Chem Factsheet

www.curriculum-press.co.uk Number 112

Acid Base Reactions of Transition Metal Complexes

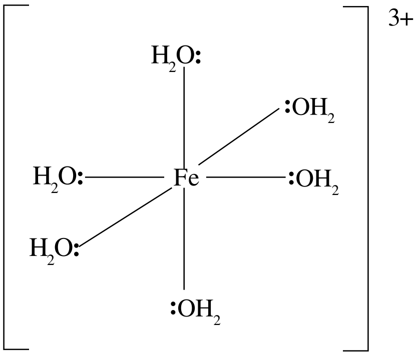
It is perhaps surprising at first sight that, whereas many common salts such as sodium chloride are neutral, solutions of transition metal ions are usually acidic. Like other acids, solutions of transition metal ion solutions contain H^+ ions and may react with bases, with carbonates to give carbon dioxide and even with reactive metals such as magnesium to give hydrogen.

Why are complexes of transition metals acidic?

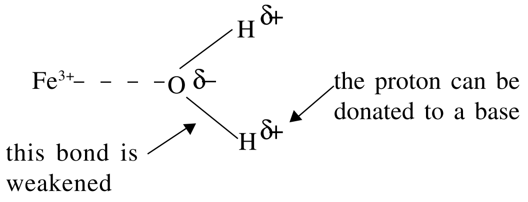
Recall that complex ions are formed by a central metal ion surrounded by several ligands. The ligands bind to the central metal ion by dative (co-ordinate) bonds. The lone pairs of electrons from the ligands are donated into the empty orbitals of the metal ion.

Ligands are molecules or ions which have one or more lone pairs of electrons which they can donate to a transition metal ion to form the dative bond. They are electron pair donors or Lewis bases. Water is a common ligand.

When transition metals ions are dissolved in water they form complex ions in which water is the ligand. For example, solutions of iron(III) salts contain the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$



Hexaaqua complexes of transition metal ions are *hydrolysed* in aqueous solution. This means that the co-ordinated water molecule ligands split up and donate protons to the solvent. This occurs because the central metal atom is small and highly charged. It polarises the co-ordinated water molecules and weakens the oxygen to hydrogen bond.



This process can be represented by the following sequence of equations. The hexaaquairon(III) ion,$[Fe(H_2O)_6]^{3+}$, donates a proton to a water molecule to form the hydrated proton H_3O^+.

e.g. $[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+$

acid — base

proton donor — proton acceptor

The $[Fe(H_2O)_6]^{3+}$ ion is behaving as an acid in the Lowry Bronsted sense of being a proton donor and the solvent water molecules behave as the base, the proton acceptor.

Notice that the Fe containing ion which is formed has one fewer positive charges because it has lost a proton. (This does not mean, of course, that its oxidation state has changed)

The reaction sequence continues with the ion $[Fe(H_2O)_5OH]^{2+}$ behaving as an acid and donating a proton to the solvent water molecule. However this process takes place to a much lesser extent than the first reaction.

$[Fe(H_2O)_5OH]^{2+} + H_2O \rightarrow [Fe(H_2O)_4(OH)_2]^+ + H_3O^+$ etc.

The extent to which hexaaqua ions are hydrolysed depends on the charge on the ion and on its size.

- Ions with a higher charge are more polarising than those with a smaller charge.
- Smaller ions are more polarising than larger ions.

Hexaaqua ions are therefore ***acidic*** in aqueous solution since they are acting as proton donors. The pH of the solution is related to the charge and size of the ion. As a rough guide, hexaaqua ions with a charge of 2+ have a pH of about 6; hexaaqua ions with a charge of 3+ have a pH of about 3.

$[M(H_2O)_6]^{2+}(aq) \rightarrow \cong pH\ 6$
$[M(H_2O)_6]^{3+} \rightarrow pH \cong 3$

Reaction of Transition Metal Complexes with Strong Bases

Hydroxide Ions

Hydroxide ions are strongly basic and so have a strong tendency to remove protons from the acidic hexaaqua ions. All solutions of transition metal ions (2+ and 3+) react with hydroxide ions to give a precipitate of the hydroxide; some transition metal ions form a precipitate which re-dissolves in excess of the hydroxide.

Ions in oxidation state 2

$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(H_2O)_4(OH)_2 + 2H_2O$
pale green solution → green precipitate

$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(H_2O)_4(OH)_2 + 2H_2O$
pink solution → blue precipitate (turns pink on standing)

$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(H_2O)_4(OH)_2 + 2H_2O$
blue solution → blue precipitate

Mn^{2+} and Ni^{2+} behave in a similar way. Mn^{2+} give a buff coloured precipitate which darkens on standing due to oxidation; Ni^{2+} gives a green precipitate.

Ions in oxidation state 3

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow Cr(H_2O)_3(OH)_3 + 3H_2O$
ruby solution → green precipitate

The precipitate dissolves in excess OH^- to give the hexahydroxy complex:

$Cr(H_2O)_3(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-} + 3H_2O$
green precipitate → deep green solution

$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow Fe(H_2O)_3(OH)_3 + 3H_2O$
violet → orange/brown precipitate

This precipitate does not re-dissolve

Aluminium, although not a transition metal, behaves like chromium:

$[Al(H_2O)_6]^{3+} + 3OH^- \rightarrow Al(H_2O)_3(OH)_3 + 3H_2O$
colourless solution → white precipitate

$Al(H_2O)_3(OH)_3 + 3OH^- \rightarrow [Al(OH)_6]^{3-} + 3H_2O$
white precipitate → colourless solution

Aluminium hydroxide and chromium hydroxide are said to be ***amphoteric*** since they will react both with acid (to give the hexaaqua ion) and strong base (to give the hexahydroxy chromium(III) ion or hexahydroxyaluminium(III) ion).

Reaction of Transition Metal Complexes with Weak Bases

Ammonia

Ammonia is a weak base. It removes protons from hexaaqua metal ions but to a lesser extent than the hydroxide ion. It always reacts with transition metal ions to give a precipitate of the hydroxide but it is not sufficiently basic to cause the precipitate to re-dissolve to form a soluble hydroxy complex. (However, it may react by a ligand exchange reaction to form a soluble complex.)

Ions in oxidation state 2

$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow Fe(H_2O)_4(OH)_2 + 2NH_4^+$
pale green solution → green precipitate

$[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow Co(H_2O)_4(OH)_2 + 2NH_4^+$
pink solution → blue precipitate

This blue precipitate then redissolves. This is because a ligand exchange reaction occurs to give the hexaammine cobalt(II) ion. This is not related to the acidity of the ion.

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$
pink solution → straw solution

This is then readily oxidised by oxygen from the air to hexaammine cobalt(III) ion

$[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + e$
straw solution → orange solution

$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(H_2O)_4(OH)_2 + 2NH_4^+$
blue solution → blue precipitate

The precipitate again dissolves because a ligand exchange reaction occurs to give the tetraamminecopper(II) ion

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
pale blue solution → deep blue solution

Mn^{2+} and Ni^{2+} behave in a similar way. Mn^{2+} gives a buff coloured precipitate which darkens on standing due to oxidation; Ni^{2+} gives a green precipitate which dissolves in excess ammonia to give a blue solution. This is due to a ligand exchange reaction.

Ions in oxidation state 3

$[Cr(H_2O)_6]^{3+} + 3NH_3 \rightarrow Cr(H_2O)_3(OH)_3 + 3NH_4^+$
ruby solution → green precipitate

The precipitate dissolves slowly in excess conc. NH_3 to give the hexaamine complex. This is again a ligand exchange reaction.

$[Cr(H_2O)_6]^{3+} + 6NH_3 \rightarrow [Cr(NH_3)_6]^{3+} + 6H_2O$
green solution → purple solution

$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow Fe(H_2O)_3(OH)_3 + 3NH_4^+$
violet solution → orange/brown precipitate

$[Al(H_2O)_6]^{3+} + 3NH_3 \rightarrow Al(H_2O)_3(OH)_3 + 3NH_4^+$
colourless solution → white precipitate

Reaction of Transition Metal Complexes with Weak Bases

Carbonate Ions

Carbonate ions are weakly basic.

Ions in oxidation state 2

Hexaaqua ions of transition metal ions in oxidation state 2 react with carbonate ions to give a precipitate of the carbonate. The carbonates do not redissolve in excess.

$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow FeCO_3 + 6H_2O$
green solution — green precipitate

$[Co(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CoCO_3 + 6H_2O$
pink solution — pink precipitate

$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CuCO_3 + 6H_2O$
blue solution — green precipitate

The hexaaqua 2+ ion solutions are *not* sufficiently acidic to displace carbon dioxide.

Ions in oxidation state 3

Hexaaqua ions of transition metal ions in oxidation state 3 are more acidic than those in oxidation state 2. They are sufficiently acidic to decompose the carbonate to carbon dioxide and water and they give a precipitate of the ***metal hydroxide***.

$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Fe(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$
violet solution — orange brown precipitate

$2[Cr(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Cr(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$
ruby solution — green precipitate

$2[Al(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Al(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$
colourless solution — white precipitate

Questions

1. Give an approximate value for the pH of the following solutions. Select your answer from the following choices: approximately 6, approximately 3 or approximately neutral. Assume that all the solutions are 1M.
   (a) chromium(III) sulphate (b) iron(II) chloride
   (c) potassium chloride (d) copper(II) sulphate
   (e) cobalt(II) sulphate (f) iron(III) chloride

2. A solution containing nickel(II) ions (such as nickel(II) sulphate) reacts with a solution of sodium hydroxide to give a green precipitate of nickel(II) hydroxide. Write an equation for this reaction using $[Ni(H_2O)_6]^{2+}$ for the nickel(II) ion.

3. A solution containing manganese(II) ions (such as manganese(II) sulphate) reacts with a solution of ammonia to give a buff coloured precipitate of manganese(II) hydroxide. Write an equation for this reaction using $[Mn(H_2O)_6]^{2+}$ for the manganese(II) ion.

4. When iron(III) chloride reacts with sodium carbonate an orange/brown precipitate is seen and bubbles of gas are evolved. Explain these observations and write an equation for the reaction.

5. If sodium hydroxide is added slowly to a solution of aluminium sulphate, a white precipitate is formed which redissolves in excess sodium hydroxide to give a colourless solution. Explain these observations and write equations for the reactions. What would you expect to see if dilute hydrochloric acid were slowly added to the resulting solution? Write equations to explain the expected observations.

Answers

1. (a) approx. 3 (b) approx. 6 (c) approx. neutral
   (d) approx. 6 (e) approx. 6 (f) approx. 3

2. $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(H_2O)_4(OH)_2 + 2H_2O$

3. $[Mn(H_2O)_6]^{2+} + 2NH_3 \rightarrow Mn(H_2O)_4(OH)_2 + 2NH_4^+$

4. The hexaaquairon(III) ion is sufficiently acidic to decompose the carbonate ion to give carbon dioxide gas. The carbonate ion behaves as a base and removes protons from the hexaaquairon(III) ion to give iron(III) hydroxide $Fe(H_2O)_3(OH)_3$

   $2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Fe(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$

5. Addition of sodium hydroxide forms a white precipitate of aluminium hydroxide:

   $[Al(H_2O)_6]^{3+} + 3OH^- \rightarrow Al(H_2O)_3(OH)_3 + 3H_2O$
   colourless solution — white precipitate

   The precipitate redissolves in excess sodium hydroxide to give the aluminate ion:

   $Al(H_2O)_3(OH)_3 + OH^- \rightarrow [Al(OH)_4]^- + 3H_2O$
   white precipitate — colourless solution
   On addition of dilute acid, these reactions are reversed:

   The aluminate ion reacts with the acid to give a precipitate of aluminium hydroxide:

   $[Al(OH)_4]^- + H^+ + 2H_2O \rightarrow Al(H_2O)_3(OH)_3$
   colourless solution — white precipitate

   The aluminium hydroxide redissolves in excess of the acid to give the hexaaquaaluminium ion.

   $Al(H_2O)_3(OH)_3 + 3H^+ \rightarrow [Al(H_2O)_6]^{3+}$
   white precipitate — colourless solution

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