Acidity or hydrolysis reactions

Metal(II) ions in aqueous solution

When a metal(II) aqua-ion is placed in water, this equilibrium is set up:

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

A water molecule has been broken into OH^{-} and H^{+} ions, so the reaction is called a **hydrolysis** reaction. It is also called an **acidity** reaction because H_3O^{+} ions are produced.
The position of equilibrium lies to the left. K_a varies between 10^{-6} and 10^{-11}, producing a pH of about 6. Only about 1 in a million aqua-ions have undergone the hydrolysis reaction.

Further hydrolysis can occur, especially if a base is present:

$$[M(H_2O)_5(OH)]^{+} + H_2O \rightleftharpoons [M(H_2O]_4(OH)_2] + H_3O^{+}$$

Metal(III) ions in aqueous solution

When a metal(III) aqua-ion is placed in water, this equilibrium is set up:

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

K_a varies between 10^{-2} and 10^{-5}, producing a pH of about 3. About 1 in a thousand aqua-ions have undergone the hydrolysis reaction. Further hydrolysis can occur, especially if a base is present:

$[M(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [M(H_2O]_4(OH)_2]^{+} + H_3O^{+}$ … and …

$[M(H_2O)_5(OH)]^{3+} + H_2O \rightleftharpoons [M(H_2O]_3(OH)_3] + H_3O^{+}$

Note that for metal(IV) ions this stage goes to completion, producing a pH of less than 1, and that $[M(H_2O]6]^{4+}$ ions do not exist in solution – they hydrolyse to $[M(OH)_4]$.

Factors affecting the acidity of metal ions

Two factors affect the acidity of metal ions:

- the charge on the metal ion – acidity increases with charge
- the size of the metal ion – acidity decreases as size increases

The **charge:size ratio** can be used to predict the relative acidities of metal ions: highly charged, small cations are the strongest acids in aqueous solution. This is because the greater the power of the metal ion to attract electron density from the oxygen atom of a co-ordinated water molecule, the weaker the O–H bond of this molecule, and the easier it is to break so releasing an H^{+} ion.

Transition metal hydroxides

The final transition metal hydroxides have no charge, and are insoluble, and so appear as precipitates. You can write them as $M(OH)_2$ and $M(OH)_3$. However, $M(OH)_2$ do actually occur in the solid state, metal(III) hydroxides lose water on drying, and usually occur in the solid state as [MO(OH)]. For example, iron(III) hydroxide occurs as FeO(OH), which is "rust".

