## Chlorine, Sulfur and Nitrogen

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<table>
<thead>
<tr>
<th>Mark the following statements True (T), False (F) or Unsure (U)</th>
<th>Before Lessons</th>
<th>After Lessons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen is obtained by filtration of air</td>
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<tr>
<td>Nitrogen and oxygen react in the hot parts of a car engine</td>
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<td>The triple bond in nitrogen makes it very unreactive</td>
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<tr>
<td>The major use of nitrogen is in the Haber Process to produce ammonia</td>
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<td>A temperature ranging from 350 °C to 500 °C is used in the Haber Process, together with a pressure of 200 atm.</td>
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<td>Ammonia and hydrogen chloride are very soluble in water</td>
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<td>Ammonia solution is strongly alkaline</td>
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<tr>
<td>Ammonia reacts with both sulfuric and nitric acids to form compounds which are widely used in fertilisers</td>
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<td>A colourless gas which reacts with oxygen to give a brown gas can be NO</td>
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<td>Nitric acid is a strong oxidizing agent as illustrated by its reaction with copper</td>
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<td>Dilute nitric acid reacts very differently when compared to other dilute acids</td>
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<tr>
<td>A gas which reduces orange dichromate to green would be SO₂</td>
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<td>Sulfur dioxide and nitrogen monoxide are acidic</td>
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<td>Sulfuric acid is hygroscopic, an oxidizing agent and a dehydrating agent</td>
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<td>Sulfur dioxide dissolves in water to give sulfuric acid</td>
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<td>Chloride ions can be oxidized to yield chlorine gas</td>
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<td>Chlorine dissolves in water to give pure hydrochloric acid solution</td>
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<td>Hydrogen chloride dissolves in methyl benzene to give a neutral solution</td>
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<td>Conc. sulfuric acid can be used to produce hydrogen chloride from salt</td>
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<tr>
<td>A gas that turns moist blue litmus paper red and then bleaches it white is chlorine. The bleaching effect is due to chloric (I) acid.</td>
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<td>Diprotic acids can be used to make acid salts</td>
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</table>
Chlorine as a Halogen and Oxidizing Agent

- Chlorine is one of the halogens and undergoes reactions similar to those of bromine and iodine. It occurs as a pungent, yellow-green gas, but is not found pure in nature due to its high reactivity.
- All halogens are oxidizing agents, with chlorine being the strongest due to its smaller atomic size. Since chlorine is the most reactive halogen, the chloride ion is the most stable halide ion. Thus chlorine gas can displace both bromide and iodide ions in solution.

\[
\text{Cl}_2(g) + 2 \text{Br}^-(aq) \rightarrow \text{Br}_2(l) + 2 \text{Cl}^-(aq)
\]

- Due to its strong oxidizing nature, chlorine oxidizes iron directly to iron (III) to form iron (III) chloride. Bromine undergoes a similar reaction, but iron (III) bromide is less stable than iron (III) chloride. Iron (III) iodide is not formed as it is unstable.

\[
3 \text{Cl}_2(g) + 2 \text{Fe(s)} \rightarrow 2 \text{FeCl}_3(s)
\]

- Chlorine can also oxidized the sulfide ion to give a yellow deposit of sulfur, it can oxidize metals to give metal chlorides and oxidize iron (II) to iron (III).

\[
\text{Cl}_2(g) + \text{H}_2\text{S}(aq) \rightarrow 2 \text{HCl}(aq) + \text{S}(s)
\]

\[
\text{Cl}_2(g) + \text{Mg}(s) \rightarrow \text{MgCl}_2(s)
\]

\[
\text{Cl}_2(g) + 2 \text{FeCl}_2(aq) \rightarrow 2 \text{FeCl}_3(aq)
\]

- The test for chlorine is that it turns damp blue litmus red and then bleaches it white. This is as chlorine dissolves in water to give hydrochloric and chloric (I) acid, a component of bleach. A similar reaction is undergone to a lesser extent by bromine but not by iodine.

\[
\text{Cl}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{HCl}(aq) + \text{HOCl}(aq)
\]

- The test for chlorine is that it turns damp blue litmus red and then bleaches it white. This is as chlorine dissolves in water to give hydrochloric and chloric (I) acid, a component of bleach. A similar reaction is undergone to a lesser extent by bromine but not by iodine.

- In industry, chlorine, along with hydrogen and sodium hydroxide, are prepared by the electrolysis of brine.

- In the lab, chlorine can be prepared by the oxidation of chloride ions using an oxidizing agent such as manganese (IV) oxide. This is reacted with concentrated hydrochloric acid.

\[
4 \text{HCl}(aq) + \text{MnO}_2(s) \rightarrow \text{MnCl}_2(aq) + \text{Cl}_2(g) + 2 \text{H}_2\text{O}(l)
\]

- A dropping funnel is removed to add HCl(aq) slowly since the reaction produces a lot of heat.

- The gas is passed through two wolf bottles: one containing water to remove impurities of hydrogen chloride gas and the other with concentrated sulfuric acid to remove impurities of water. Chlorine can be collected by downward delivery or in a gas syringe.
Exercise 11.1

1. The diagram below shows the apparatus used for the preparation of chlorine gas in the laboratory.

![Diagram of chlorine preparation apparatus]

   a. Name the apparatus labelled A, B, C and D
   b. Why is apparatus A used to add the reagent?
   c. Name another apparatus that could be used instead of A to add the reagent
   d. Name another apparatus that could be used instead of D to collect the gas
   e. Give the names of the reagents that are mixed in apparatus B.
   f. Give a balanced chemical equation for the reaction taking place
   g. Give two observations that would be observed as the reaction proceeds in apparatus B
   h. What is the function of passing the gas produced through water?
   i. What is the function of passing the gas produced through concentrated sulfuric acid?
   j. What would be the effect of dry chlorine on dry blue litmus paper?
   k. What would be the effect of dry chlorine on damp red litmus paper?

2. In industry, chlorine is prepared by the electrolysis of brine (concentrated sodium chloride solution) rather than by the method in (4).

   a. Write ionic half equations for the reactions taking place at each electrode.
   b. Which ions would remain in solution after electrolysis is complete.

3. Do some research and list three uses of chlorine.

4. How can iron (II) chloride and iron (III) chloride be prepared? Why are different methods needed to produce these two similar compounds?

5. Excess concentrated sulfuric acid is added to 3.5 g of sodium chloride. Calculate the mass of chlorine that will be produced in the reaction.  

   (Ans: 2.124g)
Hydrogen Chloride

- Hydrogen chloride is a gas with a pungent smell. It is colourless. When in contact with moist air it dissolves in the water to form hydrochloric acid. It is thus often observed as misty fumes. It has a pungent, acidic smell. Hydrogen chloride turns moist blue litmus paper red, but does not bleach it white since it does not produce or contain chloric (I) acid. The test for hydrogen chloride is that it forms white fumes with ammonia.

\[ \text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s) \]

- Hydrogen chloride is very soluble in water. It dissociates completely in water and is thus a strong acid. Hydrogen chloride can also dissolve in other solvents such as methyl benzene, however when dissolved in methyl benzene, hydrogen chloride does not dissociate and is not acidic.

\[ \text{HCl}(aq) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \]

- Hydrogen chloride can be prepared by the reaction between chlorine and hydrogen or by that between chlorine and hydrogen sulfide, as shown earlier.

- However it is more easily prepared by the action of concentrated sulfuric acid on a chloride.

\[ \text{H}_2\text{SO}_4(l) + \text{NaCl}(s) \rightarrow \text{NaHSO}_4(s) + \text{HCl}(g) \]

- The gas produced is passed through concentrated sulfuric acid to dry it. Thus, concentrated sulfuric acid is used as a reactant and as a drying agent in this reaction.

- Hydrogen chloride, like chlorine, can be collected in a gas syringe or by downward delivery.

- If the hydrogen chloride produced is needed dissolved in water an inverted funnel is used to dissolve in water. This is because hydrogen chloride is very soluble and will cause back suction of the solution if dissolved directly in water using a delivery tube.
**Exercise 11.2**

1. Fill in the blanks using words from below. Each item can be used once, more than once or not at all.

   - **Fluorine**
   - **Positive**
   - **Reduced**
   - **Losing**
   - **Non-metals**
   - **Gaining**
   - **Negative**
   - **Seven**
   - **More**
   - **Displace**
   - **Neutralization**
   - **Negative**
   - **Neutral**
   - **Neutral**
   - **Neutral**
   - **Displace**
   - **Neutral**
   - **Neutral**
   - **Displace**
   - **Neutral**
   - **Displace**
   - **Neutral**
   - **Displace**
   - **Neutral**
   - **Displace**

Halogens are ___(a)___ and thus react by ___(b)___ electrons. All halogens have ___(c)___ outermost electrons and thus need to gain ___(d)___ electron to gain the stability of a full shell.

Atoms gain electrons as their nuclear ___(e)___ charge attracts ___(f)___ electrons. Thus, the smaller the atom is, the ___(g)___ it can attract electrons. This makes ___(h)___ the most reactive halogen and ___(i)___ the least reactive one.

As chlorine is ___(j)___ reactive than bromine, it can ___(k)___ bromide ions in solution. This is a redox reaction whereby chlorine is ___(l)___ and bromide ions are ___(m)___.

2. The three halogens, chlorine, bromine and iodine, have different physical state and appearance. Give the colour and physical state of each of these elements.

3. ‘Chlorine occurs naturally as diatomic molecules.’ Explain the term in *italics* and draw a dot-and-cross diagram for the bonding in a molecule of chlorine.

4. Write down balanced chemical equations for the following reactions.
   
   a. **Magnesium burns violently in chlorine**
   
   b. **When bromine is added to a solution of sodium iodide, a black solid forms**
   
   c. **When chlorine gas is mixed with hydrogen sulfide gas, a yellow solid forms**
   
   d. **When chlorine gas is bubbled through a solution of iron (II) chloride, the solution turns from pale green to yellow**
   
   e. **Hydrochloric acid is oxidized by manganese (IV) oxide**
   
   f. **A solution of chlorine is acidic and bleaching**
   
   g. **Hydrogen chloride forms white fumes with ammonia**
   
   h. **Hydrogen chloride can be prepared by the action of concentrated sulfuric acid on potassium chloride**

5. When hydrobromic acid, HBr, is added to copper (II) oxide, a solution A is formed. When chlorine gas is bubbled trough A, a dense brown liquid B and a solution C are formed.

   a. **Write chemical equations for the changes taking place.**
   
   b. **Deduce the identity of substances A, B and C.**
   
   c. **Describe tests to identify the anions in A and C.**
Sulfur

- Sulfur is the element in group 6, period 2 of the periodic table.
- Solid sulfur exists as two allotropes (different forms of the same element in the same physical state).
  - Rhombic sulfur is a granular yellow solid. This is the sulfur commonly available in labs.
  - Monoclinic sulfur is found as amber, needle-like crystals.
- Sulfur burns in oxygen with a blue flame to produce a gas with a choking smell. This gas is sulfur dioxide which can be tested using dichromate paper. Sulfur dioxide changes orange dichromate to green:
  \[ S(s) + O_2(g) \rightarrow SO_2(g) \]
- Sulfur dioxide is also produced when fossil fuels burn since sulfur is present as a contaminant in oil. Sulfur dioxide dissolves in water to give sulfurous acid, and hence sulfur dioxide is one of the pollutants responsible for acid rain:
  \[ SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq) \]
- Sulfur can form the sulfide ion by gaining two electrons. This is formed when sulfur reacts with metals:
  \[ Mg(s) + S(s) \rightarrow MgS(s) \]
- Metal sulfides react with acids to give a salt and a gas with the smell of rotten eggs. This gas is hydrogen sulfide. It is an extremely toxic gas:
  \[ 2HCl(aq) + FeS(s) \rightarrow FeCl_2(aq) + H_2S(g) \]
- Uses of Sulfur include:
  - In the contact process to produce sulfuric acid
  - Pesticide and fungicide. It is considered as a natural substance and thus organic farmers can use sulfur and still claim to be organic.
  - To vulcanize rubber to be used in car tires, shoe soles, hoses etc.
  - As a fertilizer
  - In gunpowder and fireworks

Flatulence consists mainly of carbon dioxide, hydrogen and methane. It is minute amounts (less than 1%) of hydrogen sulfide or other sulfur containing compounds which results in a smelly product.
(The Joy of Chemistry, p 158)
Wine makers add Campden tablets (potassium or sodium metabisulfite) to their musts. This releases sulfur dioxide which prevents wine from spoiling and alcohol from getting oxidized into vinegar.

Sulfur Dioxide

- Sulfur dioxide is the most common oxide of sulfur. In the lab it can be produced by any of three methods:
  - Burning sulfur in air. This however results in some of the sulfur dioxide getting oxidized to sulfur trioxide.
    \[ \text{S}_\text{(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \]
  - Adding a dilute acid to a sulfite
    \[ 2 \text{HCl}_{\text{(aq)}} + \text{K}_2\text{SO}_3(\text{aq}) \rightarrow 2 \text{KCl}_{\text{(aq)}} + \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \]
  - Adding concentrated sulfuric acid to copper
    \[ 2 \text{H}_2\text{SO}_4(\text{l}) + \text{Cu}_\text{(s)} \rightarrow \text{CuSO}_4(\text{s}) + \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \]

- The resulting gas can be passed through a drying agent such as concentrated sulfuric acid or calcium chloride if needed dry.
- Sulfur dioxide is soluble in water and cannot be collected over water. It can be dissolved in water using the inverted funnel method.
- Sulfur dioxide is easily oxidized to sulfur trioxide and thus it acts as a reducing agent. In fact, the test for SO₂ is that it reduces orange dichromate (VI) to green chromate (III) ions. Sulfur dioxide also reduces purple permanganate (VII) to light pink manganese (II) ions. SO₂ also reduces iron (III) to iron (II).
  \[ 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g}) \]
- Sulfur trioxide produced by the oxidation of sulfur dioxide is more acidic and soluble than sulfur dioxide. It dissolves in water to give sulfuric acid.
  \[ \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) \]
- Since sulfur dioxide is a reducing agent, it is used as a food preservative to prevent oxidation. It is also used in the production of sulfuric acid (Contact process) and in the bleaching of paper.
**Exercise 11.3**

1. Sulfur occurs as two allotropes
   a. Define the term allotropes
   b. Which are the two main allotropes of sulfur?
   c. What is the appearance of these two allotropes?

2. Write balanced chemical equations for the following reactions.
   a. *Sulfur is burnt in a good supply of air*
   b. *The oxidation of sulfur dioxide to sulfur trioxide*
   c. *Sulfur trioxide dissolves in water to give an acidic solution*
   d. *Sulfur is mixed with iron and the mixture is heated strongly*
   e. *Hydrochloric acid is added to iron sulfide*
   f. *Hydrochloric acid is added to sodium sulfite*
   g. *Hydrogen sulfide gas is oxidized by chlorine gas to give a yellow precipitate and an acidic gas*

3. List three uses of sulfur.

4. Sulfur is placed in a combustion spoon and burnt in a gas jar as shown in the diagram on the right hand side. A piece of damp blue litmus paper is attached to the walls of the container while some orange potassium dichromate is placed at the bottom of the gas jar. Predict
   a. *What happens when the sulfur is burnt?*
   b. *What happens to the damp blue litmus paper? Why?*
   c. *What happens to the orange potassium dichromate? Why?*
   d. *Is this a good way to prepare sulfur in the lab? Why?*

5. Write equations for each chemical change taking place and hence identify compounds A to F.

*Some sulfur is mixed with some iron and the mixture is heated. A black solid (A) is formed as the main product. When dilute hydrochloric acid is added to solid (A), a colourless gas (B) with the smell of rotten eggs is evolved. Gas (B) is placed in a gas jar and mixed with chlorine gas. A yellow solid (C) and an acidic gas (D) are formed. Gas (D) can be dissolved in water using an inverted funnel to produce an acidic solution. When this solution is added to sodium sulfite, a gas (E) with a choking smell is produced. This gas (E) can also be produced by the action of concentrated sulfuric acid on a reddish brown metal (F).*
Sulfuric Acid and the Contact Process

- Sulfuric acid is a very important substance. It is used to make fertilisers, paints, pigments, dyes, detergents and artificial fibres amongst other products. Sulfuric acid is also the acid used in car batteries.
- While dilute sulfuric acid is a normal diprotic acid, concentrated sulfuric acid acts differently. Concentrated sulfuric acid can act as a:
  
  ⇒ Concentrated sulfuric acid is hygroscopic. If a volume if left exposed to air, it absorbs moisture and the volume of the liquid can be seen to increase. As a result, sulfuric acid is used as a drying agent in the laboratory preparation of pure, dry chlorine, hydrogen chloride and sulfur dioxide.

  ⇒ Concentrated sulfuric acid is a dehydrating agent, which means that it can take away water from a number of substances. These include hydrated salts and sugar. With sugar a black mass of carbon is left.

\[
\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}(\text{aq}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{CuSO}_4(\text{aq}) + 5 \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{SO}_4(\text{aq})
\]

\[
\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{C}(\text{s}) + 6 \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{SO}_4(\text{aq})
\]

⇒ Concentrated sulfuric acid is strong oxidizing agent, getting itself reduced to sulfur dioxide in the process. It can, for example, oxidize copper:

\[
2 \text{H}_2\text{SO}_4(\text{l}) + \text{Cu}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})
\]

⇒ Concentrated sulfuric acid is such a strong acid that it can be used to prepare other acids. For example, its action on chlorides:

\[
\text{H}_2\text{SO}_4(\text{l}) + \text{NaCl}(\text{s}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HCl}(\text{g})
\]

- Sulfuric acid is produced in the Contact process which is composed of four main steps:

1. Sulfur is burnt in a good supply of air
   \[
   \text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})
   \]

2. Sulfur dioxide with more oxygen is heated to high temperatures and passed over a vanadium (V) oxide (V_2O_5) catalyst. This is done at a temperature of 400-450°C and a pressure of 2atm.
   \[
   2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})
   \]

3. If sulfur trioxide is added directly to water, sulfuric acid will be produced. However the reaction gives a large amount of energy, is difficult to control and results in the sulfuric acid evaporating. Instead, sulfur trioxide is added to concentrated sulfuric acid to produce oleum.
   \[
   \text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})
   \]

4. Oleum can be added to the correct amount of water to produce sulfuric acid of the needed concentration.
   \[
   \text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2\text{SO}_4(\text{aq})
   \]
Exercise 11.4

1. Fill in the blanks using words from below. Each item can be used once, more than once or not at all.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>2</th>
<th>450</th>
<th>600</th>
<th>Vanadium (V) oxide</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>Sulfur trioxide</td>
<td>Allotropes</td>
<td>Oxygen</td>
<td>Water</td>
</tr>
<tr>
<td>Rhombic</td>
<td>Monoclinic</td>
<td>Iron</td>
<td>Fertilisers</td>
<td>Sulfur dioxide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sulfur has two ___(a)___ with the most common one being yellow, ___(b)___ sulfur. The other allotrope is ___(c)___ sulfur, which exists as amber needle like crystals.

In the first stage of the Contact process, sulfur is burned in air to form ___(d)___ . This gas is then used in the second stage of the process. It is mixed with ___(e)___ gas, then passed over the catalyst ___(f)___ at a temperature of ___(g)___ °C and ___(h)___ atmospheres pressure. The product of this reaction is ___(i)___ gas. Finally, this gas is absorbed in concentrated sulfuric acid forming a liquid called ‘oleum’ to which the correct amount of ___(j)___ is added in order to obtain ordinary concentrated sulfuric acid. One use of sulfuric acid is to make ___(k)___.

2. Write balanced chemical equations for all the steps involved in the Contact process.

3. These are some reactions of sulfuric acid:
   Reaction 1. A + sulfuric acid → copper sulfate + water
   Reaction 2. B + sulfuric acid → copper sulfate + water + sulfur dioxide
   Reaction 3. C + sulfuric acid → sodium sulfate + water + carbon dioxide
   Reaction 4. D + sulfuric acid → sodium hydrogensulfate + hydrogen chloride
   Reaction 5. E + sulfuric acid → carbon + water

   a. Name the reagents A to E
   b. State whether sulfuric acid has to dilute or concentrated in reactions 1 to 5
   c. What is the role of sulfuric acid in reaction 2?
   d. What is the role of sulfuric acid in reaction 5?
   e. Write balanced chemical reactions for equations 1 to 5

4. Sulfuric acid is a strong oxidizing agent. It can oxidize bromide ions to bromine and iodide ions to iodine. However, sulfuric acid cannot oxidize chloride ions to chlorine. Explain why this is so.
Nitrogen

- Nitrogen is the main constituent of air, making up 78% of the air around us. It is a colourless, odourless, tasteless gas that is very unreactive. The unreactivity of nitrogen is due to nitrogen being made up of diatomic molecules held together by triple covalent bonds.

- Nitrogen can react with very reactive metals to form nitrides.
\[ \text{N}_2(\text{g}) + 6 \text{Na}_\text{(s)} \rightarrow 2 \text{Na}_3\text{N}_\text{(s)} \]

- Nitrogen can only react with oxygen under extreme conditions, such as in lightning and in the hot parts of a car engine. The product of this reaction is colourless, neutral nitrogen monoxide.
\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) \]

- Nitrogen monoxide quickly gets oxidized to nitrogen dioxide, which is a brown, toxic, acidic, pungent/sharp smelling gas.
\[ 2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) \]

- Nitrogen dioxide is a common pollutant and one of the pollutants responsible for acid rain since it dissolves in water to give nitric acid.
\[ 4 \text{NO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightarrow 4 \text{HNO}_3(\text{aq}) \]

- Nitrogen, along with oxygen and the noble gases, is obtained by the fractional distillation of liquid air. The steps are as follows:
  1. Air is filtered to remove dust.
  2. Air is cooled at -80°C to remove carbon dioxide and water as solids.
  3. Air is liquefied at a high pressure and low temperature.
  4. Liquid air is fractionally distilled.

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling Point in °C</th>
<th>Some Uses</th>
</tr>
</thead>
</table>
| Oxygen    | -183                | * Hospitals to help with breathing difficulties  
* Oxyacetylene flame for welding  
* Mountaineers, divers, astronauts and fire-fighters  
* Sewage treatment  
* Production of steel  
* Rocket fuel along with hydrogen |
| Nitrogen   | -196                | * Production of ammonia (Haber process)  
* As an inert atmosphere in oil tanks to prevent fires  
* In food packaging |
| Helium     | -269                | * Fill light bulbs  
* Provide inert atmosphere even at very high temperatures |
| Neon       | -246                | * Provide inert atmosphere even at very high temperatures  
* Advertising signs  
* Lasers |
| Argon      | -186                | * Advertising signs  
* Lasers |
| Krypton    | -157                | * Helium is used in balloons and air balloons |
| Xenon      | -108                | * Helium is used in balloons and air balloons |
Ammonia

- The main use of nitrogen is in the Haber process to produce ammonia. Ammonia, NH$_3$, is a very important chemical used for fertilisers (ammonium salts), waste water treatment, manufacture of nitric acid (Ostwald Process) and in cleaning products.

- It is a pungent, colourless gas that is very soluble in water to give a weakly alkaline solution. Ammonia thus turns moist red litmus paper blue. The confirmatory test for ammonia is that it forms white fumes with hydrogen chloride

  \[
  \text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})
  \]

- The above reaction is reversible on heating.

  \[
  \text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})
  \]

- Ammonia is a reducing agent. It can reduce copper (II) oxide to copper.

  \[
  2 \text{NH}_3(\text{g}) + 3 \text{CuO}(\text{s}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l}) + 3 \text{Cu}(\text{s})
  \]

- Ammonia reacts with acids to form ammonium salts. The test for the ammonium cation is to add sodium hydroxide and heat. If the ammonium cation is present, ammonia gas will be released.

  \[
  \text{OH}^-_{(\text{aq})} + \text{NH}_4^+_{(\text{aq})} \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{g})
  \]

- The same reaction is used to produce ammonia in the laboratory. The reaction yields ammonia, salt and water.

  \[
  \text{Ca(OH)}_2(\text{s}) + 2 \text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{CaCl}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{NH}_3(\text{g})
  \]

- The main impurity will be water vapour which can be removed by passing though a drying agent such as calcium oxide or calcium chloride.
Exercise 11.5

1. Draw the bonding in the following compounds
   a. Nitrogen
   b. Ammonia
   c. Magnesium nitride

2. By looking at your answers in 1 explain why
   a. Nitrogen is so unreactive
   b. Magnesium nitride can conduct electricity when molten

3. Cars are a common source of nitrogen oxides as nitrogen reacts with oxygen in the hot parts of a car engine
   a. Where else can nitrogen react with oxygen?
   b. Write a balanced chemical equation for the reaction between nitrogen and oxygen
   c. Account for the brown colour of car exhaust. Your answer should include a balanced chemical equation.
   d. What equipment is used to reduce carbon monoxide and nitrogen oxides from car exhaust? Include a balanced chemical equation.
   e. One of the oxides of nitrogen is responsible for acid rain. Give a balanced chemical equation to illustrate this.

4. Nitrogen dioxide can be prepared in the lab by the thermal decomposition of a nitrate and passing the resulting gases through a U-tube submerged in ice-salt.
   a. Suggest a suitable nitrate for the reaction and include a balanced chemical equation for its decomposition.
   b. Draw a well labelled diagram of the apparatus used.

5. Ammonia is passed over heated copper (II) oxide. The resulting vapours are then passed over anhydrous copper (II) sulfate and collected in a gas syringe.

   a. Write a balanced chemical equation for the reaction between ammonia and copper (II) oxide.
   b. What is the role of ammonia in this reaction?
   c. What is the role of anhydrous copper (II) sulfate?
   d. Give two physical changes that will be observed as the reaction proceeds.
   e. Which gas will be collected in the gas syringe?
   f. 1 mole of any gas occupies 24 dm³ at room temperature. If the volume of gas in the syringe at the end of the experiment was 55.4 cm³, calculate the mass of copper (II) oxide that has reacted.
The Haber Process

- Ammonia is industrially prepared by the Haber Process which involves the reaction between hydrogen and nitrogen gases to give ammonia:

\[ \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) \]

- According to the above expression, nitrogen and hydrogen are mixed at a ratio of 1 : 3. However, as the reversible arrow sign indicates, the reaction does not go to completion, and thus what one obtains is a mixture of nitrogen, hydrogen and about 15% ammonia.

- Ammonia is removed by liquefaction while the hydrogen and ammonia are recirculated to produce more ammonia.

- This is done at high temperatures and pressures and using an iron catalyst.

- The temperature used is between 350°C – 500°C while the pressure used is about 200 atm.

The Ostwald Process

- The Ostwald process is used for the production of nitric acid, which is an important precursor in fertilisers, explosives, dyes and perfumes. This consists of four steps:

  ⇒ Ammonia is oxidized using a platinum-rhodium catalyst. This reaction produces a lot of heat and is thus a good heat source for the process:

\[ 4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) \]

  ⇒ Nitrogen monoxide is oxidized to yield nitrogen dioxide:

\[ 2 \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_3(\text{g}) \]

  ⇒ When nitrogen dioxide dissolves in water, it yields the desired product together with some nitrogen monoxide:

\[ 3 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HNO}_3(\text{aq}) + \text{NO}(\text{g}) \]

  ⇒ Nitrogen monoxide is recycled and nitric acid is concentrated to the required strength by distillation.

- When dilute, nitric acid acts like a normal acid. It reacts with bases to produce nitrate salts. Nitrates are generally thermally unstable as seen early and must be collected by careful recrystallization.

- On the other hand, concentrated nitric acid does not act like a dilute acid. It is a strong oxidizing agent being itself reduced to oxides of nitrogen in the process. Similar to concentrated sulfuric acid, concentrated nitric acid can oxidize:

  ⇒ Iron (II) ions to iron (III) ions
  ⇒ Copper to copper (II) ions

- The reaction between concentrated nitric acid and copper releases brown fumes of toxic nitrogen dioxide. Nitrogen dioxide can also be prepared by decomposition of metal nitrates and be collected by liquefaction in a U-tube immersed in cold salted water (ice salt) as in Chapter 2.
Exercise 11.6

1. Ammonium chloride was heated with calcium hydroxide in a boiling tube as shown. The resulting gas was passed directly into water.

   ![Diagram of Ammonium Chloride and Calcium Hydroxide Reactions](image)

   a. In the apparatus shown above, back suction is likely to occur. How can the apparatus be changed to overcome this problem?

   b. Write a balanced chemical equation for the reaction taking place and hence identify the gas being produced.

   c. Give two uses of this gas.

   d. 50g of ammonium chloride were completely used up in this reaction. What will be the concentration of the resulting solution if its final volume was 420 cm$^3$?

   e. In industry, this gas is produced in the Haber process. Give the reaction and conditions (temperature, pressure and catalyst) used in this industrial chemical process.

2. Give balanced chemical equations, which can be ionic, for the following changes:

   a. Ammonia gas reacts with hydrogen chloride

   b. Ammonia solution is added to iron (II) chloride. A mud green precipitate forms.

   c. Ammonia solution is added to dilute sulfuric acid

   d. Ammonia gas is passed over silver (I) oxide

3. Nitric acid is an important chemical that is produced by the Ostwald process.

   a. Give two uses of nitric acid

   b. Explain the steps involved in the Ostwald process

   c. ‘Concentrated nitric acid is not a normal acid’. Explain this statement by referring to two reaction of your choice. Chemical equations are not to be included.