094$ mol dm^{-3}

The concentration of ammonia in 50 cm^3 of the organic solvent

$= 6.00 \times 10^{-4} \times \frac{1000}{50}$

$= 0.012$ mol dm^{-3}

The expression for the partition coefficient, K_{pc} is:

$$K_{pc} = \frac{[NH_3(\text{organic solvent})]}{[NH_3(aq)]} = \frac{0.012}{0.094}$$

$$= 0.128 \text{ (no units)}$$

This value is less than 1, which shows us that ammonia is more soluble in water than in the organic solvent.

In general for a solute X partitioned between two solvents A and B, the equilibrium expression is given by

$$K_{pc} = \frac{[X(\text{solvent A})]}{[X(\text{solvent B})]}$$

EXCERSISE

1.
   a. Ethanol has a great number of uses. For industrial purposes, it can be manufactured via the following reversible reaction.

      $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH\ (g) \quad \Delta H = -46\ kJ\ mol^{-1}$

      The optimum pressure for this reaction is between 60 and 70 atm.

      State and explain the effect, if any, that increasing the overall pressure would have on the equilibrium yield of ethanol. Use Le Chatelier's principle to explain your answer.
   b. Although Le Chatelier's principle is used to suggest the best conditions for a reaction, often a compromise has to be made.
      i. Use Le Chatelier's principle to suggest whether a high or low temperature should be used to produce the maximum yield of ethanol in the reaction from part (a).
      ii. State a problem that may occur from using this temperature.
   c. Ethanol can be used as a reactant in another equilibrium reaction; the manufacture of ethyl ethanoate.

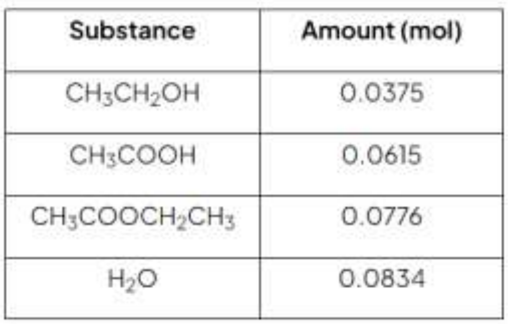
      $CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$

      Give the expression for the equilibrium constant, K_c, for this equilibrium.
   d. A student set up the esterification reaction seen in part (c), adding ethanol and ethanoic acid to a reaction vessel. They set the reaction up in a closed system, at a constant temperature and allowed equilibrium to be reached.

      The reaction was done in a container with a volume of 250 cm^3.

      Table 1.1 below shows the amount of each substance present in the equilibrium mixture.

Table 1.1



Substance	Amount (mol)
CH_3CH_2OH	0.0375
CH_3COOH	0.0615
$CH_3COOCH_2CH_3$	0.0776
H_2O	0.0834

      i. Calculate K_c for this reaction to 2 decimal places.
      ii. Deduce the units for K_c.

2.
   a. Ammonia can be manufactured from nitrogen and hydrogen gases in the Haber process. The equilibrium is shown below.

      $N_2\ (g) + 3H_2(g) \rightleftharpoons 2NH_3\ (g)\ \Delta H = -91\ kJ\ mol^{-1}$

      Write an expression for Kc for this equilibrium.
   b. A chemist carries out a series of experiments to investigate the conversion of nitrogen and hydrogen into ammonia under different conditions. The chemist mixes together 10.40 mol N_2 and 22.50 mol H_2 and pressurises the gases so that the total gas volume is 5.00 dm^3. The

mixture is allowed to reach equilibrium at constant temperature and without changing the total gas volume. The equilibrium mixture contains 5.60 mol NH_3.

i. Calculate Kc at this temperature. Give your answer to three significant figures. Show your working.

ii. State the units for Kc.

c. The chemist repeats the experiment several times. In each experiment, the chemist makes one change. The chemist heats the mixture to a higher temperature at constant pressure. Explain whether the value of Kc would be greater, smaller or the same.

d. The chemist increases the pressure of the mixture at constant temperature. Explain whether the value of Kc would be greater, smaller or the same.

3.

a. This question is about Brønsted-Lowry acids and bases.

i. Give the meaning of the term Brønsted-Lowry base.

ii. Explain the term weak acid.

b. A student titrated 0.10 mol dm^{-3} acid into a conical flask containing 25.0 cm^3 of 0.1 mol dm^{-3} of a base, recording the pH with each addition of acid.

The student repeated the procedure using different combinations of acids and bases.

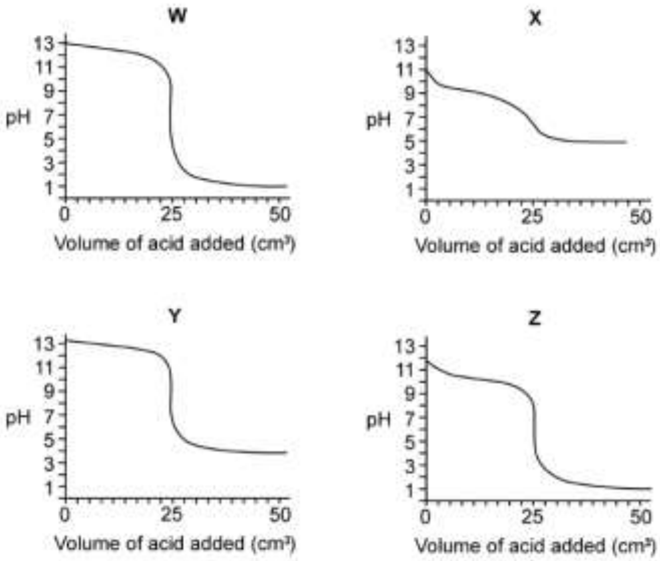


Fig. 5.1

Identify which curve shown above in Fig. 5.1, is the acid-base combination for the following:

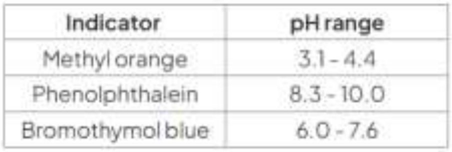
i. Ammonia and ethanoic acid.

ii. Ammonia and nitric acid.

iii. Sodium hydroxide and propanoic acid.

c. Identify which indicator given in Table 5.2 would be most suitable for curve Z. Justify your answer.

Table 5.2



Indicator	pH range
Methyl orange	3.1 - 4.4
Phenolphthalein	8.3 - 10.0
Bromothymol blue	6.0 - 7.6

d. Water is amphoteric and will react with nitric acid and ammonia.

i. Write an equation to show how water reacts with ammonia
ii. Explain the term amphoteric.

4.

a. The following dynamic equilibrium was reached at temperature, T, in a closed container.

$3A (g) + 2B (g) \rightleftharpoons 2C (g) \qquad \Delta H = - 65 \text{ kJ mol}^{-1}$

The value of Kc for the reaction was 255 mol-1 dm3 when the equilibrium mixture contained 3.34 mol of A and 4.28 mol of C.

i. Give the definition of dynamic equilibrium.
ii. Write an expression for K, for the reaction.

b. Calculate the concentration of B in the equilibrium mixture if the volume of the container is 8.00 dm^3. Give your answer to 3 significant figures.

c. Changing the conditions of a closed container can have an effect on the concentrations of the reactants, products and K_c. State the effect, if any, on the concentration of B at equilibrium if temperature, T, is increased and give a reason for your answer.

d. Calculate the equilibrium constant for the following reaction at temperature, T.

$2C (g) \rightleftharpoons 3A (g) + 2B (g)$

5.

a. A student carried out some acid-base titrations using different reactants. The indicators and their pH range are given in Table 3.1.

Table 3.1

Indicator	pH range
methyl red	4.2 - 6.3
bromothymol blue	6.0 - 7.6
bromocresol green	3.8 - 5.4
phenolphthalein	8.2 - 10.0

In the first titration, they titrated 10.0 cm3 of 0.200 mol dm^{-3} HCl against 0.200 mol dm^{-3} aqueous ammonia.

Sketch the pH curve that would be obtained from this titration.

b. Using Table 3.1, explain why methyl red is a suitable indicator for the first titration but phenolphthalein is not.

c. In a second titration, the student titrated 25.0 cm3 of 0.200 mol dm3 sodium hydroxide against 0.100 mol dm-3 ethanoic acid solution.

Sketch the graph that would be obtained for this titration.

d. Using Table 3.1, explain why phenolphthalein is a suitable indicator for the second titration but methyl orange is not.

e. Explain whether the other two indicators in Table 3.1 are suitable for use in either titration.