3. Ionic Equilibriums in Water

1 Acid-Base Buffer Solutions

An acid-base **buffer** is a solution that can resist changes in pH after the addition of small amounts of either acid or base. To do so, the buffer solution must contain appreciable amounts of both an acid (to neutralize the added OH^--ions) and a base (to neutralize the added H_3O^+-ions). However, because they should not neutralize each other the acid and base cannot be chosen at random. Suitable compounds for buffer solutions are hence conjugate acid-base pairs, such as for instance HOAc and OAc^-. The concentration of the acid base couple must be substantial (e.g. $0.1\ \frac{mol}{L}$) and the ratio [acid]/[base] must be between 10/1 and 1/10.

$0.1\ \frac{mol}{L}$ HOAc (aq) + $0.1\ \frac{mol}{L}$ NaOAc (aq)

$0.1\ \frac{mol}{L}$ NH_4Cl (aq) + $0.2\ \frac{mol}{L}$ NH_3

$0.2\ \frac{mol}{L}$ $NaHCO_3$ (aq) + $0.1\ \frac{mol}{L}$ Na_2CO_3

1.1 Mechanism of the Buffering Action

We will consider 1.0 L of an aqueous solution containing equal amounts of e.g. $1.00\ \frac{mol}{L}$ HOAc(aq) and $1.00\ \frac{mol}{L}$ NaOAc(aq). In this solution, the HOAc, Na^+, OAc^-, H^+ and OH^- are present and the following equilibrium conditions occur (at 25°C):

(a) $HOAc(aq) \rightleftharpoons H^+(aq) + OAc^-(aq)$

$$\text{with } K_a = \frac{\left[H^+\right].\left[OAc^-\right]}{\left[HOAc\right]} = 1.8\times10^{-5}$$

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

$$\text{with } K_w = \left[H^+\right].\left[OH^-\right] = 1.0\times10^{-14}$$

Because $K_a >> K_w$, the global concentration of protons $[H^+]$ will be determined by equilibrium (a) and we can write:

$$\left[H^+\right] = K_a.\frac{\left[HOAc\right]}{\left[OAc^-\right]} \qquad (1)$$

$[H^+]$ is determined by K_a and by the ratio $\frac{[HOAc]}{[OAc^-]}$.

1. When a small amount of a strong acid is added (b mole H^+) the following reaction will occur:

$$H^+(aq, added) \quad + \quad OAc^-(aq) \rightleftharpoons HOAc(aq)$$

$$-\text{ b mole} \qquad -\text{ b mole} \qquad +\text{ b mole}$$

As $K = 1/K_a = 5.6 \times 10^4$, this reaction will go to completion. The ratio of the acid and its conjugate base becomes: $\frac{[HOAc]}{[OAc^-]} = \frac{1+b}{1-b}$. When b << 1 no substantial changes will occur and $[H^+]$ in equation (1) will only increase to a very small extent.

2. Addition of a small amount of a strong base (b mol OH^-) leads to the following reaction:

$$OH^-(aq, added) \quad + \quad HOAc(aq) \rightleftharpoons OAc^-(aq) \quad + \quad H_2O\ (l)$$

$$-\text{ b mole} \qquad -\text{ b mole} \qquad +\text{ b mole}$$

Also this reaction will go to completion, because $K = K_a/K_w = 1.8 \times 10^9$. The ratio [acid]/[base] becomes: $\frac{[HOAc]}{[OAc^-]} = \frac{1-b}{1+b}$ and will hence decrease. This decrease is however very small when b << 1.

The concentration of protons $[H^+]$ in (1) will hence also decrease to a very small extent.

From the foregoing it can be concluded that, when their concentration is large enough, the acid-base compounds in the buffer mixture will virtually neutralise all extra H^+- en OH^--ions that are added to the solution Under these conditions the ratio $\frac{[\text{acidic form}]}{[\text{basic form}]}$ changes only to a very small extent and$[H^+]$ will approximately remain constant.

1.2 Henderson – Hasselbalch Equation

For an arbitrarily chosen weak acid HA we can write:

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

with $K_a = \frac{[H^+].[A^-]}{[HA]}$ (2)

Rearranging this equation and taking the logarithm gives:

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

$$\boxed{\mathbf{pH = p\mathit{K}_a + \log\frac{[A^-]}{[HA]}}} \qquad (3)$$

This relationship is called the **Henderson-Hasselbalch** equation, it is also known as the **buffer formula**.

1.3 Buffer Capacity

The capacity of any buffer is a measure of the amount of H_3O^+ or OH^- that can be added to a solution without significant change of pH. This **buffer capacity** is determined by the actual concentrations of the conjugate acid-base compounds in the solution. The larger these concentrations are, the more extra acid or base can be neutralized before the pH will exceed the limits of a given pH-range. When a buffer solution is prepared, it is necessary to determine in advance the pH-change that is acceptable, e.g. 0.1 or 0.05 pH-units. After that, the concentrations of the conjugate acid-base compounds can be calculated, taking into account the extra amount of acid or base that has to be neutralized and the desired pH of the buffer solution.

The working region of a buffer is the region where the buffer works efficiently. The more the ratio of the concentrations of the buffer components deviates from 1, the smaller the buffer capacity and the buffer efficiency. In practice this means that for a buffer system (HA, A^-) the ratio $\frac{[HA]}{[A^-]}$ has to be between $\frac{10}{1}$ and $\frac{1}{10}$. Combination with equation (3) indicates that the working pH-region of a buffer is equal to $pH = pK_a \pm 1$.

Worked example 1

1) 1 L of a mixture of $1.00\ \frac{mol}{L}$ HOAc and $1.00\ \frac{mol}{L}$ NaOAc

For this mixture we have:

$$pH = pK_a + \log\frac{[OAc^-]}{[HOAc]} = 4.75 + \log\frac{1.00\frac{mol}{L}}{1.00\frac{mol}{L}} = 4.75$$

Addition of 1 mL $1\ \frac{mol}{L}$ HCl or $1x10^{-3}$ mole HCl:

$$H^+(aq) + OAc^-(aq) \rightleftharpoons HOAc(aq)$$

mol	$H^+(aq)$	OAc^- (aq)	HOAc(aq)
Initial	0.001	1.000	1.000
Δ	– 0.001	– 0.001	+ 0.001

After reaction	-	0.990	1.001

with $V = 1\ \text{L} + 0.001\ \text{L} \approx 1\ \text{L}$

The pH of this mixture is given by:

$$\text{pH} = 4.75 + \log\frac{0.999\,\frac{\text{mol}}{\text{L}}}{1.001\,\frac{\text{mol}}{\text{L}}} = 4.749$$

ΔpH = – 0.001 and can be neglected.

2) 1 L of pure water , no buffer added.

After addition of 1 mL 1 $\frac{\text{mol}}{\text{L}}$ HCl to the water, $c_{\text{HCl}} = \frac{0.001\,\text{mol}}{1.001\,\text{L}} = 1.0\times10^{-3}\,\frac{\text{mol}}{\text{L}}$

and the pH of this mixture is equal to

pH = – log ($1.0\text{x}10^{-3}$) = 3.00

ΔpH = 3 – 7 = – 4 which is much larger than for the buffered solution.

Worked example 2

Calculate the formal concentrations of HOAc and NaOAc, needed to prepare 1.000 L of a buffer solution with pH = 4.74 and for which ΔpH does not exceed 0.10 when an extra amount of 0.15 mole of H^+ is added to the solution. For HOAc : pK_a = 4.74.

Answer

$$\text{pH} = \text{p}K_a + \log\frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

$$4.74 = 4.74 + \log\frac{[\text{OAc}^-]}{[\text{HOAc}]} = 4.74 + \log\frac{x\,\frac{\text{mol}}{\text{L}}}{x\,\frac{\text{mol}}{\text{L}}}$$

The logarimic terms in this equation have to equal zero, so the concentrations of HOAc and OAc^- are equal. We denote this unknown value as “x”.

When 0.15 mole of H^+ is added these protons will react with OAc^- to form HOAc according to HOAc(aq) $\rightleftharpoons$ H^+ (aq) + OAc^-(aq).

mole	H^+(aq)	OAc^- (aq)	HOAc(aq)
Initial	0.15	x	x
Δ	– 0.15	– 0.15	+ 0.15
After reaction	-	$x – 0.15$	$x + 0.15$

The final pH may not be lower than 4.64, we have:

$$4.64 = 4.74 + \log\frac{\left[\mathrm{OAc}^-\right]_{\mathrm{final}}}{[\mathrm{HOAc}]_{\mathrm{final}}} = 4.74 + \log\frac{(x - 0.15)\dfrac{\mathrm{mol}}{\mathrm{L}}}{(x + 0.15)\ \dfrac{\mathrm{mol}}{\mathrm{L}}}$$

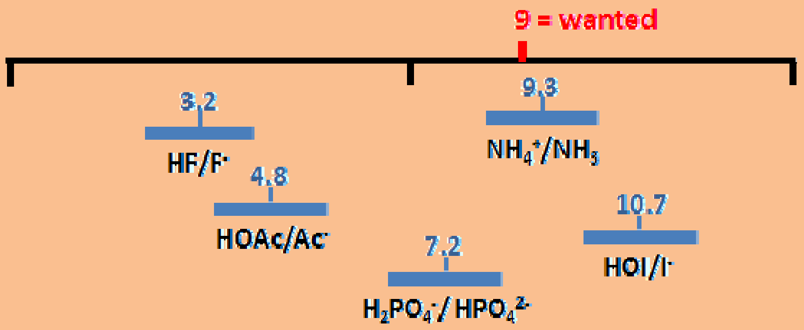
It follows that $x = 1.306\ \dfrac{\mathrm{mol}}{\mathrm{L}}$

$$\Rightarrow\ c_{\mathrm{HOAc}} = c_{\mathrm{NaOAc}} = 1.306\frac{\mathrm{mol}}{\mathrm{L}}$$

Worked example 3

Choose a suitable conjugate acid-base pair (HA, A^-) for the preparation of a buffer with pH = 9. The working region of the buffer should be $pK_a \pm 1$.

Answer



From the figure it follows that NH_4^+/NH_3 has to be chosen as the conjugate acid-base pair. The ratio NH_3/NH_4^+ is determined as follows:

$$\mathrm{pH}_{\mathrm{buffer}} = 9 = pK_{a_{\mathrm{NH}_4^+}} + \log\frac{[\mathrm{NH}_3]}{\left[\mathrm{NH}_4^+\right]} = 9.25 + \log\frac{[\mathrm{NH}_3]}{\left[\mathrm{NH}_4^+\right]}$$

⇨ $\dfrac{[NH_3]}{[NH_4^+]} = 0.56$

In the laboratory, the following solutions are available:

$0.100\ \dfrac{mol}{L}$ NaOH(aq), $0.100\ \dfrac{mol}{L}$ HCl(aq) and $0.100\ \dfrac{mol}{L}$ NH_4Cl(aq);

$0.300\ \dfrac{mol}{L}$ NH_3(aq) and $0.300\ \dfrac{mol}{L}$ $(NH_4)_2SO_4$(aq)

Possible combinations:

0.100 L NH_3(aq) + x L NH_4Cl(aq)

0.100 L NH_3(aq) + x L HCl(aq)

0.100 L NH_4Cl(aq)+ x L NaOH(aq)

0.100 L $(NH_4)_2SO_4$(aq) +x L NaOH(aq)

Take for example: 0.100 L $0.300\ \dfrac{mol}{L}$ $(NH_4)_2SO_4$(aq) + x L $0.100\ \dfrac{mol}{L}$ NaOH(aq)

Number of moles $NH_4^+ = 2 \times 0.300\ \dfrac{mol}{L} \times 0.100\ L = 0.0600$ moles

Number of moles $OH^- = x$ moles

Reaction: $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

mole	NH_4^+	OH^-	NH_3
Initial	0.0600	x	-
Δ	$-x$	$-x$	$+x$
After reaction	$0.0600 - x$	0	x

⇨ $\dfrac{[NH_3]}{[NH_4^+]} = 0.56 = \dfrac{x}{0.06 - x}$

⇨ $x = 0.0220$ mole

⇨ 0.215 L NaOH 0.100 $\frac{\text{mol}}{\text{L}}$

Conclusion: you have to mix 0.100 L 0.300 $\frac{\text{mol}}{\text{L}}$ $(NH_4)_2SO_4(aq)$ + 0.215 L 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq) to obtain 0.315 L of a buffer solution with pH = 9.

2 Acid – Base Titrations

A method to determine an unknown concentration of a compound in a solution is by means of **titration**. This method involves gradual addition of a standard solution of known concentration (the **titrant**) to an accurately known volume of the unknown solution. The endpoint of the titration is determined with a suitable method. In the case of an acid-base tritration, the pH can be monitored with for instance a pH meter and a glass electrode. A plot of the pH versus the volume of titrant added, is called an acid-base **titration curve** (see further for some examples). This curve shows a sharp swing in pH at the **stoichiometric point (SP)** or the **equivalence point (EP**) of the titration. This is the point at which the reaction is stoichiometric satisfied or, in other words, where the amount of titrant added exactly equals the amount of acid or base that is initially present. When the pH at the equivalence point is known, it is also possible to choose an acid base indicator to detect the equivalence point, this is a compound that is added to the solution and that changes colour when the endpoint is reached.

2.1 Acid-Base Indicators

The indicators used in acid-base titrations are weak organic acids for which the 'acid form' (HInd) has another colour than the conjugate 'base form' (Ind^-). Both forms have intense colours, so only a very small amount of the indicator is needed to give striking colour changes and the presence of the indicator will not influence the global pH of the test solution.

The ratio of acid and base form is determined by $[H^+]$ of the test solution by the acid-base equilibrium of the indicator:

$$HInd(aq) \rightleftharpoons Ind^-(aq) + H^+(aq)$$

acid form	base form
colour 1	colour 2

For this equilibrium we have: $K_{\text{indicator}} = \frac{\left[H^+\right].\left[Ind^-\right]}{\left[HInd\right]}$

so $$\frac{\left[HInd\right]}{\left[Ind^-\right]} = \frac{\left[H^+\right]}{K_{\text{indicator}}}$$

The visual observation of the colour change at the equivalence point is very important when indicators are used. The colour of HInd is observed when $\frac{[\mathrm{HInd}]}{[\mathrm{Ind}^-]} \geq \frac{10}{1}$ and the colour of Ind^- is seen when the ratio $\frac{[\mathrm{HInd}]}{[\mathrm{Ind}^-]} \leq \frac{1}{10}$. In-between these ratios a mixed colour is present. This means that the indicator changes colour in a pH range of approximately 2 units at the pK of the indicator.

Bromthymol Blue is yellow at pH < 6.0, blue at pH > 7.6 and greenish in-between. A sudden colour change will be observed during the titration when the titration curve shows a sharp change of at least 2 pH units at pH = 7.

From the foregoing we can conclude that, when we want to determine the equivalence point of a titration with acid base indicators, the pH at the EP should be in the pH-range of colour change of the indicator.

Indicator	Acid colour	pH-range of colour change	Base colour
Thymol Blue	**red**	1.2 – 2.8	**yellow**
Methyl Orange	**red**	3.1 – 4.8	**yellow**
Bromcresol Green	**yellow**	3.8 - 5.4	**green**
Methyl Red	**red**	4.2 – 6.3	**yellow**
Litmus	**red**	5.0 – 8.0	**blue**
Bromthymol Blue	**yellow**	6.0 – 7.6	**blue**
Phenolphtalein	**no colour**	8.3 – 10.0	**purple**

Table 1 – Colour and pH-range of colour change for some acid-base indicators

2.2 Strong Acid - Strong Base Titrations

Titration of 25.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ HCl(aq) with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq)

Reaction before the EP: $\mathbf{1}\,HCl(aq) + \mathbf{1}\,NaOH(aq) \longrightarrow H_2O + NaCl(aq)$

or, in netto-ionic form: $H^+ + OH^- \longrightarrow H_2O$

At the EP the reaction stoichiometry is satisfied. This means that, for the given case:

$$\frac{n_{\text{HCl}}}{n_{\text{NaOH}}} = \frac{\mathbf{1}}{\mathbf{1}} \Rightarrow n_{\text{HCl}} = n_{\text{NaOH}} \Rightarrow 25.00\text{ mL} \,.\, 0.100\,\frac{\text{mmol}}{\text{mL}} = V_{\text{EP}}\text{ mL} \,.\, 0.100\,\frac{\text{mmol}}{\text{mL}}$$

with V_{EP} the volume of NaOH added. It follows that EP is at V_{EP} = 25.00 mL NaOH.

The acid base titration curve shows a sharp inflection point at 25.00 mL NaOH(aq) added.

Calculation of pH during the titration

The initial pH:

Initially, only HCl(aq) is present. Because HCl is a strong acid it is completely ionised, so we have:

$$pH = -\log[H^+] = -\log(0.100) = 1.00$$

The acidic region (between initial pH and EP):

For every volume *v* of base that is added to the initial volume of acid we have:

number of mmole OH^- = *v* mL x 0.100 mol/L = 0.100 *v*

number of mmole H^+ left = 2.5 – 0.100 *v*

$$\left[H^+\right] = \frac{(2.5 - 0.100v)}{(25.00 + v)}\,\frac{\text{mmol}}{\text{mL}}$$

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

The equivalence point:

This solution contains only H_2O, Na^+(aq) en Cl^-(aq):

pH = 7.00

The alkaline region (after EP):

For every volume *v* of base that is added to the initial volume of acid we have:

number of mmole OH^- = *v* mL x 0.100 mol/L = 0.100 *v* number of mmole OH^-used for neutralisation of the acid= 2.5 mmol

number of mmole OH^- in excess = 0.100 v – 2.5

$$\left[OH^-\right] = \frac{(0.100v - 2.5)}{(25.00 + v)} \frac{mmol}{mL}$$

pOH = – log [OH^-] and pH = 14 – pOH

Table 2 gives the values of pH as a function of the added volume of base (v , calculated as described above for the given example. These values are also plotted as a titration curve in Figure 1.

Volume NaOH(aq) added (mL)	$[H^+]$ ($\frac{mol}{L}$)	$[OH^-]$ ($\frac{mol}{L}$)	pH	pH
0.0	0.1000	~ 0 (1.0×10^{-13})	- log $[H^+]$	1.00
5.0	0.0666	~ 0 (1.5×10^{-13})		1.18
10.0	0.0429	~ 0 (2.3×10^{-13})		1.37
15.0	0.0250	~ 0 (4.0×10^{-13})		1.60
20.0	0.0111	~ 0 (9.0×10^{-13})		1.95
22.0	0.0064	~ 0 (1.6×10^{-12})		2.20
24.0	0.0020	~ 0 (5.0×10^{-12})		2.69
24.5	0.0010	~ 0 (1.0×10^{-11})		3.00
24.9	0.0002	~ 0 (5.0×10^{-11})		3.70
25.0 (E.P.)	10^{-7}	10^{-7}	pH = pOH	7.00
25.1	~ 0 (5.0×10^{-11})	0.0002	pH = 14 - pOH	10.30
25.5	~ 0 (1.0×10^{-11})	0.0010		11.00
26.0	~ 0 (5.0×10^{-12})	0.0020		11.29
28.0	~ 0 (1.8×10^{-12})	0.0056		11.75
30.0	~ 0 (5.0×10^{-12})	0.0091		11.96
40.0	~ 0 (1.1×10^{-12})	0.0230		12.36

45.0	~ 0 (3.5×10^{-13})	0.0286		12.46
50.0	~ 0 (3.0×10^{-13})	0.0333		12.52

Table 2 – Titration of a strong acid with a strong base; pH as a function of the volume of base added

$$25.00 \text{ mL } 0.100 \frac{\text{mol}}{\text{L}} \text{ HCl with } 0.100 \frac{\text{mol}}{\text{L}} \text{ NaOH}$$

From the table and the figure it follows that, on addition of NaOH (aq):

- the pH increases very slowly before the equivalence point,
- the pH changes significantly in the small region round the equivalence point. At the equivalence point the curve shows an inflection point,
- after the equivalence point the pH of the solution again increases very slowly.

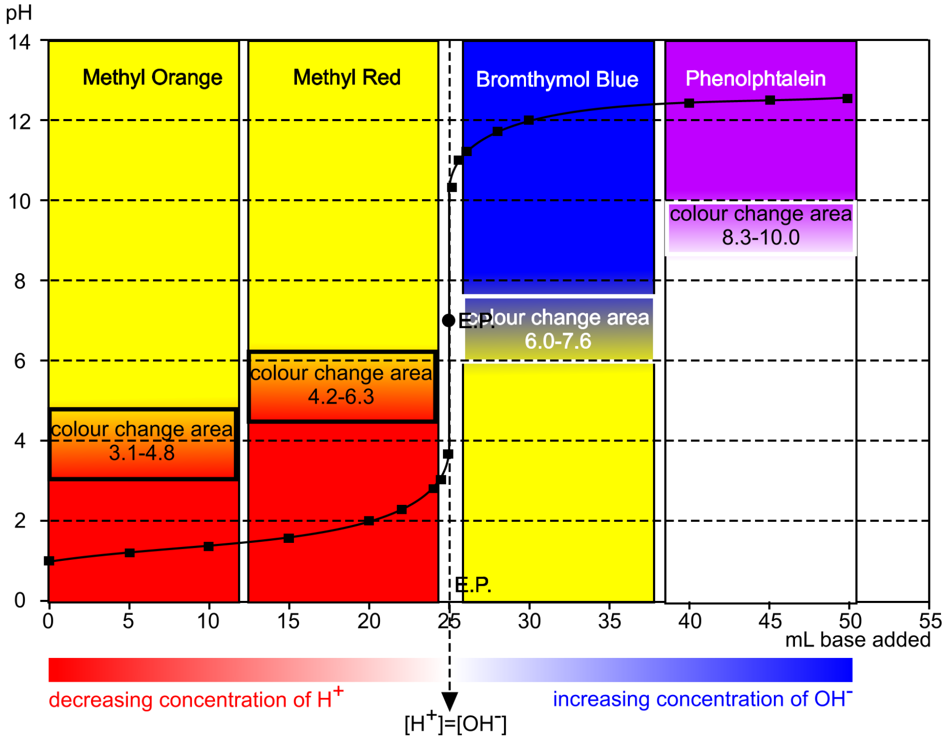


Figure 1 – Titration curve for the titration of 25.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ HCl with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH: pH as a function of the volume base added to the solution.

From the titration curve it can be seen that, at the EP, there is a sharp change in pH of approximately 6 units: from pH = 4 to pH = 10. Methyl Orange, Methyl Red, Bromthymol Blue and Phenolphtalein can be used as acid base indicators for this titration.

2.3 Weak Acid-Strong Base Titrations

Titration of 25.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ HOAc with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH

Reaction before the EP: $\mathbf{1}\ HOAc(aq) + \mathbf{1}\ NaOH(aq) \longrightarrow NaOAc(aq) + H_2O$

or more precise: $HOAc(aq) + OH^-(aq) \longrightarrow OAc^-(aq) + H_2O$

At the equivalence point we have:

$$\frac{n_{HOAc}}{n_{NaOH}} = \frac{\mathbf{1}}{\mathbf{1}} \qquad V_{HOAc}{\cdot}c_{HOAc} = V_{NaOH}{\cdot}c_{NaOH}$$, from which it follows: V_{EP} = 25.00 mL

Calculation of pH during the titration

The initial pH

Initially, only HOAc is present in solution. This acid ionizes only to a small extent according to:

$$HOAc(aq) \rightleftharpoons H^+(aq) + OAc^-(aq)$$

$\frac{\textbf{mol}}{\textbf{L}} = \frac{\textbf{mmol}}{\textbf{mL}}$	HOAc(aq)	$H^+(aq)$	$OAc^-(aq)$
Initial	0.100	-	
Δ	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	x	x

$$K_{a_{HOAc}} = \frac{[H^+].[OAc^-]}{[HOAc]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5} (\frac{\text{mol}}{\text{L}}) \Rightarrow x = 1.33 \times 10^{-3}\ \frac{\text{mol}}{\text{L}} \Rightarrow \text{pH} = 2.87$$

Between initial pH and EP:

When OH^- is added to the solution, HOAc is partially neutralised with formation of OAc^- and a buffer solution $HOAc/OAc^-$ is formed. For every volume *v* of strong base added to the solution we have :

$$HOAc(aq) + OH^-(aq) \longrightarrow OAc^-(aq) + H_2O$$

mmole	HOAc(aq)	$OH^-(aq)$	$OAc^-(aq)$
After addition of v mL base	2.500	$0.100v$	-
Δ	$-0.100v$	$-0.100v$	$+0.100v$
After reaction	(2.500–0.100v)	-	$0.100v$

The concentrations of acetic acid and it’s conjugate base in this buffer solution are given by :

$$\left[\text{OAc}^-\right]=\frac{0.100v}{(25.00+v)}\frac{\text{mmol}}{\text{mL}}$$

$$[\text{HOAc}]=\frac{(2.500-0.100v)}{(25.00+v)}\frac{\text{mmol}}{\text{mL}}$$

When we apply the buffer formula (3) it follows:

$$\text{pH}=\text{p}K_\text{a}+\log\frac{\left[\text{OAc}^-\right]}{[\text{HOAc}]}=4.74+\log\frac{0.100v}{2.500-0.100v}$$

<u>The equivalence point</u>:

At this stage of the titration only NaOAc(aq) or, more specifically, OAc^-(aq) is present in solution. This salt hydrolyses according to:

$$\text{OAc}^-(aq) + H_2O \rightleftharpoons \text{HOAc}(aq) + \text{OH}^-(aq)$$

mmole	OAc^-(aq)	HOAc(aq)	OH^-(aq)
Initial	2.500	-	-
Δ	$-x$	$+x$	$+x$
Equilibrium	$2.500-x$	x	x

$$K_{\text{b}_{\text{OAc}^-}}=\frac{[\text{HOAc}].\left[\text{OH}^-\right]}{\left[\text{OAc}^-\right]}=\frac{1.0\times10^{-14}}{1.8\times10^{-5}}=5.6\times10^{-10}$$

$$\frac{[\text{HOAc}].\left[\text{OH}^-\right]}{\left[\text{OAc}^-\right]}=\frac{\left(\frac{x}{50}\right)^2}{\frac{2.50-x}{50}}=5.6\times10^{-10}\Rightarrow x = 2.65 \times 10^{-4}$$

mmole	OAc^-(aq)	HOAc(aq)	OH^-(aq)
Equilibrium	2.500	2.65×10^{-4}	2.65×10^{-4}

$$\Rightarrow\left[\text{OH}^-\right]=\frac{2.65\times10^{-4}\,\text{mmol}}{50\text{ mL}}=5.3\times10^{-6}\,\frac{\text{mmol}}{\text{mL}}=5.3\times10^{-6}\,\frac{\text{mol}}{\text{L}}\Rightarrow \text{pOH} = 5.28 \Rightarrow \text{pH} = 8.72$$

After the equivalence point:

An excess of OH¯ is added, [OH¯] can be calculated as in the previous case.

As the pH of the solution is 8.7 at the equivalence point, Methyl Orange, Methyl Red and Bromthymol Blue are not fit to use as an indicator in this case; according to Table 1 Phenolphtalein however is still efficient.

Volume NaOH added (mL)	[OAc¯] ($\frac{\text{mol}}{\text{L}}$)	[OH¯] ($\frac{\text{mol}}{\text{L}}$)	[HOAc] ($\frac{\text{mol}}{\text{L}}$)	pH
0.0	0.0013	~ 0 (7.4×10^{-12})	0.0988	2.87
5.0	0.017	~ 0 (1.4×10^{-10})	0.066	4.15
10.0	0.028	~ 0 (3.5×10^{-10})	0.043	4.55
15.0	0.037	~ 0 (8.1×10^{-10})	0.025	4.91
20.0	0.044	~ 0 (2.0×10^{-9})	0.011	5.31
22.0	0.047	~ 0 (4.3×10^{-9})	0.006	5.63
24.0	0.049	~ 0 (1.3×10^{-8})	0.0020	6.12
24.5	0.0495	~ 0 (2.7×10^{-8})	0.0010	6.43
24.9	0.0499	~ 0 (1.3×10^{-7})	0.0002	7.13
25.0 (S.P.)	0.0500	5.2×10^{-6}	5.2×10^{-6}	8.72
25.1	0.0499	0.0002	~ 0	10.30
25.5	0.0495	0.0010	~ 0	11.00
26.0	0.049	0.0020	~ 0	11.29
28.0	0.047	0.0056	~ 0	11.75
30.0	0.045	0.0091	~ 0	11.96
40.0	0.038	0.0230	~ 0	12.36
50.0	0.033	0.0333	~ 0	12.52

Table 3 – Titration of a weak acid with a strong base: 25.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ HOAc with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH. pH as a function of volume base added

When we compare the initial pH in this titration with the initial pH in the titration of a strong acid, it can be seen that it is already significantly higher. This is to be expected as HOAc is a weak acid. In the buffer region (i.e. before the equivalence point) the pH changes only slightly. The stoichiometric point itself is at a higher pH (8.72) than pure water (7.00) because the neutralisation product (OAc^-) behaves as a weak base.

The effective concentration of the particles (HOAc and OAc^-) is in agreement with what is expected on basis of the formal reaction: HOAc is continueously neutralized to OAc^-.

From the titration curve it follows that neither Methyl Orange, Methyl Red nor Bromthymol Blue are good indicators because they already change colour before the equivalence point. Further the colour change occurs in a quite extensive volume region. Only Phenolphthalein fits the conditions in this case.

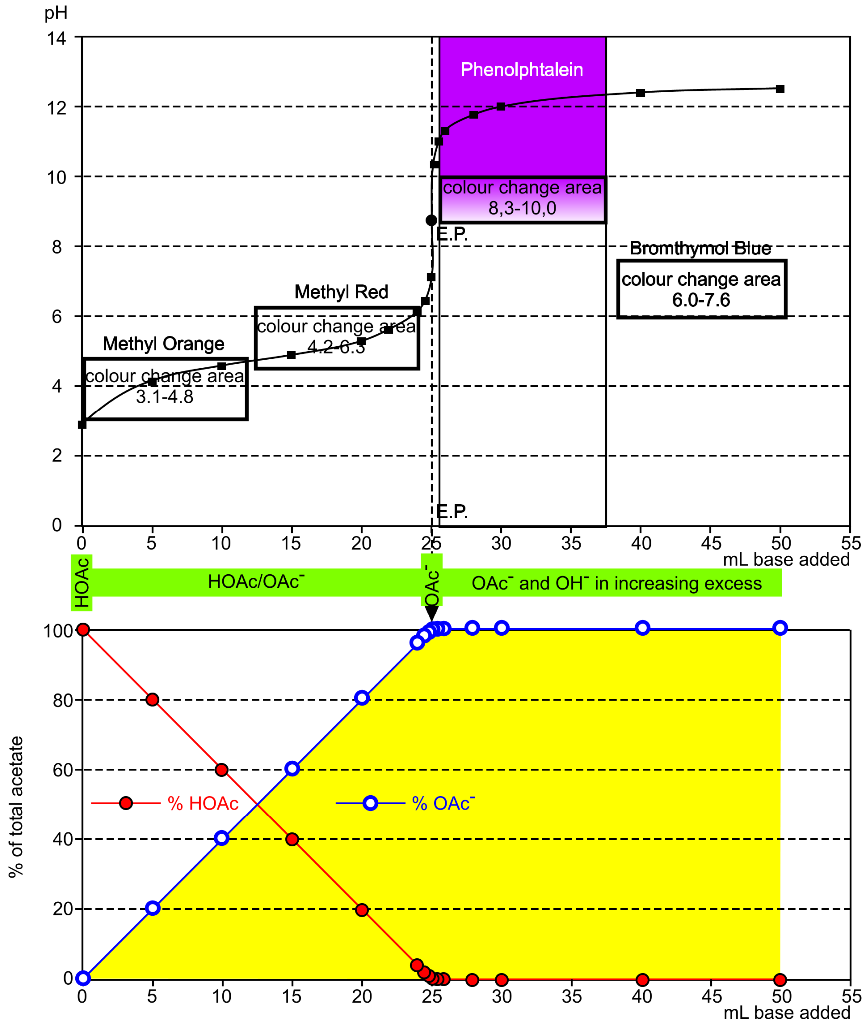


Figure 2 – Titration curve for the titration of 25.00 mL HOAc with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH. –

pH as a function of volume base added.

2.4 Titration of a Polyprotic Acid with a Strong Base

Example: 10 mL 0.100 $\frac{\text{mol}}{\text{L}}$ H_3PO_4(aq) with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH (aq)

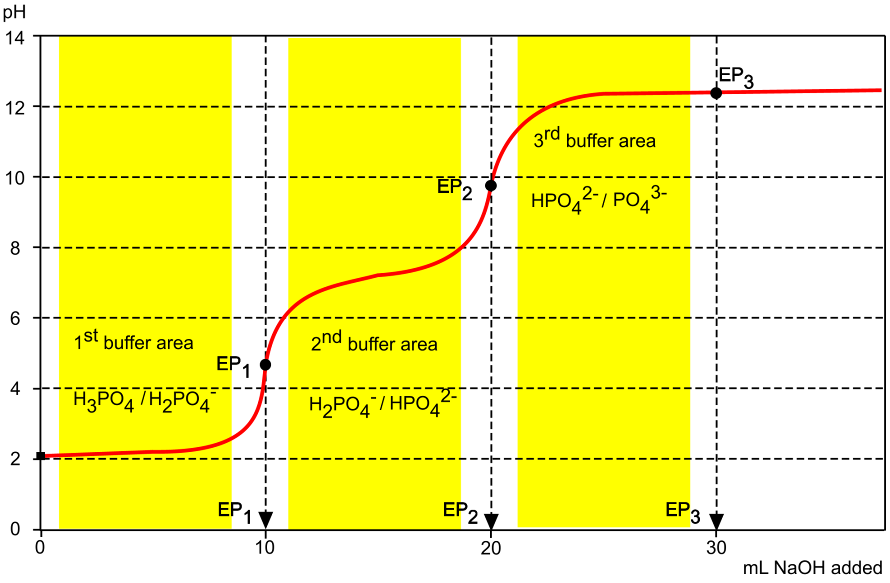


Figure 3 – Titration curve for the titration of 10.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ H_3PO_4(aq) with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq)

The titration curve is given in Figure 3. It shows 2 inflection points at pH = 4.7 and pH = 9.6 respectively and 3 buffer regions. Because the pK_a-values of H_3PO_4 are sufficiently different, ($pK_{a_1} = 2.16$; $pK_{a_2} = 7.21$ en $pK_{a_3} = 12.32$; the differences are in all cases more than 3 powers of ten), this titration curve has the appearance of three consecutive (weak acid-strong base) curves.

Original amount of H_3PO_4 = 10.0 mL x 0.100 $\frac{\text{mol}}{\text{L}}$ = 1 mmole

At the first equivalence point EP_1 , 10.0 mL 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq) is added and 1 mmole H_3PO_4 has reacted to 1 mmole NaH_2PO_4. At this point the pH is given by $pH = \frac{1}{2}\left(pK_{a_1} + pK_{a_2}\right) = \frac{1}{2}(2.16 + 7.21) = 4.69$.

For volumes v of NaOH (aq) added between 0 mL < v < EP_1 , a buffer solution $H_3PO_4/H_2PO_4^-$ is present. After the addition of 5.00 mL titrant we have : $[H_3PO_4] = [H_2PO_4^-]$ so $pH = pK_{a_1} = 2.16$.

At the second equivalence point EP_2 , 20.0 mL 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq) is added and 1 mmole H_3PO_4 has stoichiometrically been converted to 1 mmole Na_2HPO_4. At EP_2 the pH is given by $pH = \frac{1}{2}\left(pK_{a_2} + pK_{a_3}\right) = \frac{1}{2}(7.21 + 12.32) = 9.77$.

For $EP_1 < v < EP_2$ a buffer solution $H_2PO_4^{-}$ / HPO_4^{2-} is present. After the addition of 15.0 mL titrant we have $[H_2PO_4^{-}] = [HPO_4^{2-}]$ so $pH = pK_{a_2} = 7.21$.

For $EP_2 < v < 30.0$ mL a buffer solution HPO_4^{2-}/PO_4^{3-} is present.

For $v > 30.0$ mL, OH^{-} is added in excess. The phosphate anion can hydrolyse according to:

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^{-}(aq)$$

The corresponding constant $K_{b_{PO_4^{3-}}} = \dfrac{K_w}{K_{a_{HPO_4^{2-}}}} = \dfrac{K_w}{K_{a_{3_{H_3PO_4}}}} = \dfrac{1.0\times10^{-14}}{4.8\times10^{-13}} = 2.1\times10^{-2}$ is not that small. This means that the equilibrium position of this reaction is not sufficiently shifted to the left and that at EP3 a HPO_4^{2-}/PO_4^{3-} buffer is still present. As a consequence, there is no clear inflection point at v = 30.0 mL.

2.5 Titration of a Weak Base with a Strong Acid

Example: 25 mL 0.100 $\frac{\text{mol}}{\text{L}}$ NH_3 (aq) with 0.100 $\frac{\text{mol}}{\text{L}}$ HCl (aq)

The titration curve is represented in figure 4. This curve can be constructed by a reasoning, analogous as for the titration of a weak acid with a strong base.

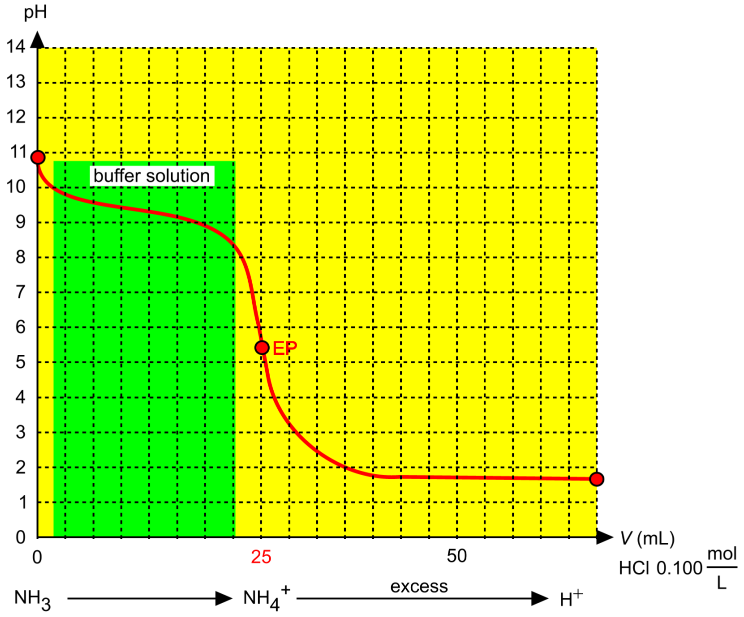
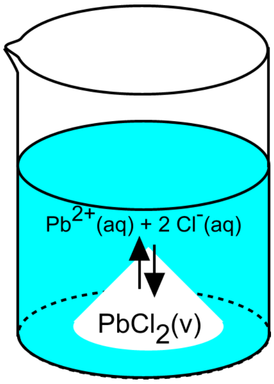


Figure 4 – Titration curve for the titration of 25.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ NH_3(aq) with 0.100 $\frac{\text{mol}}{\text{L}}$ HCl(aq)

3 Slightly Soluble Ionic Compounds

3.1 Solubility Product



Many ionic compounds or salts only show a limited solubility in aqueous solution. The part of these compounds that dissolves, readily decomposes completely into ions. In a saturated solution of such a salt, a dynamic heterogeneous equilibrium exists between the undissolved solid and the ions in solution.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$$

with $K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2$ the equilibrium constant

K_{sp} is called the **solubility product**.

The expression for the solubility product of any salt $M_pL_q(s)$ can be derived by considering the equilibrium constant for its dissolution in water:

$$M_pL_q(s) \rightleftharpoons p\ M^{m+}(aq) + q\ L^{n-}(aq)$$

and $K_{sp} = \left[M^{m+}\right]^p\left[L^{n-}\right]^q$

Values for K_{sp} at 25 °C are, for selected slightly soluble salts, given in Table 4.

Note

In reality is the part of a slightly soluble salt that is dissolved in water not always completely dissociated in ions. It has for instance been shown that a saturated solution of $PbCl_2(s)$ contains not only $Pb^{2+}(aq)$ and $Cl^-(aq)$ ions, but also $PbCl^+(aq)$ and even $PbCl_2(aq)$. In this course however, this complication will not be taken into account.

Fluorides		**Hydroxides**		**Sulphates**		**Phosphates**	
BaF_2	1.8×10^{-7}	$Al(OH)_3$	3.0×10^{-34}	Ag_2SO_4	1.2×10^{-5}	Ag_3PO_4	8.9×10^{-17}
CaF_2	3.5×10^{-11}	$Ba(OH)_2$	2.6×10^{-4}	$BaSO_4$	1.1×10^{-10}	$Ba_3(PO_4)_2$	5.8×10^{-38}
Hg_2F_2	2.4×10^{-6}	$Ca(OH)_2$	5.0×10^{-6}	$CaSO_4$	4.9×10^{-5}	$Ca_3(PO_4)_2$	2.1×10^{-33}
LiF	1.8×10^{-3}	$Cd(OH)_2$	7.2×10^{-15}	Hg_2SO_4	6.5×10^{-7}	$Cu_3(PO_4)_2$	1.4×10^{-37}
MgF_2	5.2×10^{-11}	$Co(OH)_2$	5.9×10^{-15}	$PbSO_4$	2.5×10^{-8}	$FePO_4$	9.9×10^{-16}
PbF_2	3.3×10^{-8}	$Co(OH)_3$	3.0×10^{-45}	**Chromates**		$Fe_3(PO_4)_2$	1.0×10^{-36}
Chlorides		$Cr(OH)_3$	2.0×10^{-30}	Ag_2CrO_4	1.1×10^{-12}	$Mg_3(PO_4)_2$	1.0×10^{-24}
$AgCl$	1.8×10^{-10}	$Cu(OH)_2$	4.8×10^{-20}	$BaCrO_4$	1.2×10^{-10}	$Ni_3(PO_4)_2$	4.7×10^{-32}
$CuCl$	1.7×10^{-7}	$Fe(OH)_2$	4.9×10^{-17}	$CaCrO_4$	7.1×10^{-4}	$Pb_3(PO_4)_2$	3.0×10^{-44}
Hg_2Cl_2	1.4×10^{-18}	$Fe(OH)_3$	2.8×10^{-39}	Hg_2CrO_4	2.0×10^{-9}	**Sulphides**	
$PbCl_2$	1.7×10^{-5}	$Mg(OH)_2$	5.6×10^{-12}	$CuCrO_4$	3.6×10^{-6}	Ag_2S	6.0×10^{-51}
Bromides		$Mn(OH)_2$	1.6×10^{-13}	$PbCrO_4$	1.8×10^{-14}	CdS	8.0×10^{-26}
$AgBr$	5.4×10^{-13}	$Ni(OH)_2$	5.5×10^{-16}	**Carbonates**		CoS	5.0×10^{-22}
$CuBr$	6.3×10^{-9}	$Pb(OH)_2$	1.4×10^{-20}	Ag_2CO_3	8.5×10^{-12}	Cu_2S	2.3×10^{-48}
Hg_2Br_2	6.4×10^{-23}	$Sn(OH)_2$	5.5×10^{-27}	$BaCO_3$	2.6×10^{-9}	CuS	6.0×10^{-37}
$PbBr_2$	6.6×10^{-6}	$Zn(OH)_2$	3.0×10^{-17}	$CaCO_3$	3.4×10^{-9}	FeS	6.0×10^{-19}
$HgBr_2$	6.2×10^{-20}	**Cyanides**		$CdCO_3$	1.0×10^{-12}	HgS	2.0×10^{-53}
Iodides		$AgCN$	6.0×10^{-17}	$CuCO_3$	2.3×10^{-10}	MnS	3.0×10^{-14}
AgI	8.5×10^{-17}	$CuCN$	3.5×10^{-20}	$FeCO_3$	3.1×10^{-11}	PbS	3.0×10^{-28}
CuI	1.3×10^{-12}	$Zn(CN)_2$	3.0×10^{-16}	Hg_2CO_3	3.6×10^{-17}	ZnS	2.0×10^{-25}
Hg_2I_2	5.2×10^{-29}	**Sulphites**		$MgCO_3$	6.8×10^{-6}	**Oxalates**	
PbI_2	9.8×10^{-9}	Ag_2SO_3	1.5×10^{-14}	$MnCO_3$	2.2×10^{-11}	$Ag_2C_2O_4$	5.4×10^{-12}
HgI_2	2.9×10^{-29}	$BaSO_3$	5.0×10^{-10}	$ZnCO_3$	1.5×10^{-10}	MgC_2O_4	4.8×10^{-6}
		$CaSO_3$	3.1×10^{-7}	$PbCO_3$	7.4×10^{-14}	ZnC_2O_4	1.4×10^{-9}

Table 6: solubility product for slightly soluble salts

3.2 Calculating K_{sp} from solubility data

When the **solubility *S*** of a slightly soluble salt is experimentally determined, it is possible to calculate the value of K_{sp}. The solubility equals the amount of salt (in g or in mole) dissolved in 1 L of a saturated solution at the specified temperature.

For $Ag_2CrO_4(s)$ the solubility S = 43.12 mg per liter solution. De molar mass of Ag_2CrO_4 is 331.74 $\frac{g}{mol}$ so we can calculate that $S = 1.3 \times 10^{-4}\ \frac{mol}{L}$.

Dissociation: $Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$

When $1.3 \times 10^{-4}\ \frac{mol}{L}$ Ag_2CrO_4 dissolves, $[Ag^+] = 2 \times 1.3.10^{-4}\ \frac{mol}{L}$ and $[CrO_4^{2-}] = 1.3 \times 10^{-4}\ \frac{mol}{L}$. With this values we find for K_{sp}:

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2.6 \times 10^{-4})^2(1{,}3 \times 10^{-4}) = 8.8 \times 10^{-12}\ (\frac{mol^3}{L^3})$$

3.3 Calculating Solubility from K_{sp}

$PbCl_2(s)$: $K_{sp} = 1.7 \times 10^{-5}$ for $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$

When the solubility of $PbCl_2(s)$ equals $S\ \frac{mol}{L}$, then $[Pb^{2+}] = S\ \frac{mol}{L}$ and $[Cl^-] = 2S\ \frac{mol}{L}$, and we have

$$K_{sp} = 1.7 \times 10^{-5} = [Pb^{2+}][Cl^-]^2 = S\ .\ (2S)^2 = 4S^3$$

From this it follows : $S = 1.6 \times 10^{-2}\ \frac{mol}{L}$

For any ionic compound with general formula M_pL_q , solubility product K_{sp} and solubility S ($\frac{mol}{L}$) we have:

$$M_pL_q(s) \rightleftharpoons p\ M^{m+}(aq) + q\ L^{n-}(aq)$$

For the concentrations of the ions we can write:

$[M^{m+}] = p.S$ and $[L^{n-}] = q.S$

so

$$S = \frac{\left[M^{m+}\right]}{p} = \frac{\left[L^{n-}\right]}{q}$$

When we combine this with the expression for K_{sp} we find

$$K_{sp} = \left[M^{m+}\right]^p \left[L^{n-}\right]^q = (pS)^p.(qS)^q$$

or $S = \sqrt[p+q]{\dfrac{K_s}{p^p.q^q}}$

K_{sp} for $Mg_3(PO_4)_2$ equals 1.0 x 10^{-24} at 25 °C.

In this case p = 3 and q = 2, so we find

$$S = \sqrt[5]{\frac{K_s}{3^3.2^2}} = \sqrt[5]{\frac{K_{sp}}{108}} = 6.2\times10^{-6}\,\frac{\text{mol}}{\text{L}}$$

3.4 Predicting the Formation of a Precipitate

In the chapter “Chemical equilibrium” we discussed how the value of the concentration quotient *Q* can be used to predict whether a reaction will proceed in the forward or backward direction. When two solutions containing ionic salts are mixed, we calculate *Q* by determining the concentrations of the appropriate ions immediately after mixing and comparing with the value of K_{sp} .

$Q = K_{sp}$: saturated solution, no precipitation

$Q < K_{sp}$: unsaturated solution; no precipitation

$Q > K_{sp}$: supersaturated solution; precipitation untill $Q = K_{sp}$

Worked example 4

The following solutions are mixed. Will a precipitation be formed? Calculate the equilibrium concentrations $[Ag^+]$ and $[Cl^-]$.

$$10.0\text{ mL of }1.0\times10^{-2}\,\frac{\text{mol}}{\text{L}}\ AgNO_3(aq) + 10.0\text{ mL of }1.0\times10^{-4}\,\frac{\text{mol}}{\text{L}}\ NaCl(aq)$$

$$K_{sp_{AgCl}} = 1.7\times10^{-10}$$

Answer

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ $\qquad K = \dfrac{1}{K_{sp_{AgCl}}} = 5.9\times10^{9}$ ⇨ completed reaction!

Initial concentrations: $[Ag^+] = 5.0\times10^{-3}\,\dfrac{\text{mol}}{\text{L}}$, $[Cl^-] = 5.0\times10^{-5}\,\dfrac{\text{mol}}{\text{L}}$

⇨ $Q = 2.5\times10^{-7} > K_{sp} \Rightarrow$ precipitation!

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

$\frac{\text{mol}}{\text{L}}$	Ag^+	Cl^-	AgCl
Initial	5.0×10^{-3}	5.0×10^{-5}	-
Δ	-5.0×10^{-5}	-5.0×10^{-5}	$+5.0\times10^{-5}$
Equilibrium	4.95×10^{-3}	-	↘

The final concentration of chloride ions can be calculated from the equilibrium with solid AgCl.

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

$\frac{\text{mol}}{\text{L}}$	AgCl	Ag^+	Cl^-
Initial	↘	4.95×10^{-3}	-
Δ	$-x$	$+x$	$+x$
Equilibrium	↘	$4.95\times10^{-3}+x$ $\approx 4.95\times10^{-3}$	x

$$K_{sp_{AgCl}} = 1.7\times10^{-10} = \left[Ag^+\right]\times\left[Cl^-\right] = \left(4.95\times10^{-3}\right)\times x$$

$$\Rightarrow x = [Cl^-] = 3.43\times10^{-8}\,\frac{\text{mol}}{\text{L}}$$

Equilibrium concentrations: $[Cl^-] = 3.43\times10^{-8}\,\frac{\text{mol}}{\text{L}}$; $[Ag^+] = 4.95\times10^{-3}\,\frac{\text{mol}}{\text{L}}$

3.5 Common Ion Effect

According to Le Châteliers principle we can predict that the solubility of a slightly soluble salt will decrease when an electrolyte with a common ion is added.

Worked example 5

Calculate the solubility of $BaSO_4$ in an aqueous solution of 0.050 $\frac{\text{mol}}{\text{L}}$ Na_2SO_4.

$$K_{sp_{BaSO_4}} = 1.5\times10^{-9}$$

Answer

$$K_{sp_{BaSO_4}} = 1.5\times10^{-9} = \left[Ba^{2+}\right]\times\left[SO_4^{2-}\right]$$

$$S=\left[Ba^{2+}\right]=\frac{K_{sp_{BaSO_4}}}{\left[SO_4^{2-}\right]}$$

$$\left[SO_4^{2-}\right]=0.050\frac{mol}{L}+x\frac{mol}{L}\approx 0.050\frac{mol}{L}\ \text{(amount } x \text{ from } BaSO_4 \text{ very small)}$$

$$\Rightarrow S=\frac{1.5\times 10^{-9}}{0.050}=3.0\times 10^{-8}\frac{mol}{L}$$

Compare with solubility $BaSO_4$in pure water :

$$S=\sqrt{K_{sp}}=\sqrt{1.5\times 10^{-9}}=3.9\times 10^{-5}\frac{mol}{L}$$

3.6 Influence of pH

When the slightly soluble salt contains an anion that hydrolyses in water, the solubility of the salt will depend on the pH of the solution. These anions are the conjugate base of a weak acid, examples are CO_3^{2-}, S^{2-}, PO_4^{3-}, F^- , ...

Worked example

In a saturated solution of $CaCO_3$, the following equilibrium are present:

(a) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $\qquad K_{sp}$

(b1) $CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$ $\qquad K_{b_1}=\frac{K_w}{K_{a_2}}$

(b2) $HCO_3^-(aq) + H_2O \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ $\qquad K_{b_2}=\frac{K_w}{K_{a_1}}$

(c) $H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\qquad K_w$

In these equations, K_{a_1} and K_{a_2} represent the acid dissociation constants of H_2CO_3.

When an extra amount of a strong acid, e.g. HCl(aq), is added, the equilibriums will shift according to Le Chateliers principle: equilibrium (c) will shift to the left, equilibriums (b_2) and (b_1) will shift to the right and equilibrium (a) should also shift to the right: more $CaCO_3$ (s) will dissolve. The opposite will occur when an extra amount of NaOH(aq)is added.

The solubility of $CaCO_3$ is then given by:

$$S=\left[Ca^{2+}\right]=\left[CO_3^{2-}\right]+\left[HCO_3^-\right]+\left[H_2CO_3\right]$$

$$=\left[CO_3^{2-}\right]\left\{1+\frac{\left[H^+\right]}{K_{a_2}}+\frac{\left[H^+\right]^2}{K_{a_1}.K_{a_2}}\right\}$$

$$=\frac{K_s}{\left[Ca^{2+}\right]}\left\{1+\frac{\left[H^+\right]}{K_{a_2}}+\frac{\left[H^+\right]^2}{K_{a_1}.K_{a_2}}\right\}$$

or

$$\left[Ca^{2+}\right]^2=K_s\left\{1+\frac{\left[H^+\right]}{K_{a_2}}+\frac{\left[H^+\right]^2}{K_{a_1}.K_{a_2}}\right\}$$

$$S=\left[Ca^{2+}\right]=\sqrt{K_s\left\{1+\frac{\left[H^+\right]}{K_{a_2}}+\frac{\left[H^+\right]^2}{K_{a_1}.K_{a_2}}\right\}}$$

Because the sum between the curly brackets {} is larger than 1, the solubility of $CaCO_3$ will indeed increase with increasing acidity of the solution.

An analogous method can be used to calculate the solubility of for instance metal sulfides as a function of the pH of the solution. In analytical chemistry, this pH dependence of the solubility of metal sulfides (in general denoted as MS(s)) is used for the separation of metal ions from a mixture. The following equilibriums must be considered:

$MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$ $\quad K_{sp}=\left[M^{2+}\right]\left[S^{2-}\right]$

$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$ $\quad K_{a_1}=\frac{\left[H^+\right]\left[HS^-\right]}{[H_2S]}$

$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$ $\quad K_{a_2}=\frac{\left[H^+\right]\left[S^{2-}\right]}{\left[HS^-\right]}$

A combination of the expressions for K_{a_1} and K_{a_2} gives, after rearrangement:

$$\left[S^{2-}\right]=\frac{K_{a_1}.K_{a_2}.[H_2S]}{\left[H^+\right]^2} \qquad (4)$$

and the solubility S of the metal sulfide MS is given by:

$$S=\left[M^{2+}\right]=\frac{K_{sp}}{\left[S^{2-}\right]}=\frac{K_s\cdot\left[H^+\right]^2}{K_{a_1}.K_{a_2}.[H_2S]}$$

For H_2S, the maximum solubility in water equals 0.1 $\frac{\text{mol}}{\text{L}}$. When an aqueous solution of a metal ion is saturated with H_2S, then $[H_2S]$ = 0.1 $\frac{\text{mol}}{\text{L}}$ and constant and the solubility of MS is determined by its value of K_{sp} and the solution pH. For separation of metal ions in a mixture, the pH of the solution must be adjusted so that the sulfide of one metal precipitates completely while the sulfides of the other metal ion remain dissolved.

Worked example 6

A solution contains 0.050 $\frac{\text{mol}}{\text{L}}$ Pb^{2+} and 0.050 $\frac{\text{mol}}{\text{L}}$ Fe^{2+} at pH = 0.52. This solution is saturated with H_2S until $[H_2S]$ = 0.10 $\frac{\text{mol}}{\text{L}}$. Predict which cation will precipitate.

$$K_{sp_{PbS}}=7.9\times10^{-29}$$

$$K_{sp_{FeS}}=4.0\times10^{-19}$$

Answer

Strategy: a precipitate will form when $Q > K_{sp}$

$Q = [M^{2+}][S^{2-}]$ with $[S^{2-}] = f([H_2S][H^+])$

⇨ Calculate concentration of sulphide ion first

1) $H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$

$$K_{a_1}=\frac{\left[H^+\right]\left[HS^-\right]}{[H_2S]}=1.1\times10^{-7}$$

2) $HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$

$$K_{a_2}=\frac{\left[H^+\right]\left[S^{2-}\right]}{\left[HS^-\right]}=1.0\times10^{-14}$$

A combination of the expressions for K_{a_1} and K_{a_2} gives, after rearrangement:

$$\left[S^{2-}\right]=\frac{K_{a_1}.K_{a_2}.[H_2S]}{\left[H^+\right]^2}$$

pH = 0.52 ⇨ $[H^+] = 0.30\,\dfrac{\text{mol}}{\text{L}}$

$[H_2S] = 0.10\,\dfrac{\text{mol}}{\text{L}}$

$$\Rightarrow \left[S^{2-}\right] = \frac{\left(1.1\times10^{-7}\right)\left(1.0\times10^{-14}\right)(0.01)}{(0.30)^2} = 1.2\times10^{-21}$$

Q for both cations?

$Q_{PbS} = [Pb^{2+}][S^{2-}] = (0.050)(1.2\times10^{-21}) = 6.0\times10^{-23} > K_{sp_{PbS}} = 7.9\times10^{-29}$

$Q_{FeS} = [Fe^{2+}][S^{2-}] = (0.050)(1.2\times10^{-21}) = 6.0\times10^{-23} < K_{sp_{FeS}} = 4.0\times10^{-19}$

PbS will precipitate, Fe^{2+} stays in solution!

4 Equilibriums with Complex Ions

In complex ions, a central metal cation is covalently bound (coordinated) to a number of **ligands** (either neutral molecules or negative ions). Examples are $Ag(NH_3)_2^{+}$, $CdCl_4^{2-}$, $Cu(NH_3)_4^{2+}$, $Zn(OH)_4^{2-}$, $Fe(CN)_6^{3-}$, ... The number of ligands that is directly attached to the metal ion is called the **coordination number**.

According to lewis-acid-base theory, the complex ion is formed by a combination reaction between the cation that acts as an electron pair acceptor and the ligands that act as electron pair donors. In aqueous solutions the metal ions can be considered as complex ions in which the metal ion is attached to a number of water molecules that act as ligands, e.g. $Ni(H_2O)_6^{2+}$ (aq). This complex ion is also hydrated. Because the exact number of water molecules that is bound is usually unknown, these complex ions are denoted as **M^{n+}(aq)**.

When ligands are added to the solution that form stronger covalent bonds with the cation than water, the water molecules can be displaced.

$$Cu(H_2O)_4^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 4\ H_2O(vl)$$

This reaction can be simplified to:

$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

The formation of a complex ion occurs in several subsequent steps.

$$Ag^{+}(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^{+}(aq)$$

with $K_1 = \frac{\left[\mathrm{Ag(NH_3)^+}\right]}{\left[\mathrm{Ag^+}\right]\left[\mathrm{NH_3}\right]}$

$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

with $K_2 = \frac{\left[\mathrm{Ag(NH_3)_2^+}\right]}{\left[\mathrm{Ag(NH_3)^+}\right]\left[\mathrm{NH_3}\right]}$

The equilibrium constants for the formation of metal complexes from their constituent metal ions and ligands are called **stability constants**.

When we consider the global equilibrium

$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

Then the global equilibrium condition is given by:

$$\beta_2 = K_1.K_2 = \frac{\left[\mathrm{Ag(NH_3)_2^+}\right]}{\left[\mathrm{Ag^+}\right]\left[\mathrm{NH_3}\right]^2}$$

with β_2 the global stability constant.

Worked example 7

Calculate the equilibrium concentration of Zn^{2+}-ions when 50.0 mL of a $2.0\times10^{-3}\ \frac{\text{mol}}{\text{L}}$ $Zn^{2+}(aq)$ solution is mixed with 25.0 mL of a $0.15\ \frac{\text{mol}}{\text{L}}$ $NH_3(aq)$ solution.

$\beta_4\ (Zn(NH_3)_4^{2+}) = 7.8\times10^8$

Answer

Strategy:

1. Calculate the initial concentrations of zinc ions and ammonia. Because $\beta_4 \gg 1$ this reaction will go to completion.
2. Calculate the concentrations of the Zn^{2+}-ions from the equilibrium with $Zn(NH_3)_4^{2+}$

1. $Zn^{2+}(aq)$: $c = 1.33\times10^{-3}\ \frac{\text{mol}}{\text{L}}$; $NH_3(aq)$: $c = 5\times10^{-2}\ \frac{\text{mol}}{\text{L}}$ (global volume = 75 mL)

Reaction: $Zn^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Zn(NH_3)_4{}^{2+}(aq)$

$\frac{mol}{L}$	Zn^{2+}	NH_3	$Zn(NH_3)_4{}^{2+}$
Initial	1.33×10^{-3}	5.0×10^{-2}	-
Δ	-1.33×10^{-3}	$-4\times1.33\times10^{-3}$	$+1.33\times10^{-3}$
Equilibrium	-	4.468×10^{-2}	1.33×10^{-3}

2. Equilibrium from the complex $Zn(NH_3)_4{}^{2+}$

Reaction: $Zn(NH_3)_4{}^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + 4\ NH_3(aq)$

$\frac{mol}{L}$	$Zn(NH_3)_4{}^{2+}$	Zn^{2+}	NH_3
Initial	1.33×10^{-3}	-	4.468×10^{-2}
Δ	$-x$	$+x$	$+4x$
Equilibrium	$1.33\times10^{-3}-x$	x	$4.468\times10^{-2}+4x$

$$K=\frac{1}{\beta_4}=\frac{1}{7.8\times10^{8}}=1.28\times10^{-9}=\frac{\left[Zn^{2+}\right]\left[NH_3\right]^4}{\left[Zn\left(NH_3\right)_4{}^{2+}\right]}=\frac{x.\left(4.468\times10^{-2}+4x\right)^4}{\left(1.33\times10^{-3}-x\right)}$$

x can be neglected for the expressions between brackets

⇨ $x = 4.2\times10^{-7}\ \frac{mol}{L}$

$[Zn(NH_3)_4{}^{2+}]_{final} = 1.33\times10^{-3}\ \frac{mol}{L}$

$[Zn^{2+}]_{final} = 4.2\times10^{-7}\ \frac{mol}{L}$

$[NH_3]_{final} = 4.468\times10^{-2}\ \frac{mol}{L}$

4.1 Influence of Complex Formation on the Solubility

Following Le Chatelier's principle, the solubility of a slightly soluble salt will increase when a ligand is added to the solution that preferentially forms a complex ion with the cation.

AgCl is a slightly soluble salt. In the presence of NH_3 ,the Ag^+-ion can form the complex ion $Ag(NH_3)_2{}^+$. The following equilibriums need to be considered :

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

$$K_{sp} = \left[Ag^+\right]\left[Cl^-\right] = 1.8 \times 10^{-10}$$

(b) $Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

$$\beta_2 = \frac{\left[Ag\left(NH_3\right)_2^+\right]}{\left[Ag^+\right]\left[NH_3\right]^2} = 1.7 \times 10^7$$

When NH_3 is added, reaction (b) will occur and $[Ag^+]$ will decrease. As a consequence equilibrium (a) will shift to the right : AgCl(s) dissolves.

For the global reaction

$AgCl(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) + Cl^-(aq)$

We then have: $$K = K_{sp}.\beta_2 = \frac{\left[Ag\left(NH_3\right)_2^+\right]}{\left[Ag^+\right]\left[NH_3\right]^2} = 3.1 \times 10^{-3}$$

Worked example 8

Calculate the solubility of AgBr(s) in a $1.0 \frac{mol}{L}$ solution of $Na_2S_2O_3(aq)$.

$$K_{sp_{AgBr}} = 5.0 \times 10^{-13}$$

$\beta_2(Ag(S_2O_3)_2{}^{3-}) = 4.7 \times 10^{13}$

Answer

Equilibriums: $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ K_{sp}

$Ag^+(aq) + 2\ S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq)$ β_2

Global reaction: $AgBr(s) + 2\ S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) + Br^-(aq)$ K

$$K = K_{sp} \times \beta_2 = \frac{\left[Ag\left(S_2O_3\right)_2^{3-}\right]\left[Br^-\right]}{\left[S_2 0_3^{2-}\right]^2} = 23.5$$

$$AgBr(s) \quad + \quad 2\,S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) \quad + Br^-(aq)$$

$\frac{\text{mol}}{\text{L}}$	AgBr	$S_2O_3^{2-}$	$Ag(S_2O_3)_2^{3-}$	Br^-
Initial	↘	1.0	-	-
Δ	$-x$	$-2x$	$+x$	$+x$
Equilibrium	↘	$1.0-2x$	x	x

$$K=\frac{\left[Ag\left(S_2O_3\right)_2^{3-}\right]\left[Br^-\right]}{\left[S_2O_3^{2-}\right]^2}=23.5=\frac{x^2}{(1.0-2x)^2}$$

⇨ $x = 0.453\ \frac{\text{mol}}{\text{L}} = [Ag(S_2O_3)_2^{3-}]_{eq} = [Br^-]_{eq} = S_{AgBr}$

In 1 L, it is possible to dissolve 0.453 mole of AgBr(s) in the presence of $1.0\frac{\text{mol}}{\text{L}}$ $Na_2S_2O_3(aq)$, this corresponds with (approximately) 85g.

The concentration of Ag^+ can be calculated from $K_{sp_{AgBr}}$ or from $\beta_2(Ag(S_2O_3)_2^{3-})$

From $K_{sp_{AgBr}}$: $\left[Ag^+\right]=\dfrac{K_{sp}}{\left[Br^-\right]}=\dfrac{5.0\times10^{-13}}{0.453}=1.1\times10^{-12}\,\dfrac{\text{mol}}{\text{L}}$

From $\beta_2(Ag(S_2O_3)_2^{3-})$: $\left[Ag^+\right]=\dfrac{\left[Ag\left(S_2O_3\right)_2^{3-}\right]}{\beta_2\left[S_2O_3^{2-}\right]^2}=\dfrac{0.453}{(4.7\times10^{13})(0.093)^2}=1.1\times10^{-12}\,\dfrac{\text{mol}}{\text{L}}$

4.2 Complex Ions of Amphoteric Hydroxides

Amphoteric hydroxides are compounds that are slightly soluble under their hydroxide form. However, when an extra amount of a strong acid or a strong base is added to the solution, they readily dissolve.

$Al(OH)_3$ is a slightly soluble hydroxide.

$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$ (a)

When a strong acid is added, a neutralization reaction will proceed:

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

So equilibrium (a) shifts to the right: $Al(OH)_3(s)$dissolves.

When a strong base is added, a complex is formed:

$Al(OH)_3(s) + OH^-(aq, added) \rightarrow Al(OH)_4^-(aq)$

so $Al(OH)_3$ will also dissolve.

All hydroxides will dissolve when a strong acid is added, but only the amphoteric hydroxides will dissolve in alkaline medium.

The most important amphoteric hydroxides are:

	Also denoted as
$Zn(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$	$ZnO_2^{2-}(aq)$ (zincate ion)
$Sn(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons Sn(OH)_4^{2-}(aq)$	$SnO_2^{2-}(aq)$ (stannate ion)
$Pb(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons Pb(OH)_4^{2-}(aq)$	$PbO_2^{2-}(aq)$ (plumbate ion)
$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$	(aluminate ion)
$Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$	$CrO_2^{2-}(aq)$ (chromate(III)-ion)

Based on the amphoteric nature of these hydroxides, it is possible to separate metal ions in a mixture.

A solution contains $Fe^{3+}(aq)$ and $Al^{3+}(aq)$. When a strong base, e.g. NaOH (aq) is gradually added, then first $Fe(OH)_3(s)$ will precipitate, later on also $Al(OH)_3(s)$ will be formed.

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

$Al^{3+}(aq) + 3\ OH^-(aq) \rightarrow Al(OH)_3(s)$

When extra NaOH (aq) is added to the solution, only the $Al(OH)_3$ will dissolve again.

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

Note

Many metal hydroxides that are represented here as mononuclear (1 metal ion per formula unit), are in reality polynuclear (more than one metal ion per formula unit). Also polynuclear hydroxo complex exist, e.g. $[Sn_2(OH)_2]^{2+}$, $[Cu_3(OH)_4]^{2-}$, ...

Worked example 9

You are given the following solutions (without label): $ZnCl_2(aq)$; $Al(OH)_4^-(aq)$; $Bi(NO_3)_3(aq)$ and the following testing reagents: HCl(aq); $Pb(NO_3)_2$; $NH_3(aq)$ and NaOH(aq).

Develop a strategy to identify the 3 solutions.

Answer

	HCl(aq)	$Pb(NO_3)_2(aq)$	$NH_3(aq)$	NaOH(aq)
$ZnCl_2(aq)$	soluble	↘	↘ , soluble	↘ , soluble
$Al(OH)_4^-(aq)$	↘ , soluble	soluble	soluble	soluble
$Bi(NO_3)_3(aq)$	soluble	soluble	↘	↘

1. Add $Pb(NO_3)_2$ ⇨ identification of $ZnCl_2(aq)$
2. Add $NH_3(aq)$ or NaOH(aq)⇨identification of $Bi(NO_3)_3(aq)$
3. $Al(OH)_4^-(aq)$: no precipitation (or identification with HCl(aq)).

5 Exercises[1]

1

Calculate the pH of a buffer that contains 0.55 $\frac{mol}{L}$ formic acid (HCOOH) and 0.63 $\frac{mol}{L}$ sodium formiate ($HCOO^-Na^+$).

2

A solution contains 0.20 $\frac{mol}{L}$ of a weak acid (HA) and 0.15 $\frac{mol}{L}$ of its conjugate base (A^-) and has pH = 3.35. When 1.50 mmole NaOH is added to 500 mL of this buffer solution, what is the final pH?

3

A buffer is prepared by mixing 184 mL 0.442 $\frac{mol}{L}$ HCl and 500 mL 0.400 $\frac{mol}{L}$ NaOAc.

a. What is the pH of the solution?

---

[1] For pK_a values: see chapter" acids and bases", for solubility constants: see table 6 in this chapter, for stability constants: see text.

b. How many grams of KOH must be added to this mixture if we want the pH to change with 0.15 log units?

4

Calculate the pH of a phosphate buffer, prepared by dissolving 0.800 mol NaOH in 500 mL 1.0 $\frac{\text{mol}}{\text{L}}$ H_3PO_4.

5

Calculate the pH during the titration of 20.00 mL 0.100 $\frac{\text{mol}}{\text{L}}$ propane carbonic acid (butyric acid) ($CH_3CH_2CH_2COOH$) with 0.100 $\frac{\text{mol}}{\text{L}}$ NaOH(aq) after addition of the following amounts of titrant:

a. 0.00 mL

b. 10.00 mL

c. 15.00 mL

d. 19.00 mL

e. 19.95 mL

f. 20.00 mL

g. 20.05 mL

h. 25.00 mL

6

Calculate the pH and the number of mL 0.0372 $\frac{\text{mol}}{\text{L}}$ NaOH(aq) needed to reach the EP for titration of:

a. 42.2 mL 0.0520 $\frac{\text{mol}}{\text{L}}$ HOAc

b. 18.9 mL 0.0890 $\frac{\text{mol}}{\text{L}}$ H_2SO_3

7

Sketch the titration curve(pH versus volume titrant) for the titration of

a. 20.0 mL 0,050 $\frac{\text{mol}}{\text{L}}$ arsenic acid (H_3AsO_4) with 0.050 $\frac{\text{mol}}{\text{L}}$ NaOH (aq)

b. 20.0 mL 0.050 $\frac{\text{mol}}{\text{L}}$ sodium glycinate ($H_2N\text{-}CH_2\text{-}COO^{-}Na^{+}$) with 0.05 $\frac{\text{mol}}{\text{L}}$ HCl (aq)

Glycine: K_a of the COOH-group = 4.47 x 10^{-3} ; K_b of the NH_2-group = 6.03 x 10^{-5}.

8

An amount of a monoprotic weak acid is dissolved in water and titrated with 0.125 $\frac{\text{mol}}{\text{L}}$ NaOH (aq). When 2.00 mL of titrant is added, the pH is 6.912. The EP is reached with 16.00 mL of titrant. Calculate K_a for this acid.

9

The solubility of $Ag_2Cr_2O_7$ at 15 °C equals 8.3 x 10^{-3} g/100 mL. Calculate K_{sp}.

10

Calculate the solubility (in mol.L^{-1}) of $Ca(IO_3)_2$ in

a. 0.060 $\frac{\text{mol}}{\text{L}}$ $Ca(NO_3)_2$

b. 0.060 $\frac{\text{mol}}{\text{L}}$ $NaIO_3$

K_{sp} ($Ca(IO_3)_2$) equals 7.1 x 10^{-7}

11

A solution is 0.15 $\frac{\text{mol}}{\text{L}}$ in Pb^{2+}(aq) and 0.20 $\frac{\text{mol}}{\text{L}}$ in Ag^{+}(aq). When solid Na_2SO_4 is slowly added, what will precipitate the first (neglect the change of volume when the solid is added): Ag_2SO_4 or $PbSO_4$? After that, Na_2SO_4 is further added until also the second cation precipitates. What is, at that time, the concentration of the first cation in solution?

12

Calculate the solubility (in mol.L^{-1}) of MnS in water at 25 °C and pH = 5.00, taking into account that the sulfide ion can hydrolyse in water.

13

A solution is 0.080 $\frac{\text{mol}}{\text{L}}$ in Ca^{2+} and 0.060 $\frac{\text{mol}}{\text{L}}$ in Mg^{2+} ions. Is it possible to precipitate 99,9 % of the $CaCO_3$ without the formation of $MgCO_3$?

14

Fe^{3+}(aq) forms a complex with SCN^-(aq).

Fe^{3+}(aq) + SCN^-(aq) $\rightleftharpoons$ $Fe(SCN)^{2+}$(aq) with K_1 for $Fe(SCN)^{2+}$ = 8.9 x 10^2.

Calculate $[Fe^{3+}]$ when 500 mL 1.5 x 10^{-3} $\frac{\text{mol}}{\text{L}}$ $Fe(NO_3)_3$(aq) is added to 500 mL 0.20 $\frac{\text{mol}}{\text{L}}$ KSCN(aq).

15

Calculate the solubility of AgBr in 1.0 $\frac{\text{mol}}{\text{L}}$ NH_3.

16

A phosphate and a carbonate buffer keep the pH of blood at 37°C at a value of 7.4. What are the most important phosphate and carbonate species at that pH? Calculate the [base form] / [acid form] for every buffer.

6 Answers

1

3.80

2

3.36

3

a. pH = 4.91

b. 0.87 g KOH

4

7.39

5

a. 2.91

b. 4.81

c. 5.29

d. 6.09

e. 7.41

f. 8.76

g. 10.10

h. 12.05

6

a. pH = 8.54 ; 59.0 mL

b. pH = 4.53 en 45.2 mL at 1st EP; pH = 9.69 and 90.4 mL at 2nd EP

7

Arsenic acid		**Sodium glycinate**	
Volume OH^- added (mL)	pH	Volume HCl added (mL)	pH
0	1.84	0	11.23
10	2.22	10	9.78
20	4.59 = EP1	20	6.06 = EP1
25	6.48	25	2.83
30	6.69	30	2.35
40	9.09 = EP2	40	2.18 = EP2
45	10.74	50	2.15
60	11.58 = EP3		
70	11.74		
90	12.13		

8

$K_a = 1.74 \times 10^{-8}$

9

$K_{sp} = 2.84 \times 10^{-11}$

10

a. $1.7 \times 10^{-3}\ \frac{\text{mol}}{\text{L}}$

b. $2.0 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}$

11

$PbSO_4$; $8.3 \times 10^{-5}\ \frac{\text{mol}}{\text{L}}$

12

$5.8 \times 10^{-2}\ \frac{\text{mol}}{\text{L}}$

13

yes

14

$8.4 \times 10^{-6}\ \frac{\text{mol}}{\text{L}}\ \text{Fe}^{3+}$

15

$3.0 \times 10^{-3}\ \frac{\text{mol}}{\text{L}}$

16

$H_2PO_4^{-}$, HPO_4^{2-} and HCO_3^{-}

$$\frac{\left[\text{HPO}_4^{2-}\right]}{\left[\text{H}_2\text{PO}_4^{-}\right]}=1.55\ ,\ \frac{\left[\text{HCO}_3^{-}\right]}{\left[\text{H}_2\text{CO}_3\right]}=11$$