

Soil pH

Acidity, alkalinity and pH

All aqueous solutions contain both hydrogen ions, $\text{H}^+(\text{aq})$, and hydroxide ions, $\text{OH}^-(\text{aq})$.

- Neutral solutions contain equal but tiny amounts of both $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. They are both about $1 \times 10^{-7} \text{ mol dm}^{-3}$.
- Acidic aqueous solutions contain $\text{H}^+(\text{aq})$, and negligible quantities of $\text{OH}^-(\text{aq})$.
- Alkaline aqueous solutions contain $\text{OH}^-(\text{aq})$, and negligible quantities of $\text{H}^+(\text{aq})$.

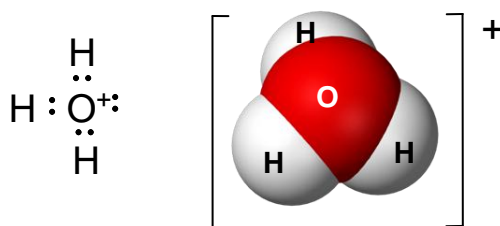


Figure 1 Electronic structure of the hydroxonium ion, H_3O^+ , a space-filling model of the ion.

Hydrogen ions, $\text{H}^+(\text{aq})$, are sometimes called hydroxonium ions, represented as $\text{H}_3\text{O}^+(\text{aq})$.

This is to make it clear that 'free' protons do not exist in aqueous solution. Nonetheless, $\text{H}^+(\text{aq})$ is still used commonly.

pH is related to the concentration of hydroxonium ions in solution:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})]$$

often written more simply as

$$\text{pH} = -\log_{10}[\text{H}^+]$$

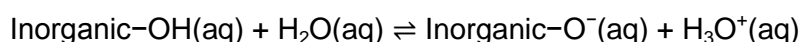
Note: To be accurate, $\text{pH} = -\log_{10}(a_{\text{H}^+})$

where a_{H^+} is the activity of hydrogen ions. It approximates to but is always slightly less than $[\text{H}^+]$. It is affected by the presence of other ions in solution.

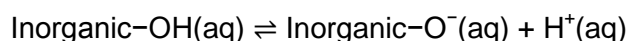
Soil particles and acidity

Soil particles are negatively charged. This is because of their structures.

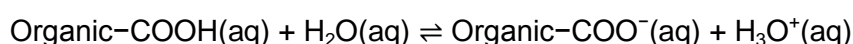
Giant lattices have to stop somewhere and so the surfaces of inorganic particles often have hydroxyl groups. These can act as proton donors to water molecules, leaving negatively charged sites:



often written more simply as:



Organic particles have, for example, carboxylic acid groups in them. These can also act as proton donors leaving negatively charged sites:



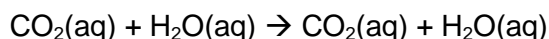
Often written more simply as:



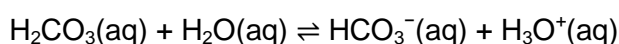
The reactions that happen at the surfaces of soil particles are examples of dynamic equilibrium and respond in the same way as any equilibrium reactions to changing conditions.

Rain and acidity

Plants need water and, depending on where and when the crops are being grown, much comes from rainfall. Rain is naturally acidic because it contains dissolved carbon dioxide.

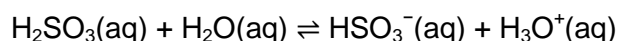


This solution is sometimes called carbonic acid and written as H_2CO_3 . Ionisation occurs and equilibrium is established:

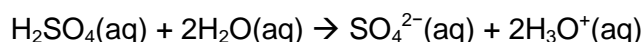


Gases such as sulfur dioxide and nitrogen dioxide may be present in air, formed when fossil fuels are burned. They also dissolve in water to give acidic solutions.

Sulfur dioxide, for example, dissolves in water to form sulphurous acid, $\text{H}_2\text{SO}_3(\text{aq})$. This is a weak acid (it does not ionise completely in water) and equilibrium is established as follows:



Sulfuric acid, $\text{H}_2\text{SO}_4(\text{aq})$, may also form in rainwater when sulfurous acid is oxidised. Sulfuric acid is a strong acid that ionises completely in water:



Rain containing acids formed by dissolving carbon dioxide, sulfur dioxide and oxides of nitrogen is often called acid rain.

Dissolved salts: ammonium compounds

Ammonium salts are often used as nitrogen-containing fertilisers. Ammonium salts of strong acids dissolve to give aqueous solutions of their ions:

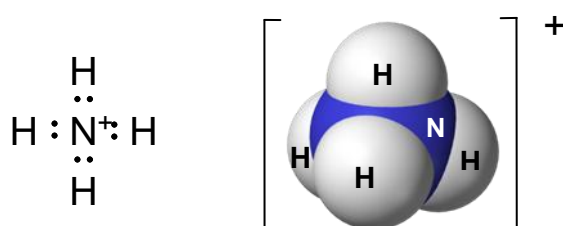
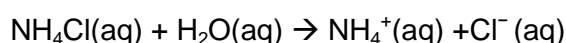
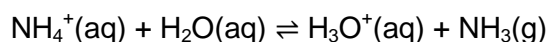


Figure 2 Lewis (electronic) structure of the ammonium ion, NH_4^{+} , a space-filling model of the ion.

The ammonium ion is a proton donor and a proton is transferred to a water molecule, producing an acidic solution.



The equilibrium constant, K , is given by:

$$K = \frac{[H_3O^+][NH_3]}{[NH_4^+][H_2O]}$$

However, since water is in a very large excess its concentration remains constant.

So the equation becomes:

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

where K_a is the acid equilibrium constant. It equals $5.7 \times 10^{-10} \text{ mol dm}^{-3}$.

The value of K_a tells us that position of equilibrium is well to the right, in other words that far more protons are bonded to ammonium molecules forming ammonium ions than are bonded to water molecules as hydroxonium ions. The equilibrium is dynamic.

To make the number easier to represent, pK_a values are often given rather than K_a values.

$$pK_a = -\log_{10}K_a$$

Therefore, the pK_a value for NH_4^+ is 9.2

Dissolved salts: metal salts

Sometimes metal salts are added to soil, for example, to provide essential micronutrients. These tend to be added in very small quantities, however.

Other sources of metal salts found in soil include water waste rock from mines.

The British Geological Survey has said “*Historically, mining to extract metals has produced wastes which contain toxic chemicals. For example, water leaching from wastes may be highly acidic or alkaline and might carry many toxic metals, such as lead, copper, zinc and cadmium. Such wastes often pose a significant risk to the health of vegetation, animals and humans. In most developed countries, such as the UK, the hazards represented by these wastes mainly reflect historical mining activities.*”

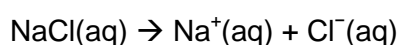


Figure 3 The Rio Tinto in Spain has been polluted by iron compounds leached from neighbouring disused iron mines.

Non-toxic metals such as iron may also be leached from mine wastes.

Another source of metal ions is sea water. Soil salinity poses a problem for growers. It occurs mainly in arid or semi-arid areas as a result of weathering of minerals found in rocks. They may also be present due to excessive use of, for example, potassium fertilisers.

Salts of group 1 and group 2 metals dissolve in water to give neutral solutions. For example:



Their hydrated ions do not have distinct structures and the hydrated ions are poor proton donors. As a result, solutions of these ions are more or less neutral.

However, some other metal salts change the pH of water when they dissolve. They are usually salts of transition metals, though aluminium salts also dissolve to give acidic solutions.

Hydrated metal ions such as $\text{Fe}^{3+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ have a metal ion surrounded by six water molecules in an octahedral arrangement. This is often represented as $[\text{M}(\text{H}_2\text{O})_6]^{x+}$. They are proton donors and the higher the charge on the metal ion, the stronger donors they are.

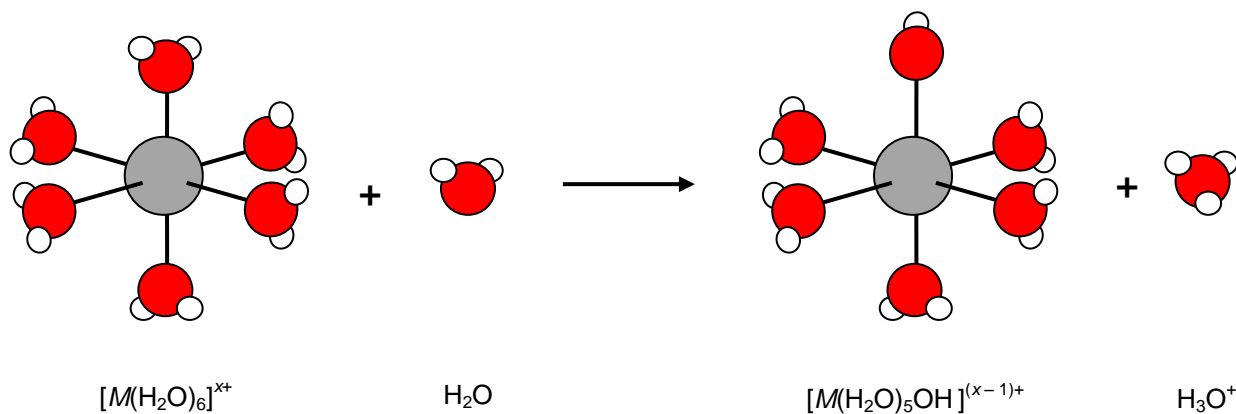
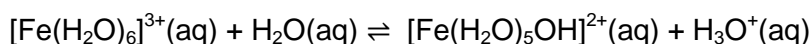


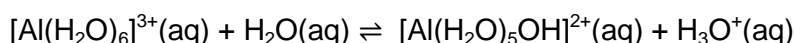
Figure 4 Solutions of hexa-aquometal ions are acidic. The hexa-aquometal ion is a proton donor, transferring a proton to a water molecule to produce a hydroxonium ion.

For example:



$$K_a = \frac{[\text{H}_3\text{O}^+][[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}]}{[[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})]} = 6.3 \times 10^{-3} \text{ mol dm}^{-3}$$

Therefore, the $\text{p}K_a$ value for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is 2.2.



$$K_a = \frac{[\text{H}_3\text{O}^+][[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}]}{[[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})]} = 7.9 \times 10^{-6} \text{ mol dm}^{-3}$$

Therefore, the $\text{p}K_a$ value for $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is 5.1.

Finding out

To put these values for the two examples above into perspective compare them with the $\text{p}K_a$ values for some commonly used weak acids. Examples could be:

- monobasic acids: benzoic acid, ethanoic acid, hydrogensulfate ion, phenol;
- dibasic acids (two $\text{p}K_a$ values): carbonic acid, maleic acid (*cis*-but-2-enedioic acid), oxalic acid (ethanedioic acid).