Chem Factsheet

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Ions in solution II: The properties & reactions of transition metal ions in solution

To succeed in this topic you need to:-

- Be familiar with the electronic configurations of the first transition series elements
- Be familiar with the ability of these elements to exhibit variable oxidation states.
- Be familiar with the concept of dative covalent (coordinate) bonding.
- Be familiar with the Brønsted-Lowry and Lewis definitions of acids and bases.

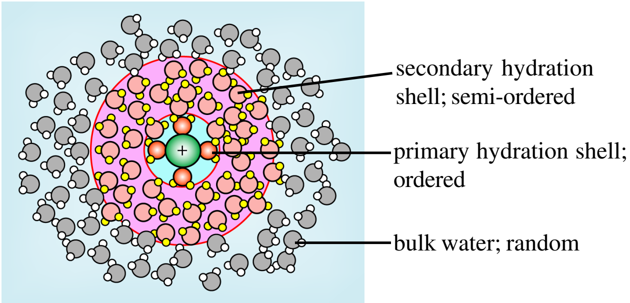
After working through this Factsheet you will:-

- Be familiar with the typical behaviour associated with a variety of transition element ions in solution.

Introduction

This Factsheet will present an overview of the behaviour of ions in solution.

Ions in Solution



For most simple ions in solution there are between four and eight water molecules held relatively tightly to the ion, forming the *primary hydration shell*. At a greater distance there is then a less tightly held group of water molecules, whose behaviour is nonetheless influenced by the presence of the ion, forming the *secondary hydration shell*. Water molecules further away from an ion than this simply behave as they would in pure water.

Transition Metal Complex Ions

The metal ions formed by the elements in the d-block of the Periodic Table are relatively small with high charge densities. Coupled with the incompletely filled outer d-subshell of such ions, this leads to a different kind of interaction with water molecules when salts of d-block elements dissolve in water compared to when Group I or II metal salts dissolve.

The d-block metal ions attract the water molecules (also some other molecules and anions - generally referred to as *ligands*), so strongly that dative covalent (coordinate) bonds form by donation of lone pairs from the water into vacant d-orbitals in the outer shell of the cation. This results in *complex ion* formation with a central metal cation attached by *dative covalent* bonds to the surrounding *ligand* molecules or ions. The electronegativity of the ligands attracts the bond electrons such that the metal cation is effectively neutral with the charge dispersed to the outside of the ion.

The complex ion is then itself surrounded by a *primary* and *secondary hydration shell* in the same way as for a simple ion.

The *co-ordination number* of a complex refers to the number of dative bonds formed by the central cation – normally 2, 4 or 6 – for example.

Co-ordination number 2: $[Ag(NH_3)_2]^+$, $[AgCl_2]^-$
Co-ordination number 4: $[CoCl_4]^{2-}$, $[PtCl_2(NH_3)_2]$
Co-ordination number 6: $[Cu(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$

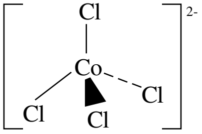
The overall charge of such complexes depends on the balance between the charge of the central cation and the charges, if any, of the ligands. Neutral ligands, such as H_2O and NH_3 have no effect on the overall charge while negative ligands such as Cl^- and CN^- cancel out some or all of the cation change and can form neutral or negative complexes.

Shapes of Complexes

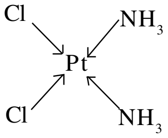
- 2 attached ligands give a *linear* complex - 180° bond angle.

  $H_3N{\rightarrow}Ag^+{\leftarrow}NH_3$

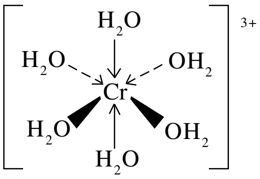
- 4 attached ligands give a *tetrahedral* complex – 109.5° bond angle



  (although some are *square planar* such as $[PtCl_2(NH_3)_2]$ and $[Ni(CN)_4]^{2-}$ - 90° bond angle)

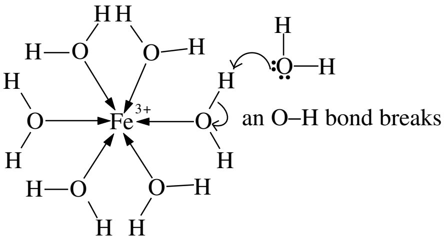


- 6 attached ligands give an *octahedral* complex - 90° bond angle.



Hydrolysis Reactions of Complex Ions

If the O–H bond in an aqua complex ion breaks then a hydrogen ion is released. This is more likely as the charge density of the central cation increases, as the higher the charge density the greater the polarising effect, which weakens the O–H bonds in the aqua ligands.



This type of reaction explains why solutions of salts of M^{3+} d-block metals are acidic, as the following equilibrium is established in aqueous solution.

$[M(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$ — (1)

e.g. $[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$
$K_a = 1.48\times10^{-3}$ mol dm^{-3}

A similar equilibrium is established for M^{2+} but the lower polarising power of the 2+ ion means that the proton-donating ability of the complex is greatly reduced and so the equilibrium lies much further to the left and the solution is only very weakly acidic, if at all!.

$[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5OH]^{+}(aq) + H_3O^+(aq)$ — (2)

e.g. $[Fe(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5OH]^{+}(aq) + H_3O^+(aq)$
$K_a = 1.82 \times 10^{-7}$ mol dm^{-3}

Reactions of Complex Ions with Alkali

In the presence of hydroxide ions [i.e. addition of NaOH(aq)], further proton donation is possible because the OH^- ions react with H_3O^+ ions in equilibria (1) or (2), "pulling" those equilibrium positions further to the right. This leads to the formation of precipitates of the metal hydroxides, the colours of which can often help with the identification of aqueous metal ions.

$[M(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + 2H_2O(l)$
$[M(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [M(H_2O)_3(OH)_3](s) + 3H_2O(l)$

e.g. $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$
Blue-green ppt. (gelatinous)

$[Co(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Co(H_2O)_4(OH)_2](s) + 2H_2O(l)$
Blue ppt.

$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Fe(H_2O)_4(OH)_2](s) + 2H_2O(l)$
Pale green ppt.

$[Ni(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Ni(H_2O)_4(OH)_2](s) + 2H_2O(l)$
Green ppt. (gelatinous)

$[Zn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Zn(H_2O)_4(OH)_2](s) + 2H_2O(l)$
White ppt.

$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Mn(H_2O)_4(OH)_2](s) + 2H_2O(l)$
Pale brown ppt.

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

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

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

In some cases, the higher polarising power of the central cation, especially for M^{3+} ions, makes further proton donation possible so that the precipitate re-dissolves.

e.g. $[Zn(H_2O)_4(OH)_2](s) + 2OH^-(aq) \rightleftharpoons [Zn(H_2O)_2(OH)_4]^{2-} + 2H_2O(l)$
Colourless solution

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

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

Reactions of Complex Ions with Carbonates

With carbonate ions, the greater charge density and acidity of M^{3+} ions compared with M^{2+} ions gives rise to very different behaviour. With the 2+ ions, a metal carbonate precipitates.

$[M(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons MCO_3(s) + 6H_2O(l)$

e.g. $[Fe(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons FeCO_3(s) + 6H_2O(l)$
Pale green ppt

$[Cu(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CuCO_3(s) + 6H_2O(l)$
Blue ppt

$[Co(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CoCO_3(s) + 6H_2O(l)$
Violet ppt

$[Zn(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons ZnCO_3(s) + 6H_2O(l)$
White ppt

However, with the 3+ ions, the solution is sufficiently acidic to displace carbon dioxide gas from the carbonate, resulting in precipitation of the metal hydroxide.

$2[M(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightleftharpoons 2[M(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$

e.g.
$2[Fe(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightleftharpoons 2[Fe(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$
Brown ppt

$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightleftharpoons 2[Al(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$
White ppt

$2[Cr(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightleftharpoons 2[Cr(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$
Green ppt

Unlike the addition of NaOH(aq), addition of excess aq carbonate does not result in dissolution of the hydroxides of aluminium and chromium. The basicity of the carbonate ion is too low to allow the continued proton transfer needed.

Reactions of Complex Ions with Aqueous Ammonia

The polarity of an ammonia molecule together with the lone pair on the nitrogen atom make it capable of acting both as a ligand in ligand-exchange reactions and also as a base.

When aqueous ammonia is gradually added to an aqueous solution of a transition metal salt the first stage involves the ammonia acting as a Brønsted-Lowry base, accepting protons from water ligands to form NH_4^+ ions. This leads to precipitation of the metal hydroxide [as above with NaOH(aq)].

$[M(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
$[M(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightleftharpoons [M(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$

e.g. $[Ni(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Ni(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
Green ppt

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
Blue ppt

$[Zn(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Zn(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
White ppt

$[Fe(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Fe(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
Pale green ppt

$[Mn(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Mn(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
Pale brown ppt

$[Co(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Co(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$
Blue ppt

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

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

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

Ammonia is not a strong enough base to enable any of the amphoteric hydroxides (Al and Cr) to re-dissolve by further proton donation, but *some* of the precipitates re-dissolve due to ligand exchange (in which case the ammonia now behaves as a Lewis base – electron pair donor). The exchange of water ligands for ammonia ligands may be complete or partial (e.g. Cu)

e.g. $[Co(H_2O)_6]^{2+}(aq) + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}(aq) + 6H_2O\,(l)$
Pale yellow soln.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O\,(l)$
Dark blue soln.

$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O\,(l)$
Violet soln.

$[Cr(H_2O)_6]^{3+}(aq) + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+}(aq) + 6H_2O\,(l)$
Purple soln.

A Level questions will, depending on your syllabus, expect you to remember some of these examples but it is very unlikely that you will need to produce a detailed explanation of why some of the precipitated hydroxides re-dissolve.

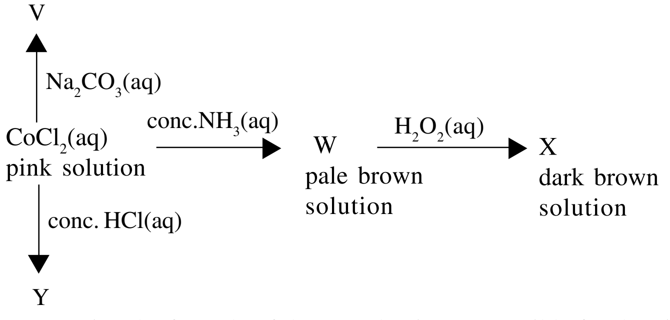
It does, in fact, depend on a balance between two competing equilibria.
e.g. taking the example of cobalt(II)
$[Co(H_2O)_6]^{2+}(aq) + 2NH_3 \rightleftharpoons [Co(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$ —(3)
(NH_3 acting as a Brønsted-Lowry base in an acid-base reaction)

$[Co(H_2O)_6]^{2+}(aq) + 6NH_3 \rightleftharpoons [Co(NH_3)_6](aq) + 6H_2O(l)$ ——(4)
(NH_3 acting as a Lewis base in a ligand exchange reaction)

In an excess of ammonia the position of the equilibrium [(4)] for the ligand exchange lies well to the right. This greatly reduces the concentration of $[Ni(H_2O)_6]^{2+}(aq)$ so, in accordance with Le Chatelier's principle, the position of equilibrium [(3)] for the acid-base reaction will shift to the left – dissolving the precipitate previously formed.

So, whether or not a precipitate re-dissolves in excess ammonia, depends on the relative positions of these equilibria. For the precipitate to re-dissolve, the ligand exchange equilibrium [(4)] must lie well to the right, while the acid-base equilibrium [(3)] must be easy to shift to the left.

Practice Questions



(a) Give the formula of the complex ion responsible for the pink colour in aqueous $CoCl_2$ and name its shape.
(b) Give the formula of the cobalt-containing compound V and describe its appearance.
(c) Write an equation for the reaction that takes place when the pink solution of $CoCl_2$ is converted into W.
(d) Give the formula of the cobalt-containing complex in X and state the role of the H_2O_2 in this reaction.
(e) Identify the cobalt-containing complex in the solution Y and explain why its co-ordination number is different from that in the pink solution of $CoCl_2$.

2. Which of the following reagents would enable you to separate iron(III) hydroxide from a mixture of iron(III) hydroxide and copper(II) hydroxide?
   A Dilute hydrochloric acid
   B Aqueous ammonia
   C Dilute nitric acid
   D Sodium hydroxide solution

3. This question is about some complex ions of several transition metals.
   (a) The transition metal rhodium forms the complex ion $[RhCl(NH_3)_5]^{2+}$.
   State the coordination number and the oxidation number of rhodium in $[RhCl(NH_3)_5]^{2+}$.
   (b) A student dissolved some cobalt(II) chloride crystals in water. A pink solution was formed.
   She then added concentrated hydrochloric acid to this solution. A blue solution was formed.
      (i) Give the formula of the complex ion in each solution.
      (ii) Write a balanced equation to illustrate the equilibrium that exists between these two complex ions in solution.
      (iii) The student added an excess of aqueous silver nitrate, $AgNO_3(aq)$, to the blue solution.
      A white precipitate formed and the solution turned pink. Suggest an explanation for these observations.

Answers

1. (a) $[Co(H_2O)_6]^{2+}$. Octahedral.

   (b) $CoCO_3$ Purple / violet solid (allow pink)
   (Allow pink precipitate)

   (c) $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$
   (Allow $[Co(NH_3)_5H_2O]^{2+}$)

   (d) $[Co(NH_3)_6]^{3+}$ Oxidising agent – changes Co(II) to Co(III).
   (Allow $[Co(NH_3)_5H_2O]^{3+}$)

   (e) $[CoCl_4]^{2-}$ Cl^- ligand too big to fit more than 4 round Co^{2+}
   (Allow Cl^- is bigger)

2. B – Only the copper(II) hydroxide will dissolve in the ammonia; forming $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$, so the iron(III) hydroxide can then be separated by filtration.

3. (a) Co-ordination number = 6
   Oxidation state = +3

   (b) (i) $[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$
      (ii) $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$

      (iii) White precipitate is silver chloride/AgCl
      Chloride ions are removed/chloride concentration reduced so equilibrium moves to the left/towards $[Co(H_2O)_6]^{2+}$

      Accept idea that adding aq silver nitrate adds water which pushes equilibrium to the left / toward $[Co(H_2O)_6]^{2+}$

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