Chem Factsheet

www.curriculum-press.co.uk Number 86

Deprotonation (Acid-Base Reactions)

To succeed in this topic you need to understand:
- the Brønsted-Lowry theory of acids and bases (Factsheet 25);
- the basics of transition elements and complex ions (Factsheet 28);
- salt hydrolysis (Factsheet 85).

After working through this Factsheet you will:
- have a more extensive knowledge of deprotonation reactions (Factsheet 46);
- be able to describe what is observed when solutions containing each of the following cations:
  Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}
  is reacted with each of the following reagents:
  NaOH(aq)
  NH_3(aq)
  Na_2CO_3(aq)
- understand the chemistry of each reaction in terms of deprotonation, ligand substitution or precipitation.

> ***Exam Hint** - You may be asked to describe what you would observe when any of the three reagents is added to a solution containing any of these cations, and then explain the chemistry.*
> *To describe observations accurately, it is important that you have either carried out the tests yourself or seen them demonstrated by a teacher.*

What exactly is a deprotonation reaction?
- M^{2+} and M^{3+} cations exist in solution as aqua-complexes; $[M(H_2O)_6]^{2+}$ or $[M(H_2O)_6]^{3+}$.
- Nearly all such cations form precipitates of metal hydroxides when treated with OH^-(aq), NH_3(aq) or CO_3^{2-}(aq). (M^{2+}(aq) with CO_3^{2-}(aq) is an exception.)
- In these reactions the hydrated metal cation loses one or more protons to the reagent. For this reason, they are termed *deprotonation* reactions.
- The hydrated metal cation behaves as an acid on the Brønsted-Lowry theory, i.e. a proton donor. OH^-, NH_3 or CO_3^{2-} behaves as a base, i.e. proton acceptor.
- Consequently, the changes can also be referred to as *acid-base reactions*.

Cations with dilute NaOH(aq)

> **Practical 1 - Metal salt solutions with dilute NaOH(aq)**
> Carry out the following experiment on each of the cations Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.
> - Pour into a test tube, to a depth of about 2 cm, a salt solution containing the cation under investigation.
> - Add dilute aqueous sodium hydroxide *dropwise*, with shaking, until a precipitate is formed.
> - Record the colour of this precipitate.
> - Continue to add the reagent, with further shaking, until it is eventually present in excess.
> - Record whether or not the precipitate dissolves and, if so, what colour solution is formed.

Table 1 shows the precipitates that are formed with *limited* amounts of NaOH(aq).

Table 1 - Some insoluble metal hydroxides

Cation	Formula of precipitate	Colour
Al^{3+}(aq)	$Al(OH)_3$	White
Cr^{3+}(aq)	$Cr(OH)_3$	Grey-green
Fe^{2+}(aq)	$Fe(OH)_2$	Green*
Fe^{3+}(aq)	$Fe(OH)_3$	Brown
Co^{2+}(aq)	$Co(OH)_2$	Blue
Ni^{2+}(aq)	$Ni(OH)_2$	Green
Cu^{2+}(aq)	$Cu(OH)_2$	Blue

* On standing, this precipitate changes colour, first to bottle-green and then to brown, because of aerial oxidation.

> *In all cases deprotonation occurs.Protons are transferred successively from coordinated water molecules to hydroxide ions. This gives, initially, hydroxo-complex ions in solution, and finally molecules of solid, hydrated metal hydroxides.*

Ionic equations can be written for each stage, e.g.

$[Al(H_2O)_6]^{3+}(aq) + OH^-(aq) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_2O(l)$ ....(1)

$[Al(OH)(H_2O)_5]^{2+}(aq) + OH^-(aq) \rightleftharpoons [Al(OH)_2(H_2O)_4]^{+}(aq) + H_2O(l)$ ....(2)

$[Al(OH)_2(H_2O)_4]^{+}(aq) + OH^-(aq) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + H_2O(l)$.....(3)

> ***Remember** - When writing the formulae of complex ions with two sorts of ligands, anionic ligands (e.g. OH^-) are put before molecular ligands (e.g. H_2O).*

Bearing in mind that aluminium salts are extensively hydrolysed in solution (Factsheet 85), the first of these equations can be written as follows:

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

For examination purposes, an overall equation is generally sufficient:

$$[Al(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + 3H_2O(l)$$

> ***Exam Hint** - Do not write:*
>
> $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$
>
> *Equations of this sort represent* precipitation reactions*, i.e. those brought about by an attraction between oppositely charged ions in solution. For the formation of insoluble metal hydroxides, this is quite simply wrong.*

With excess NaOH(aq)

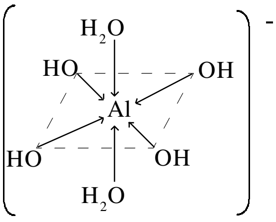
Practical 1 shows that precipitates formed with dilute NaOH(aq) **may** dissolve in excess reagent.

> *For a metal oxide or hydroxide to dissolve in alkali, it must be* amphoteric, *i.e. it must have both basic and acidic character.*
> *The only metal hydroxides from Table 1 which dissolve in excess dilute NaOH(aq) are $Al(OH)_3$ and $Cr(OH)_3$.*
>
> ***Note** - Some other hydroxides, notably $Fe(OH)_2$, $Fe(OH)_3$, $Co(OH)_2$ and $Cu(OH)_2$, will dissolve in **concentrated** NaOH(aq).*

Aluminium hydroxide dissolves in excess dilute NaOH(aq) to give a colourless solution of sodium diaquatetrahydroxoaluminate(III), commonly called 'sodium aluminate'. The reaction is a deprotonation that follows logically from Reactions (1), (2) and (3):

$$[Al(OH)_3(H_2O)_3](s) + OH^-(aq) \rightleftharpoons [Al(OH)_4(H_2O)_2]^-(aq) + H_2O(l) \text{ ....(4)}$$

Fig. 1 The diaquatetrahydroxoaluminate(III) ion



> ***Exam Hint** - Do not confuse complex aluminates with simple aluminates. Complex aluminates, such as $Na[Al(OH)_4(H_2O)_2]$, exist in solution only. On evaporation of the solution, water is lost: first, solvent water, then coordinated water, and finally H_2O between OH groups. This leaves a solid residue of the simple salt, $NaAlO_2$.*

If aluminium hydroxide is treated with concentrated NaOH(aq), deprotonation goes to completion:

$$[Al(OH)_3(H_2O)_3](s) + 3OH^-(aq) \rightleftharpoons [Al(OH)_6]^{3-}(aq) + 3H_2O(l)$$

Chromium(III) hydroxide is more susceptible than aluminium hydroxide to attack by NaOH(aq), and gives a green solution containing an equilibrium mixture of $[Cr(OH)_4(H_2O)_2]^-$, $[Cr(OH)_5(H_2O)]^{2-}$ and $[Cr(OH)_6]^{3-}$ even with dilute NaOH(aq).

> ***Exam Hint** - Do not confuse green chromate(III) solutions with the more common yellow solutions of chromate(VI) ions, CrO_4^{2-}*

Reverse changes

> *All the above reactions are reversible (notice the two half-arrows in the equations) and can be reversed by adding an acid. $H^+(aq)$ ions from the acid remove $OH^-(aq)$ ions ($H^+ + OH^- = H_2O$) and hence disturb the equilibria to the left hand side. Eventually, the original hydrated cation is reformed.*

> **Practical 2 - Reversing the changes**
> Add excess NaOH(aq) to a solution of an aluminium salt and then add a dilute acid, dropwise with shaking, to the resultant aluminate(III) solution. Notice the formation of a white precipitate of aluminium hydroxide, which dissolves in excess acid.
> Repeat the experiment with a solution of a chromium(III) salt.

Cations with dilute NH_3(aq)

> **Practical 3 - Metal salt solutions with dilute NH_3(aq)**
> Repeat Practical 1 with the same salts as before, but with dilute aqueous ammonia instead of NaOH(aq).

Practical 3 shows that, with a limited amount of reagent, precipitates are formed which, in all cases, appear similar to those formed with dilute NaOH(aq).

> *With a limited amount of dilute NH_3(aq), hydrated cations behave exactly as they do with NaOH(aq). The same precipitates (Table 1) are formed.*

Again, deprotonation (acid-base) reactions occur, the only difference being that the base is the NH_3 molecule instead of the OH^- ion, e.g.

$$[Al(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$$

With excess NH_3(aq)

Some metal hydroxides dissolve in excess dilute NH_3; some do not. **Those which dissolve are not the same as those that dissolve in dilute NaOH(aq).**

> *Metal hydroxides which dissolve in aqueous ammonia do so, not because NH_3 is a base (it is a much weaker base than OH^-), but because it is a ligand, which can coordinate to cations to give soluble ammonia complexes called* ammines.

Ammine formation is largely restricted to d-block elements towards the right of the Periodic Table. On progressing from left to right across the first series of d-block elements, cations become smaller and the density of positive charge on their surfaces ('surface charge density') becomes greater. They therefore exert a stronger attraction for NH_3 molecules, and ammines are formed more readily.

> ***Exam Hint** - Do not confuse ammines with amines.*
> *Ammines are complex ions or salts formed by the coordination of ammonia to cations of d-block elements.*
> *Amines are organic derivatives of ammonia.*

For practical purposes, there is a cut-off line between iron and cobalt:

Sc Ti V Cr* Mn Fe	Co Ni Cu Zn
Hydroxides are insoluble in dilute NH_3(aq).	Hydroxides dissolve in dilute NH_3(aq).
← Ammines are not formed.	Ammines are formed. →

> * $Cr(OH)_3$ is partially soluble in **concentrated** NH_3(aq) to give a violet solution containing the complex ion $[Cr(NH_3)_6]^{3+}$.

Table 2 shows the formulae and colours of the ammines that are formed.

Table 2 - Some common ammines

Cation	Formula	Colour
Co^{2+}	$[Co(NH_3)_6]^{2+}$	Pale red-brown
Ni^{2+}	$[Ni(NH_3)_6]^{2+}$	Blue
Cu^{2+}	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Dark blue
Zn^{2+}	$[Zn(NH_3)_4]^{2+}$	Colourless

Ammines are formed by ligand substitution; **not deprotonation**. The reactions can be represented by the following type of equation:

$$[Co(OH)_2(H_2O)_4](s) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 2OH^-(aq) + 4H_2O(l)$$

> ***Exam Hint -*** *You are more likely to be asked for an equation for the* overall *change, e.g.*
>
> $[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$

The ammines of cobalt and copper need more detailed study.

Cobalt

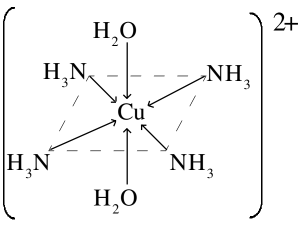
The pale red-brown solution of hexaamminecobalt(II) ions darkens on standing because of aerial oxidation:

$$\underset{\text{Pale red-brown solution}}{[Co(NH_3)_6]^{2+}(aq)} \rightarrow \underset{\text{Dark brown solution}}{[Co(NH_3)_6]^{3+}(aq)} + e^-$$

Copper

The hexaamminecopper(II) ion, $[Cu(NH_3)_6]^{2+}$, is formed only with liquid ammonia. The common ammine is $[Cu(NH_3)_4(H_2O)_2]^{2+}$; Fig. 2.

Fig. 2 The tetraamminediaquacopper(II) ion



> ***Exam Hint -*** *Do not describe the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion as 'square planar'. It is true that the four NH_3 molecules lie at the corners of a square with Cu^{2+} at the centre, but the H_2O molecules, above and below the plane but relatively distant from it, should not be ignored. The ion therefore has a distorted octahedral structure.*

> **Practical 4 -**
> **Preparation of tetraammine copper(II) sulphate-1-water**
> Add aqueous ammonia, until in excess, to an aqueous solution of copper(II) sulphate.Then add ethanol to precipitate $[Cu(NH_3)_4]SO_4.H_2O$, filter off the crystals and allow them to dry at room temperature.
>
> Afterwards, leave the crystals exposed to the atmosphere for a few days and note any change in their appearance. Try to explain this.

Cations with $Na_2CO_3(aq)$

> ***Exam Hint -*** *Reactions of cations with $Na_2CO_3(aq)$ may not be in your specification. If in doubt, check with your teacher.*

> **Practical 5 - Metal salts solutions with $Na_2CO_3(aq)$**
> Repeat Practical 1 with the same salts as before, but with sodium carbonate solution instead of sodium hydroxide. If there is effervescence, collect the gas in a squeezed-out teat pipette and bubble it slowly through a small amount of limewater in an ignition tube.

Practical 5 shows that, in all cases, precipitates are formed, but the observations (Table 3) are quite different from those with both NaOH(aq) and $NH_3(aq)$.

Table 3 - Cations with $Na_2CO_3(aq)$

Cation	Observation(s)	Product(s)
$Al^{3+}(aq)$	White precipitate + effervescence	$Al(OH)_3 + CO_2$
$Cr^{3+}(aq)$	Grey-green precipitate + effervescence	$Cr(OH)_3 + CO_2$
$Fe^{2+}(aq)$	Pale green precipitate*	$FeCO_3$
$Fe^{3+}(aq)$	Brown precipitate + effervescence	$Fe(OH)_3 + CO_2$
$Co^{2+}(aq)$	Blue precipitate	$CoCO_3$
$Ni^{2+}(aq)$	Green precipitate	$NiCO_3$
$Cu^{2+}(aq)$	Blue precipitate	$CuCO_3$

* On standing, this precipitate changes colour, first to bottle-green and then to brown, because of aerial oxidation.

A glance at Table 3 shows that what happens with Na_2CO_3 depends on whether the cation is of the kind M^{2+} or M^{3+}.

> *M^{2+} cations form metal carbonates.*
> *M^{3+} cations form metal hydroxides + carbon dioxide.*

$M^{2+}(aq)$

Metal carbonates are formed in precipitation reactions; not deprotonation. The general equation is:

$$M^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MCO_3(s)$$

$M^{3+}(aq)$

These ions are more acidic than $M^{2+}(aq)$ ions (Factsheet 85) and, with CO_3^{2-} ions, undergo deprotonation reactions. The simplest general equations you can write to show the formation of both a metal hydroxide and carbon dioxide are as follows:

$$[M(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [M(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

$$[M(OH)(H_2O)_5]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow [M(OH)_3(H_2O)_3](s) + H_2O(l) + CO_2(g)$$

> ***Remember -*** *With $Na_2CO_3(aq)$:*
> *M^{2+} ions undergo precipitation reactions.*
> *M^{3+} ions undergo deprotonation.*

With excess $Na_2CO_3(aq)$

Practical 5 should have shown that, in all cases, no further changes occur.

> *Precipitates formed with $Na_2CO_3(aq)$* ***never*** *dissolve in excess reagent.*

Questions

1 Given NaOH(aq), but no other reagents, describe how you could distinguish between solutions of chromium(III) sulphate, iron(II) sulphate and nickel sulphate.

2 Solutions of sodium carbonate are strongly alkaline because of salt hydrolysis, i.e. $[OH^-(aq)] > [H^+(aq)]$. Why, therefore, is it wrong to represent the reaction between sodium carbonate and a solution of an aluminium salt by the equation:

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

3 Vanadium(III) salts dissolve in water to give green solutions containing the ion $[V(H_2O)_6]^{3+}(aq)$. Describe what you would expect to observe when each of the following reagents is added, until in excess, to a solution of a vanadium(III) salt. Write balanced ionic equations for all the reactions you describe.

(a) Dilute NaOH(aq)

(b) Dilute $NH_3(aq)$

4 Suggest two reasons why precipitates of metal hydroxides, formed by adding $Na_2CO_3(aq)$ to aqueous solutions of M^{3+} salts, never dissolve in excess reagent.

Answers

1 $Cr_2(SO_4)_3$ gives a green precipitate which dissolves in excess NaOH(aq) to give a green solution.

$FeSO_4$ gives a green precipitate, insoluble in excess reagent, which turns brown on standing in air.

$NiSO_4$ gives a green precipitate which is insoluble in excess reagent and which does not change colour on standing.

2 The equation should show not only the formation of a precipitate of aluminium hydroxide but also the evolution of carbon dioxide.

3 (a) Green precipitate, insoluble in excess dilute NaOH(aq):

$$[V(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [V(OH)_3(H_2O)_3](s) + 3H_2O(l)$$

(b) Green precipitate, insoluble in excess dilute $NH_3(aq)$:

$$[V(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightleftharpoons [V(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$$

4 CO_3^{2-} is a weaker base than OH^-, so further deprotonation cannot occur. Also, CO_3^{2-}, unlike NH_3, is not a ligand, so complexes similar to ammines cannot be formed.

Acknowledgements:** This Factsheet was researched and written by John Brockington.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***