Module 2: The Acidic Environment

Supplementary material

(The material under this heading is not part of the HSC syllabus but is included because of its interest and close relation to syllabus material.)

1. Amphoteric and amphiprotic

Of these two terms only amphiprotic is used in the HSC syllabus. However amphoteric is often used in chemistry texts (probably more frequently than amphiprotic) so what is the difference between them?

The standard definitions are as follow: amphoteric substances are ones that can react with both acids and bases; for example ZnO, Al₂O₃, NaHCO₃, KH₂PO₄.

 $\begin{array}{l} \mathsf{ZnO} + 2\mathsf{HCI} \rightarrow \mathsf{ZnCI}_2 + \mathsf{H}_2\mathsf{O} \\ \mathsf{ZnO} + 2\mathsf{NaOH} \rightarrow \mathsf{Na}_2\mathsf{ZnO}_2 \text{ (sodium zincate)} + \mathsf{H}_2\mathsf{O} \\ \mathsf{NaHCO}_3 + \mathsf{HCI} \rightarrow \mathsf{NaCI} + \mathsf{H}_2\mathsf{O} + \mathsf{CO}_2(g) \\ \mathsf{NaHCO}_3 + \mathsf{NaOH} \rightarrow \mathsf{Na}_2\mathsf{CO}_3 + \mathsf{H}_2\mathsf{O} \end{array}$

Amphiprotic substances are ones that can act both as proton donors and as proton acceptors: for example $NaHCO_3$ (page 143) and KH_2PO_4 .

$$H_{2}PO_{4}^{-} + H_{2}O \rightleftharpoons H_{3}O^{+} + HPO_{4}^{2-}$$
$$H_{2}PO_{4}^{-} + H_{2}O \rightleftharpoons H_{3}PO_{4} + OH^{-}$$

Amphiprotic substances are therefore a sub-set of amphoteric substances: of the four amphoteric substances listed above, ZnO, Al_2O_3 , $NaHCO_3$, KH_2PO_4 , only the last two are also amphiprotic (ZnO, Al_2O_3 cannot act as proton donors – no protons to donate).

2. Amphoteric oxides

The common amphoteric oxides are ZnO, Al₂O₃, PbO, PbO₂, SnO, SnO₂, and Cr₂O₃. As just mentioned amphoteric oxides react with sodium hydroxide.

Zinc oxide forms sodium zincate, Al₂O₃ forms sodium aluminate while PbO, PbO₂, SnO, SnO₂, Cr₂O₃ form plumbite, plumbate, stannite, stannate and chromite respectively.

Different formulae

Sometimes different formulae are written for the same compound in this set. Sodium zincate can be written as Na_2ZnO_2 as above or as $Na_2Zn(OH)_4$ (= $2NaOH + Zn(OH)_2$ or $2Na^+ + Zn(OH)_4^{2^-}$). This is because the composition of the compound formed depends upon the conditions used. When ZnO is dissolved in excess aqueous sodium hydroxide solution, the $Zn(OH)_4^{2^-}$ ion forms in the solution. However depending upon how the substance is crystallised, the composition of the solid can vary from Na_2ZnO_2 to $Na_2Zn(OH)_4$. ($Zn(OH)_4^{2^-} = ZnO_2^{2^-} + 2H_2O$). Similarly when Al_2O_3 reacts with sodium hydroxide solution, $Al(OH)_4^-$ forms in the solution. The solid crystallised from this solution may be $NaAlO_2$ or $NaAl(OH)_4$.

Because of this we often write the formula that leads to the simplest equation; for example, as above $ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$ We could have written $\begin{array}{l} ZnO + 2NaOH + H_2O \rightarrow Na_2Zn(OH)_4 \\ Similarly \\ Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \ or \\ Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4 \end{array}$

The same compounds are formed when the metals themselves (e.g. aluminium and zinc) react with sodium hydroxide.

lons such as $Zn(OH)_4^{2-}$ and $Al(OH)_4^{-}$ are **complex ions** (explained in the next section).

This reaction in the home

This reaction of aluminium oxide with sodium hydroxide is the reason we should not put aluminium saucepans and cooking ware in automatic dishwashers. Such saucepans and cooking utensils like all aluminium articles are coated with a thin layer of aluminium oxide. It is this oxide that makes aluminium objects so durable and corrosion resistant. The detergents used in automatic dishwashers are quite alkaline (mainly so they can dissolve congealed fat) and so they react with the oxide coating on aluminium pots and pans. This spoils their appearance (they become blotchy) and leads to much more rapid corrosion of the objects. This is one reason why aluminium saucepans are much less common today than they were twenty years ago.

A good use for this reaction

This reaction of aluminium oxide with sodium hydroxide, while a nuisance in the home, is extremely useful in the extraction of aluminium from naturally occurring ores. The common ore of aluminium is bauxite, a red pebbly material that is a mixture of aluminium oxide, iron(III) oxide (the red colour) and dirt. Aluminium oxide, also called alumina, is extracted from this by mixing the bauxite with hot concentrated sodium hydroxide solution which dissolves the Al_2O_3 ; the insoluble iron(III) oxide and dirt are filtered off as red mud. The hot solution of $Al(OH)_4^-$ is cooled and aluminium hydroxide precipitates out:

Al(OH)₄⁻(*aq*) Al(OH)₃(*s*) + OH⁻(*aq*) (This is a reversible exothermic reaction: use Le Chatelier's principle.)

This Al(OH)₃ is filtered off then heated to form aluminium oxide $2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$

The right-hand photo on page 311 shows this dissolution of alumina in sodium hydroxide solution at the alumina plant in Gladstone, Queensland.

This Al_2O_3 is heated and mixed with cryolite, K_3AlF_6 , to lower the melting point, then the molten mixture is electrolysed to form aluminium (*CCPC* page 123–4).

Photos of bauxite, alumina and aluminium are on page 6 of CCPC.

Hydroxides of these metals react similarly

The insoluble hydroxides of Zn, Al, Pb and Cr also react with sodium hydroxide solution to form clear solutions – colourless for Zn, Al and Pb and green for Cr. Consequently if sodium hydroxide solution is slowly added to solutions containing the cations of these metals, a precipitate of the hydroxide first forms then as more hydroxide is added the precipitate redissolves to form a clear solution (but if you add the hydroxide too quickly you won't see the precipitate at all). The reactions are similar to those give above: for example

Zn²⁺(aq) + 2OH⁻(aq) → Zn(OH)₂(s) Zn(OH)₂(s) + 2OH⁻(aq) → Zn(OH)₄²⁻(aq)

A use for this

This reaction of certain insoluble hydroxides with sodium hydroxide solution to form clear solutions can be used to identify cations present in water samples. Such tests are listed in Table 8.3 on page 281.

Complex ions

lons such as $Zn(OH)_4^{2-}$, $Al(OH)_4^{-}$ are examples of what are called **complex ions.** A complex ion is an ion that forms when one or more small molecules or ions attach to a metal ion to form a species that has completely different properties from those of the ions or molecules making it up. The complex ions $Zn(OH)_4^{2-}$, $Al(OH)_4^{-}$ are made from Zn^{2+} and $4OH^{-}$ and from Al^{3+} and $4OH^{-}$ respectively.

Complex ions are introduced on page 209 and their structure (involving coordinate covalent bonds) is discussed on page 243.

3. Neutralisation

CC sticks with the simple definition of neutralisation as acid + base \rightarrow water + salt.

In Brönsted–Lowry terms neutralisation is often written as

acid(1)	+	base(2) →	conjugate acid of base(2)	+	conjugate base of acid(1)
examples a	are				
HNO ₃	+	$NH_3 \rightarrow$	NH_4^+	+	NO_3^-
CH ₃ COOF	+	$OH^{-} \rightarrow$	H ₂ O	+	CH₃COO [−]

If the reaction moves well to the right (as these two examples do) then acid(1) is a stronger acid than is the 'conjugate acid of base(2)' Similarly base(2) is a stronger base than is the 'conjugate base of acid(1)'. In these examples,

 HNO_3 is a stronger acid than is NH_4^+ NH_3 is a stronger base than is $NO_3^ CH_3COOH$ is a stronger acid than is H_2O OH^- is a stronger base than is CH_3COO^-