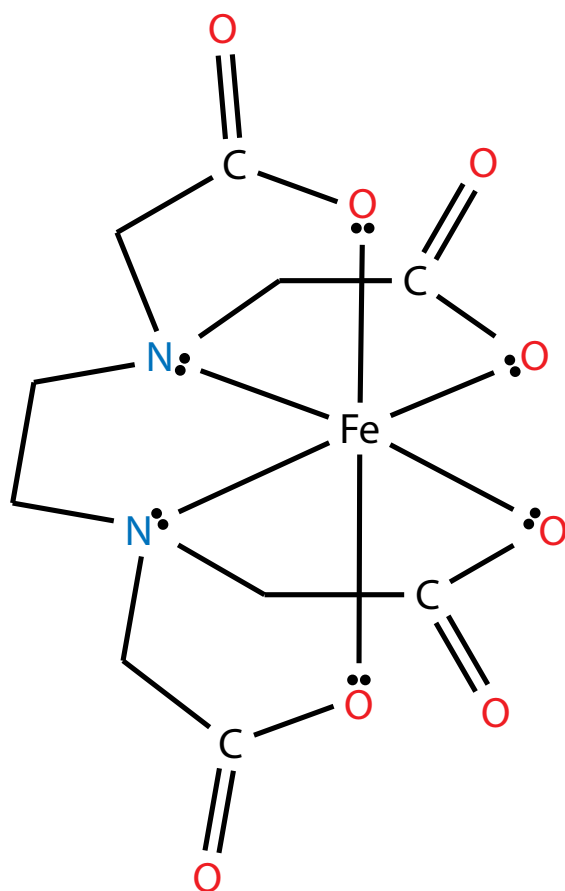


# Inorganic Chemistry



Fe-EDTA Complex

*compiled:* 2018-08-26

*git:* 58c5ac50084fca897204f028a98580d93a3bba96



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# The Third Period

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## 1 Overview

This chapter will examine the 7 elements in the third period; sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), and chlorine (Cl). Argon is... inert. Mostly.

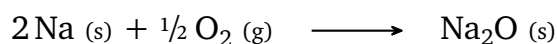
## 2 Elemental Reactions

Generally speaking, the reactivity of the elements with both oxygen and chlorine *decrease* across the period. Since reducing power decreases across the period, elements are less likely to be oxidised by oxygen and chlorine.

### 2.1 Reaction with Oxygen

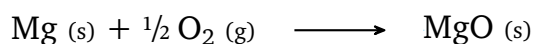
#### 2.1.1 Sodium

Sodium metal tarnishes rapidly in air, and burns readily with a *bright yellow* flame.



#### 2.1.2 Magnesium

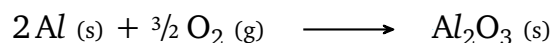
Magnesium metal tarnishes in air, albeit less readily than sodium. It burns very strongly with a *bright white* flame, and its combustion is highly exothermic.



### 2.1.3 Aluminium

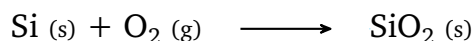
Aluminium metal is readily oxidised by air, and forms a protective layer of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) that shields the metal inside from further oxidation.

High temperatures (above  $800^\circ\text{C}$ ) are required to fully oxidise aluminium.



### 2.1.4 Silicon

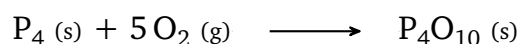
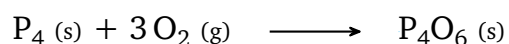
Silicon *does not* react with oxygen at room temperature. When strongly heated, some silicon dioxide ( $\text{SiO}_2$ ) can be formed. Silicon is a giant covalent molecule, so large amounts of energy need to be supplied to allow any reaction to take place.



### 2.1.5 Phosphorus

There are two predominant forms of elemental phosphorus; white phosphorus, which are discrete molecules of  $\text{P}_4$ , and red phosphorus, which takes a polymeric form.

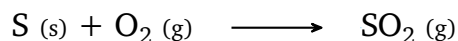
The former *spontaneously combusts* in air with a bright white flame, due to the strained tetrahedral bonds in the molecule. On the other hand, red phosphorus is more stable, and will burn on heating with a soft orange flame; the products for both forms of phosphorus are identical:



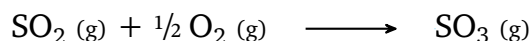
With limited oxygen, the predominant product will be  $\text{P}_4\text{O}_6$ ; in excess oxygen, the major product will be  $\text{P}_4\text{O}_{10}$ .

## 2.1.6 Sulphur

Sulphur is stable at room temperature, and requires some heating to burn — with a pale blue flame:



With a catalyst (eg. vanadium oxide  $\text{V}_2\text{O}_5$ ),  $\text{SO}_2$  can be further oxidised:



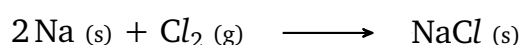
## 2.1.7 Chlorine

Chlorine rarely reacts directly with oxygen, because it is a stronger oxidising agent than oxygen and hence unlikely to be oxidised.

## 2.2 Reaction with Chlorine

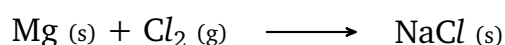
### 2.2.1 Sodium

Sodium metal is readily oxidised by chlorine and burns in it, with highly exothermic reaction:



### 2.2.2 Magnesium

Magnesium's reaction with chlorine is similar to that of sodium:



### 2.2.3 Aluminium

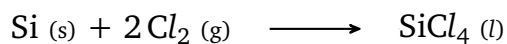
Aluminium does not *quite* react readily with chlorine. The reaction can be sped up by passing *dry* chlorine gas over heated aluminium foil (larger surface area):



$\text{AlCl}_3$  typically sublimes into the gaseous state.

## 2.2.4 Silicon

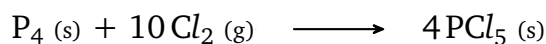
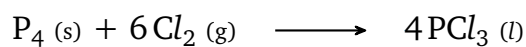
The reaction of silicon with chlorine is even slower than with aluminium, but if heated silicon powder is used, the reaction can be sped up slightly.



Silicon tetrachloride is a liquid at room temperature.

## 2.2.5 Phosphorus

White phosphorus ( $\text{P}_4$ ) burns vigorously in chlorine gas to form  $\text{PCl}_3$  and  $\text{PCl}_5$ :

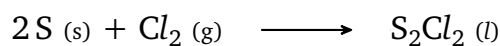


The formation of  $\text{PCl}_5$  occurs in an equilibrium, so excess chlorine gas should be used to favour the production of the latter, or limited chlorine to prefer the former:



## 2.2.6 Sulphur

Heated sulphur can react with chlorine gas:

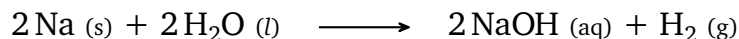




## 2.3 Reaction with Water

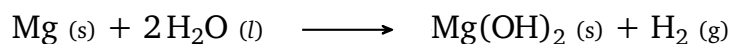
### 2.3.1 Sodium

Sodium, characteristic of group 1 metals, reacts vigorously even with cold water.

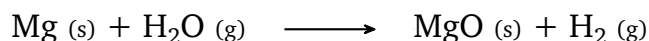


### 2.3.2 Magnesium

Magnesium reacts slowly with cold water, due to the formation of a mostly-insoluble hydroxide layer around the metal.



With steam however, magnesium reacts directly to form magnesium oxide:



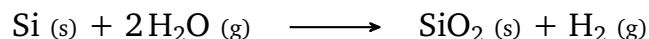
### 2.3.3 Aluminium

Aluminium does not appear to react with water, but this is due to the strong and unreactive layer of  $\text{Al}_2\text{O}_3$  on the surface, which is formed by the fast oxidation of aluminium by oxygen in the air.

If the coating is not present, aluminium will form  $\text{Al(OH)}_3$  and  $\text{H}_2$  as usual.

### 2.3.4 Silicon

Silicon is fairly unreactive towards water, due to the strong bonds in its giant covalent structure. However, when heated strongly with steam, silicon dioxide can be formed:

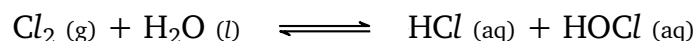


### 2.3.5 Phosphorus and Sulphur

Neither phosphorus nor sulphur react with water.

### 2.3.6 Chlorine

Chlorine disproportionates reversibly in water, as covered in the previous chapter on halogens:



## 3 Properties of the Oxides

In general, the acidities of the oxides increase across the period. Sodium and magnesium oxide are basic, aluminium oxide is amphoteric, and the other oxides are acidic. This is due to the decreasing ionic character, or conversely, the increasing covalent character in the bonding of the oxides.

The sections below will also cover the reactions of the hydroxides when appropriate.

### 3.1 Bonding, Structure, and Melting Points

Across the period, the bonding in the oxides moves from ionic to covalent. This is due to the decreasing difference in electronegativity between the element and oxygen; thus it is less likely to *completely lose* electrons, and hence covalent bonds become prevalent.

The change in bonding naturally creates a change in structure, from ionic lattices to discrete covalent molecules. Hence, this also causes a general decrease in melting points across the period.

Thing	Structure	Melting Point / °C
Na <sub>2</sub> O	ionic	1130
MgO	ionic	2850
Al <sub>2</sub> O <sub>3</sub>	ionic	2070
SiO <sub>2</sub>	giant covalent	1700
P <sub>4</sub> O <sub>6</sub>	covalent	24
P <sub>4</sub> O <sub>10</sub>	covalent	360 (sublimes)
SO <sub>2</sub>	covalent	-75
SO <sub>3</sub>	covalent	17

The melting point of MgO is much larger than that of Na<sub>2</sub>O due to the much higher charge density of Mg<sup>2+</sup>, which greatly increases the lattice energy of MgO.

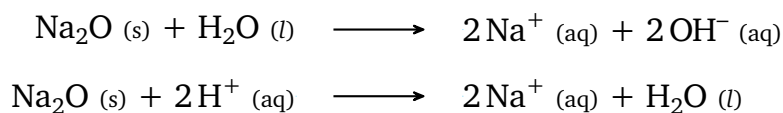
However, the *even higher* charge density of Al<sup>3+</sup> instead serves to *polarise* the O<sup>2-</sup> ion, resulting in some *covalent character*, hence *reducing* the lattice energy of Al<sub>2</sub>O<sub>3</sub>.

The reason for the high melting point of silicon dioxide is simply due to its giant covalent structure.

## 3.2 Sodium Oxide

Sodium oxide dissolves completely in water to give  $\text{OH}^-$  ions, and as such it will give a pH of around 13. This reaction is vigorous and exothermic, occurring even with cold water.

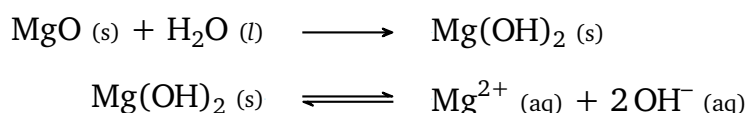
Sodium oxide also reacts directly with acids, to give an aqueous salt solution.



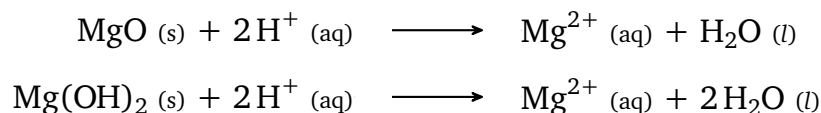
## 3.3 Magnesium Oxide

Magnesium oxide dissolves much less readily in water, and reacts *very slowly*. This is due to the high lattice energy of  $\text{MgO}$ , which naturally needs a lot of energy to break to create ions.

Furthermore, whatever tiny amounts of  $\text{Mg(OH)}_2$  formed *barely* dissociates to give  $\text{OH}^-$  ions, and so the reaction mixture is a mostly solid lump with a slightly-higher-than-neutral pH of around 9. This is due to the similarly high lattice energy of  $\text{Mg(OH)}_2$ .



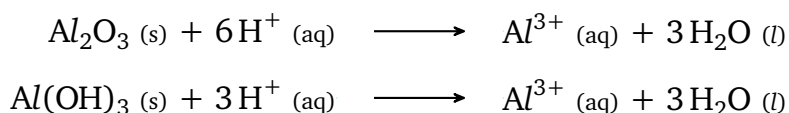
On the other hand, both  $\text{MgO}$  and  $\text{Mg(OH)}_2$  can react directly with acids to form aqueous salt solutions:



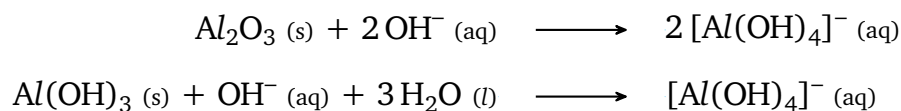
### 3.4 Aluminium Oxide

Aluminium oxide,  $\text{Al}_2\text{O}_3$ , is partially covalent, due to the polarising power of the  $\text{Al}^{3+}$  ion. Thus, the combination of ionic and covalent characters allows  $\text{Al}_2\text{O}_3$ , as well as  $\text{Al}(\text{OH})_3$ , to be amphoteric; ie. they react with both acids and bases.

Due to the high lattice energy of both  $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{OH})_3$ , they are insoluble in water. However, they both react with acids to form an aqueous salt solution containing  $\text{Al}^{3+}$  ions:

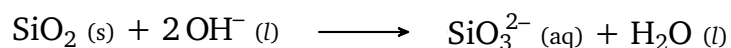


They can react with strong bases as well, to form *aluminate complex ions*,  $[\text{Al}(\text{OH})_4]^-$ :



### 3.5 Silicon Dioxide

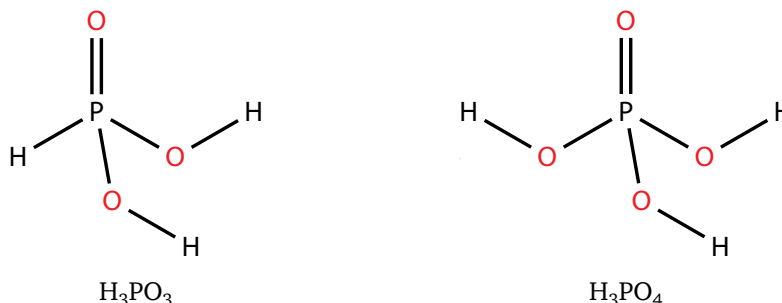
Silicon dioxide neither reacts with nor dissolves in water, due to the strong covalent bonds between the Si and O atoms. In fact, it does not succumb even when heated with aqueous bases. For any reaction to take place, there must be strong heating with concentrated bases, eg. NaOH.



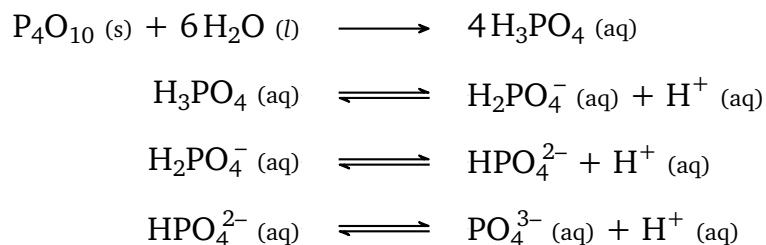
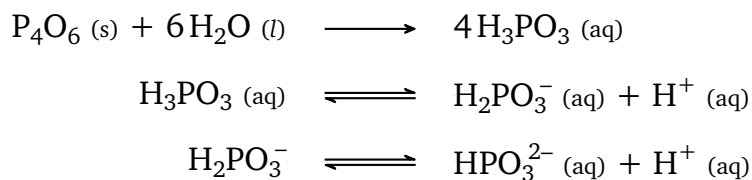
When it does react, a silicate ion is formed.

## 3.6 Phosphorus Oxides

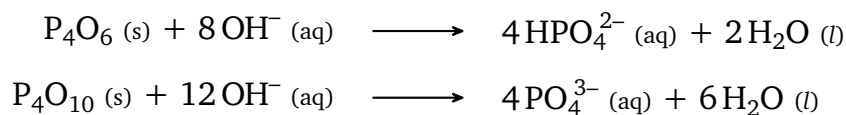
Both forms of phosphorus oxide,  $P_4O_6$  and  $P_4O_{10}$ , react with water to give acidic solutions. Both react with cold water, although the reaction of  $P_4O_{10}$  is a lot more violent than that for  $P_4O_6$ .



$H_3PO_3$  and  $H_3PO_4$  are both weak acids.  $H_3PO_3$  is a diprotic acid, and its  $pK_a$  values are 1.1 and 6.7;  $H_3PO_4$  is a triprotic acid, with  $pK_a$  values of 2.15, 7.20, and 12.32. Note that the third hydrogen in  $H_3PO_3$  isn't attached to anything electronegative, so it does not dissociate.



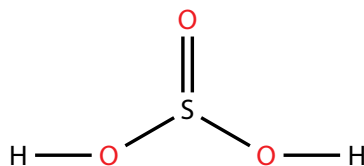
Both  $P_4O_6$  and  $P_4O_{10}$  can react directly with bases to give a salt solution, containing anions of the fully deprotonated acids ( $HPO_3^{2-}$  and  $PO_4^{3-}$  respectively):



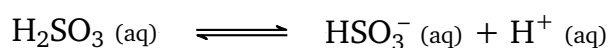
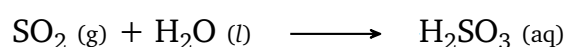
## 3.7 Sulphur Oxides

### 3.7.1 Sulphur Dioxide (SO<sub>2</sub>)

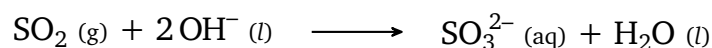
Sulphur dioxide is mostly soluble in water, giving a solution of the weak diprotic sulphurous acid, H<sub>2</sub>SO<sub>3</sub>. It has a  $pK_a$  value of around 1.8, so it is slightly stronger than H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>.



Sulphurous acid, H<sub>2</sub>SO<sub>3</sub>

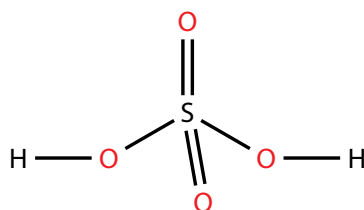


SO<sub>2</sub> (g) can react directly with bases to form a salt solution containing the sulphite ion, SO<sub>3</sub><sup>2-</sup>, which is the fully deprotonated version of the acid.



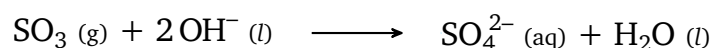
### 3.7.2 Sulphur Trioxide (SO<sub>3</sub>)

Sulphur trioxide, on the other hand, reacts violently with water, producing a mist of H<sub>2</sub>SO<sub>4</sub> droplets.



Sulphuric acid, H<sub>2</sub>SO<sub>4</sub>

Sulphuric acid is the strong acid that we know and love; SO<sub>3</sub> (g) can also react directly with bases to form an aqueous salt solution with sulphate ions.



It should be noted that while the first proton of H<sub>2</sub>SO<sub>4</sub> is undoubtedly a strong acid with a  $pK_a$  of  $-3$ , the second proton (from HSO<sub>4</sub><sup>-</sup>) has a  $pK_a$  of only 1.99, which is technically a weak acid. In most cases however, H<sub>2</sub>SO<sub>4</sub> will still fully deprotonate to give the sulphate ion.

## 4 Properties of the Chlorides

### 4.1 Bonding, Structure, and Melting Points

The trend for the chlorides is mostly identical to that for the oxides; bonding moves from ionic to covalent due to decreasing electronegativity difference between the element and chlorine, causing a shift from ionic solids to discrete covalent molecules.

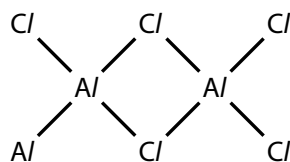
Thing	Structure	Melting Point / °C	Boiling Point / °C
$\text{NaCl}$	ionic	801	1413
$\text{MgCl}_2$	ionic	714	1412
$\text{AlCl}_3$	discrete covalent	—	180 (sublimes)
$\text{SiCl}_4$	discrete covalent	−70	58
$\text{PCl}_3$	discrete covalent	−112	76
$\text{PCl}_5$	discrete covalent	—	160 (sublimes)
$\text{SO}_2$	discrete covalent	−72	−10
$\text{SO}_3$	discrete covalent	16.9	45

#### 4.1.1 Aluminium Chloride

In the solid state (at room temperature), it is a very pale solid, and exists as an ionic lattice with a *very high* degree of covalent character.

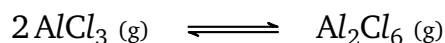
However, at around 180 °C, the heat causes the ionic lattice to expand, dissolving the ionic character of the compound. Thus,  $\text{AlCl}_3$  sublimes immediately into a gas, since the electrostatic forces have now disappeared, leaving only id-id interactions for intermolecular bonding.

A caveat, however, is that the Al atom in  $\text{AlCl}_3$  is *electron deficient*, having only 3 electron pairs. Thus, it tends to form dative bonds with another molecule of  $\text{AlCl}_3$ , creating a dimer of  $\text{Al}_2\text{Cl}_6$ .



The dimer  $\text{Al}_2\text{Cl}_6$ .

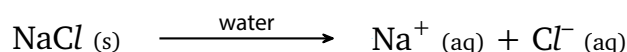
$AlCl_3$  and  $Al_2Cl_6$  actually exist in an equilibrium:



At higher temperatures, the equilibrium shifts to the left, and  $AlCl_3$  exists predominantly as discrete molecules, with no dimerisation.

## 4.2 Sodium Chloride

Sodium chloride,  $NaCl$ , should be familiar; it unremarkably dissolves in water to give  $Na^+_{(aq)}$  and  $Cl^-_{(aq)}$  ions:



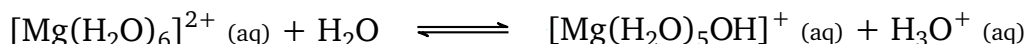
The pH of the solution is 7 — neutral.

## 4.3 Magnesium Chloride

Magnesium chloride,  $MgCl_2$ , dissolves in water as well to give  $Mg^{2+}_{(aq)}$  and  $Cl^-_{(aq)}$  ions. Note that because of magnesium's somewhat high charge density, it forms a hydrated aqua complex in water:



In a mechanism similar to that of the hydrolysis of aqua complex ions of metals with high charge density, magnesium is strong enough to polarise the O—H bond slightly, forming a slightly acidic solution:



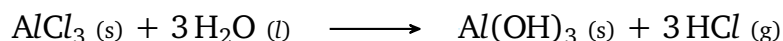
Note that the polarising power is much weaker than, for instance,  $Al^{3+}$  or  $Cr^{3+}$ , so the pH of such a solution is only around 6.5.

## 4.4 Aluminium Chloride

The reactions of  $AlCl_3$  with water differ mainly based on the amount of water or base used.

### 4.4.1 Limited Water

When *a few drops* of water are added to  $AlCl_3$ , white fumes of  $HCl$  are formed, leaving behind a white precipitate of  $Al(OH)_3$ . The aluminium hydroxide formed is insoluble in water.



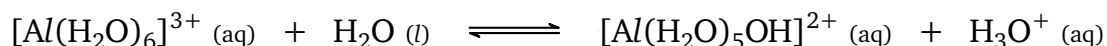


### 4.4.2 Excess Water

In excess water,  $\text{AlCl}_3$  instead forms the hydrated aluminium complex ion, and chloride ions:



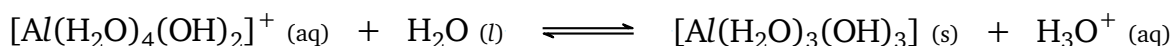
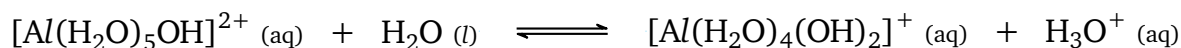
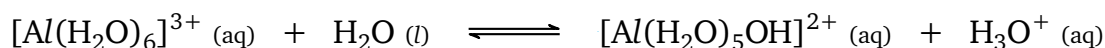
As covered previously, this hydrated aluminium ion can undergo hydrolysis to give an acidic solution:



The extent of hydrolysis is much greater than for  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ , so the pH is typically around 3.

### 4.4.3 Limited $\text{OH}^-$

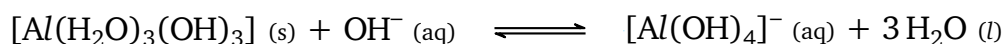
When a limited amount of base ( $\text{OH}^-$ ) is added,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq})$  behaves as a triprotic acid, being able to release 3  $\text{H}^+ (\text{aq})$  ions before being depleted and forming a precipitate of  $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3] (\text{s})$ .



A solution of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq})$  is usually acidic enough to react with carbonate ions to liberate carbon dioxide gas (which, remember, neither alcohols nor phenols can do), forming the insoluble precipitate.

### 4.4.4 Excess $\text{OH}^-$

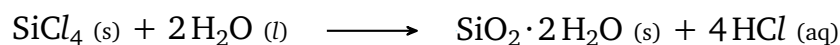
When faced with excess amounts of base, the white precipitate of  $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3] (\text{s})$  will appear to dissolve, instead forming the aluminate complex ion  $[\text{Al}(\text{OH})_4]^- (\text{aq})$ .



Note that, since this is an equilibrium reaction, the concentration of  $\text{OH}^-$  must be high enough to move the position of equilibrium to the right, to favour the formation of the soluble aluminate ion.

## 4.5 Silicon Chloride

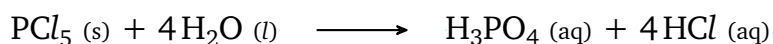
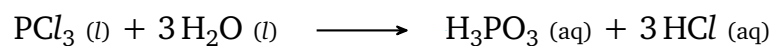
Silicon chloride *readily* and *violently* hydrolyses in water completely, forming  $\text{HCl}$ , which can either effervesce away as gaseous hydrogen chloride, or dissolve in the water to form a strongly acidic solution of pH 1.



$\text{SiO}_2 \cdot 2 \text{H}_2\text{O} (\text{s})$  is a hydrated form of silicon dioxide, but it is still in the solid state.

## 4.6 Phosphorus Chlorides

Both phosphorus chlorides,  $\text{PCl}_3$  and  $\text{PCl}_5$ , completely hydrolyse in water in a similar fashion to silicon chloride, forming  $\text{HCl}$  and hence a strongly acidic solution.



Note that, of course, the contributions of  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  to the pH of the solution will not be forgotten, but they are quite insignificant in the face of  $\text{HCl}$ .

Furthermore, on dropwise addition of water with  $\text{PCl}_5$ , it tends to form  $\text{POCl}_3$ , phosphorus oxychloride, instead.

