Fertilisers providing primary and secondary nutrients

Primary nutrients

Various nitrogen compounds are used in fertilisers as sources of the essential primary nutrient nitrogen. These include liquid ammonia, various ammonium salts, nitrates and urea.

- Ammonia is manufactured by the Haber-Bosch process:
  \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

- Ammonium nitrate is made by neutralising nitric acid with ammonia. It is chemically simple, but technologically challenging.
  \[ \text{HNO}_3(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq) \]
  Ammonium nitrate is a simple salt. It is an example of straight fertiliser as it is a source of only one nutrient – nitrogen.

- Ammonium sulfate is made by neutralising sulfuric acid with ammonia:
  \[ \text{H}_2\text{SO}_4(aq) + 2\text{NH}_3(aq) \rightarrow (\text{NH}_4)\text{}_2\text{SO}_4(aq) \]
  Ammonium sulfate is a simple salt, but unlike ammonium nitrate it is an example of complex fertiliser as it is a source of more than one nutrient – nitrogen and sulfur.

- Potassium nitrate
  Potassium nitrate, another simple salt, is manufactured by the reaction between sodium nitrate and potassium chloride:
  \[ \text{NaNO}_3 + \text{KCl} \rightarrow \text{KNO}_3 + \text{NaCl} \]
  The method depends on the differing solubility of the salts at different temperature.

- Urea is manufactured by the Bosch-Meiser process.
  The process involves two main reactions.
  Liquid ammonia is reacted with solid carbon dioxide (dry ice) to make ammonium carbamate:
  \[ 2\text{NH}_3(l) + \text{CO}_2(s) \rightleftharpoons \text{NH}_2\text{COONH}_4(s) \]
  The forward reaction is fast and exothermic and the position of equilibrium is far to the right. The reaction goes to completion under industrial reaction conditions.
  Ammonium carbamate then decomposes to form urea and water:
  \[ \text{NH}_2\text{COONH}_4(s) \rightleftharpoons (\text{NH}_2)\text{}_2\text{CO}(s) + \text{H}_2\text{O}(l) \]
  The forward reaction is endothermic and relatively slow. Under industrial conditions the equilibrium mixture contains about 50-80% of products.
Phosphate rock is used to describe ores that contain minerals such as fluorapatite, \( \text{Ca}_5(\text{PO}_4)_3\text{F} \), and francolite, \( \text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F,OH})_{2+x} \). It can be used directly as a fertiliser.

Phosphoric (V) acid is made industrially by reacting phosphate rock with concentrated sulphuric acid. The other product of the reaction is calcium sulfate (commonly known as gypsum), which is insoluble and separated from the phosphoric acid by filtration. This is a simplified equation for the reaction:

\[
\text{Ca}_3(\text{PO}_4)_{2} + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4
\]

Superphosphate is made by reacting powdered phosphate rock with concentrated sulfuric acid.

\[
\text{Ca}_3(\text{PO}_4)_{2}(s) + 2 \text{H}_2\text{SO}_4(aq) \rightarrow 2 \text{CaSO}_4(aq) + \text{Ca(H}_2\text{PO}_4)_{2}(aq)
\]

Potassium sulfate is manufactured from potassium chloride by one of these two processes:

Mannheim process – stoichiometric amounts of potassium chloride and 100% sulfuric acid are fed into a furnace and heated at 840 °C.

\[
2\text{KCl} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HCl} + \text{K}_2\text{SO}_4
\]

Hargreaves process – a mixture of air and sulfur dioxide are passed counter-current through a concentrated solution of potassium chloride.

\[
4\text{KCl} + 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HCl} + 2\text{K}_2\text{SO}_4
\]

**Secondary nutrients**

Magnesium sulfate is made by various processes, such as the reactions of magnesium oxide with sulfuric acid and magnesium carbonate with sulfuric acid. It may be made in the form of Epsom salts (the most common form), \( \text{MgSO}_4.7\text{H}_2\text{O} \), or kieserite, \( \text{MgSO}_4.\text{H}_2\text{O} \).

Calcium nitrate is manufactured by dissolving a calcium salt such as calcium carbonate (usually in the form of limestone) in nitric acid. It is an example of a complex fertiliser, being a source of both calcium and nitrogen.

A mixture of calcium carbonate and ammonium nitrate is also used. It is made by stirring a mixture of calcium carbonate and ammonium nitrate solution and evaporating the stirred mixture to leave a white solid. The solid is called ‘calcium ammonium nitrate’, but it is a mixture and not a compound.

**Finding out**

What quantities of fertilisers are used annually in the UK?

Why is the use of urea increasing, but the use of nitrate fertilisers is decreasing?

Devise and carry out an experiment to obtain potassium nitrate from a solution containing potassium nitrate and sodium chloride.