

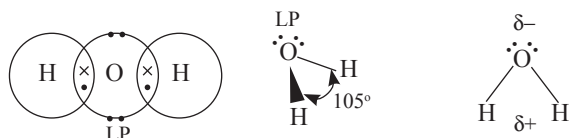
## Water as a Reagent

### Structure of water

As with all molecules, its basic properties, behaviour and reactions are determined by its structure. Thereafter, its reactivity can be adjusted by varying reaction conditions such as temperature, pressure and use of a catalyst. Temperature and pressure in particular will control whether water reacts in the liquid or gaseous state.

The water molecule ( $\text{H}_2\text{O}$ ) consists of two hydrogen atoms covalently bonded to an oxygen atom as shown in the dot-and-cross diagram (Fig. 1). The O-H bonds are relatively strong with a mean bond enthalpy of  $+465 \text{ kJ mol}^{-1}$ .

Figure 1

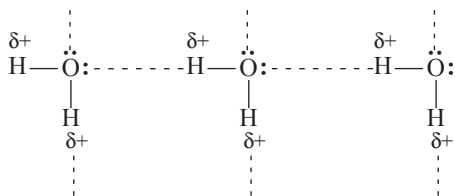


The molecule is actually v-shaped as shown because the four electron pairs around the oxygen atom arrange in a basic 3D tetrahedral shape. However, the two lone pairs (LP) repel each other more strongly than the bond electron pairs repel each other resulting in the 2 O-H bonds being pushed together slightly and the usual tetrahedral angle being reduced from the tetrahedral  $109.5^\circ$  to  $105^\circ$ .

Oxygen is the second most electronegative atom in the Periodic Table resulting in the O-H bonds being polar and, because of the v-shape, there is an overall molecular dipole with the O having a  $\delta^-$  charge and the H atoms a  $\delta^+$  charge.

In fact, the polarity of the molecule is sufficiently high for the intermolecular forces between water molecules to be classified as hydrogen bonds (see Fig. 2) rather than weaker dipole-dipole forces.

Figure 2



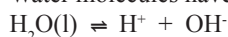
These hydrogen bonds give rise to a lot of water's surprisingly high physical properties for such a small molecule. Melting point, boiling point, viscosity and surface tension are examples of this.

The reactions and reactivity of water are controlled by some or all of the aspects of structure described so far – the strength of the O-H bond, the polarity of the O-H bonds and the overall molecule and the presence of lone pair electrons are particularly important.

### 1. Water as an acid

A Bronsted-Lowry acid is defined as a **proton ( $\text{H}^+$ ) donor**.

Water molecules have very little tendency to donate protons.



Pure water contains about one ionised molecule in every million molecules. In other words, it is a very weak acid.

However, in the presence of a weak base such as ammonia or an amine, water acts as a Bronsted-Lowry acid by donating a proton to bond to the ammonia or amine by forming a coordinate (dative) bond with the N atom via its lone pair.

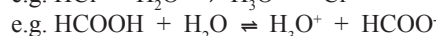


Hence, aqueous solutions of ammonia and amines are weakly alkaline because of the free  $\text{OH}^-$  ions.

### 2. Water as a base

A Bronsted-Lowry base is defined as a **proton ( $\text{H}^+$ ) acceptor**.

In the presence of a stronger acid water will act as a Bronsted-Lowry base by accepting a proton from the acid molecule, forming a coordinate bond between the proton and a lone pair on the O atom of water resulting in the formation of the hydronium ion (also called a hydroxonium ion),  $\text{H}_3\text{O}^+$ .



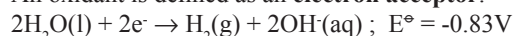
Hence, aqueous solutions of such substances have acid pH values because of the free  $\text{H}_3\text{O}^+$  ions.

Note: Water has 2 lone pairs on the O atom but it is very unlikely that both will be used to accept protons to give  $\text{H}_4\text{O}_2^+$ . This is because, once formed by the acceptance of the first proton, the  $\text{H}_3\text{O}^+$  ion will repel the second  $\text{H}^+$  ion.

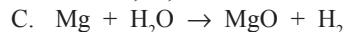
Note: 1. and 2. show that water can act as both an acid and a base depending on circumstances. As a result it is described as amphiprotic.

### 3. Water as an oxidant

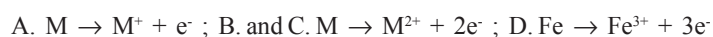
An oxidant is defined as an **electron acceptor**.



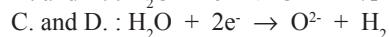
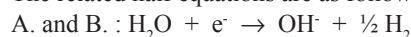
Water can act as an oxidant when reacted with a strong reductant ( $E^\ominus$  more negative than  $-0.83\text{V}$ ). The reactions with more reactive metals such as group 1 metals (Li, Na, K etc), group 2 metals (Mg, Ca, Sr, Ba etc) and iron are examples.



The metal atoms are oxidised as they lose electrons to form metal ions. The related half equations are as follows.



The water molecules cause the oxidation by accepting electrons to form either hydroxide ( $\text{OH}^-$ ) or oxide ( $\text{O}^{2-}$ ) ions and hydrogen molecules. The related half equations are as follows.



In all cases the oxidation states of the metals become more positive (oxidation) while the hydrogen atoms in water change their oxidation states from +1 to 0 (reduction).

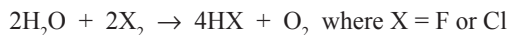
Note: Magnesium and iron only react with water in the form of steam. The associated higher temperature results in the formation of oxide rather than hydroxide.

#### 4. Water as a reductant

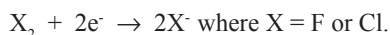
A reductant is defined as an **electron donor**.



Water can act as a reductant when reacted with a strong oxidant ( $E^\circ$  more positive than +1.23V). The reactions with the halogens  $\text{F}_2$  and  $\text{Cl}_2$  in the presence of UV light are good examples.



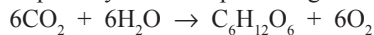
The halogen atoms (F or Cl) are reduced to halide ions ( $\text{F}^-$  or  $\text{Cl}^-$ ) by gaining electrons from water.



Note:  $\text{Cl}_2$  without UV light and  $\text{Br}_2$  undergo disproportionation instead where the halogen is simultaneously reduced to halide and oxidised to halate(I).



Note: water can also be seen as the reductant in the vital natural process of photosynthesis to produce glucose and oxygen.



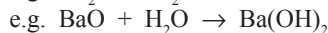
Water Reduces The Oxidation State Of Carbon From (+4) In  $\text{CO}_2$  To (0) In  $\text{C}_6\text{H}_{12}\text{O}_6$ .

#### 5. Water in hydrolysis reactions

“Hydro” implies water and “lysis” implies splitting. Hence, hydrolysis reactions involve water as a reactant where it results in being split into parts, usually H and OH, without redox reactions occurring. They are very common and very diverse reactions.

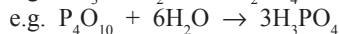
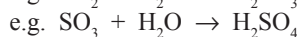
##### (a) Hydrolysis of metal oxides

Oxides of metals with soluble hydroxides react with water to form those hydroxides. This includes group 1 oxides and the oxides of group 2 from Ca to Ba.



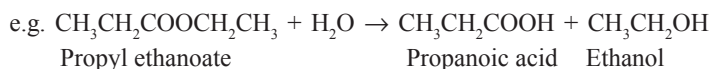
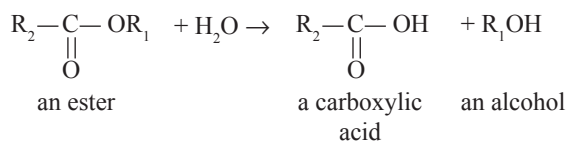
##### (b) Hydrolysis of non-metal oxides

Oxides of non-metals typically react with water to form an acid.

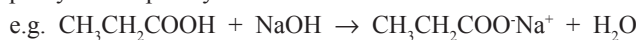


##### (c) Hydrolysis of esters

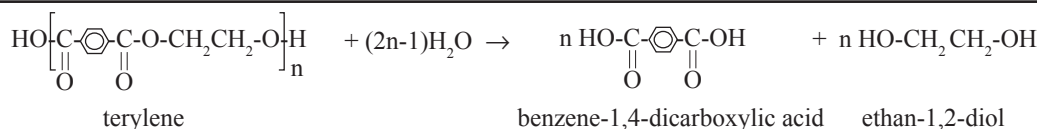
Esters react with hot water to form a carboxylic acid and an alcohol.



These hydrolyses are catalysed by dilute acid (e.g.  $\text{H}_2\text{SO}_4$ ) or alkali (e.g. NaOH). When alkali is used the carboxylic acid product is converted partly or completely to the salt.



Similar hydrolysis applies to polyesters such as Terylene, although the reaction is much slower for such large molecules.

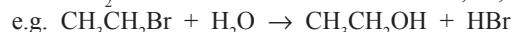


Note: Ester hydrolysis is particularly important in the case of polyesters. Such synthetic polymers are, unlike polyalkenes, biodegradable and this reduces problems of landfill disposal significantly.

However, leaching of the hydrolysis products from landfill is a problem. Overall, it is better to use the materials as fuels or feedstock.

##### (d) Hydrolysis of haloalkanes

Haloalkanes are hydrolysed to alcohols.



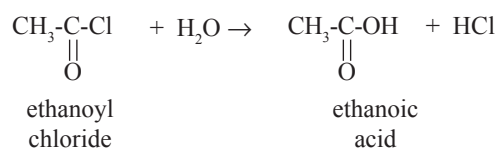
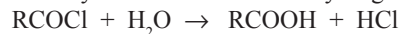
This involves the water, by way of its lone pairs, acting as a nucleophile resulting in a nucleophilic substitution. The reaction becomes significantly faster if X is Br rather than Cl or I rather than Br. This is because the C-X bond becomes weaker in the order C-Cl > C-Br > C-I. Hence, reflux is needed for Cl and Br compounds whereas I compounds react quite rapidly at room temperature.

These hydrolyses are also catalysed by acid or alkali. In the case of alkali, the acidic HX will be converted to a salt.

Note: This reaction is often used as a test to distinguish chloro-, bromo- and iodoalkanes. After hydrolysis using NaOH solution and acidification with nitric acid, the reaction mixture is treated with silver nitrate solution. The colour of the silver halide precipitate formed will show the type of haloalkane present. Chloroalkanes → white AgCl; bromoalkanes → cream AgBr; iodoalkanes → yellow AgI.

##### (e) Hydrolysis of acyl chlorides

Acyl halides (usually chlorides;  $\text{RCOCl}$ ) are hydrolysed instantly and vigorously by cold water producing the corresponding carboxylic acid and fumes of hydrogen chloride.



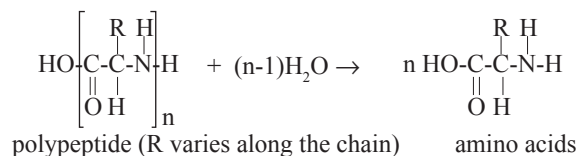
Again the water acts as a nucleophile resulting in an overall nucleophilic substitution. However, the reaction mechanism is referred to as a nucleophilic addition-elimination.

Note: This reaction is often used as a test for acyl chlorides since the vigorous reaction and “fuming” is unique to acyl chlorides.

##### (f) Hydrolysis of polypeptides and polyamides

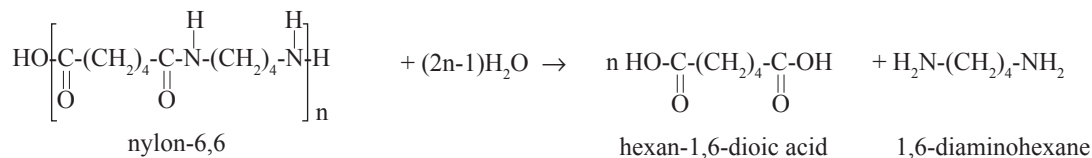
Polypeptides are polymers derived by polymerisation of amino acids. In fact, they provide the primary structure of a protein. Polyamides (e.g. nylon) are co-polymers of a dicarboxylic acid and a diamine. Polypeptides and polyamides are related in that the linkage groups are  $-\text{CO}-\text{NH}-$  in both. It is this group that undergoes hydrolysis, releasing either the individual amino acids or the dicarboxylic acid and the diamine.

##### (i) Polypeptide hydrolysis



Note: The hydrolysis of polypeptides is the reaction occurring during the digestion of protein-rich foods in the alimentary canal. The hydrolysis is catalysed by various digestive enzymes. Acid catalysed hydrolysis of polypeptides is the first step in protein structure determination. The polypeptide chain is broken down into its component amino acids which are then identified and counted by chromatography.

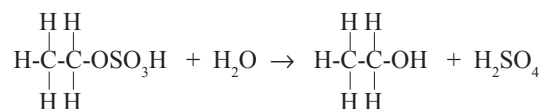
## (ii) Polyamide hydrolysis



Note: Polyamide hydrolysis is particularly important because, like polyesters, it makes such plastics biodegradable, reducing problems of landfill disposal significantly. Such hydrolysis and biodegradation is slow but catalysed by acid.

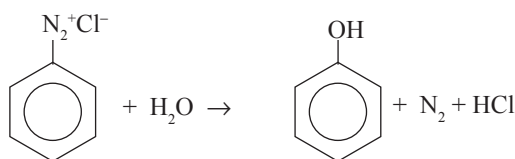
## (g) Hydrolysis of ethyl hydrogen sulphate

Ethyl hydrogen sulphate ( $\text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$ ) is formed when ethene undergoes electrophilic addition with concentrated sulphuric acid. This is then hydrolysed by addition of water to produce the very useful molecule, ethanol.



## (h) Hydrolysis of benzene diazonium chloride

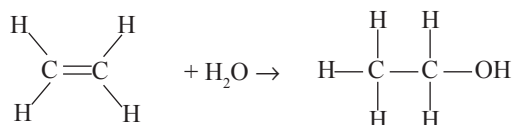
Benzene diazonium chloride ( $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ ) is kinetically stable in acid solution at temperatures below  $5^\circ\text{C}$ . As temperature increases, it is hydrolysed to form phenol (hydroxybenzene,  $\text{C}_6\text{H}_5\text{OH}$ ) and evolve nitrogen gas. This hydrolysis is a "nuisance" if the aim is to make azo-dyes from the diazonium compound but, if the aim is to introduce an OH group into a benzene ring, it is very useful.

**6. Water as a hydrating agent**

A hydration reaction is a reaction involving the addition of a water molecule to an organic molecule to form a single new product.

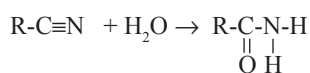
## (a) Hydration of alkenes

Alkenes are hydrated by water in the form of steam using concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ ) catalyst at  $300^\circ\text{C}$  to form alcohols. For example, ethene is converted to ethanol.

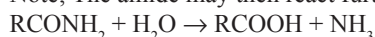


## (b) Hydration of nitriles

Nitriles ( $-\text{CN}$ ) are hydrated by refluxing with an acid catalyst to form amides.



Note; The amide may then react further to form a carboxylic acid by hydrolysis.

**7. Water as a catalyst**

Water is created explosively when hydrogen reacts with oxygen.  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

This reaction is even faster in the presence of a small amount of water. Hence, water catalyses its own production – it acts as an autocatalyst! Hopefully, this Chem Factsheet has provided an insight into the versatility and usefulness of water as a reagent, not just as a solvent!

*Acknowledgements:* This Factsheet was researched and written by Mike Hughes.

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