Mastering Chemistry

- Book 6
- Topic 13 Industrial Chemistry

Content

Continued on next page

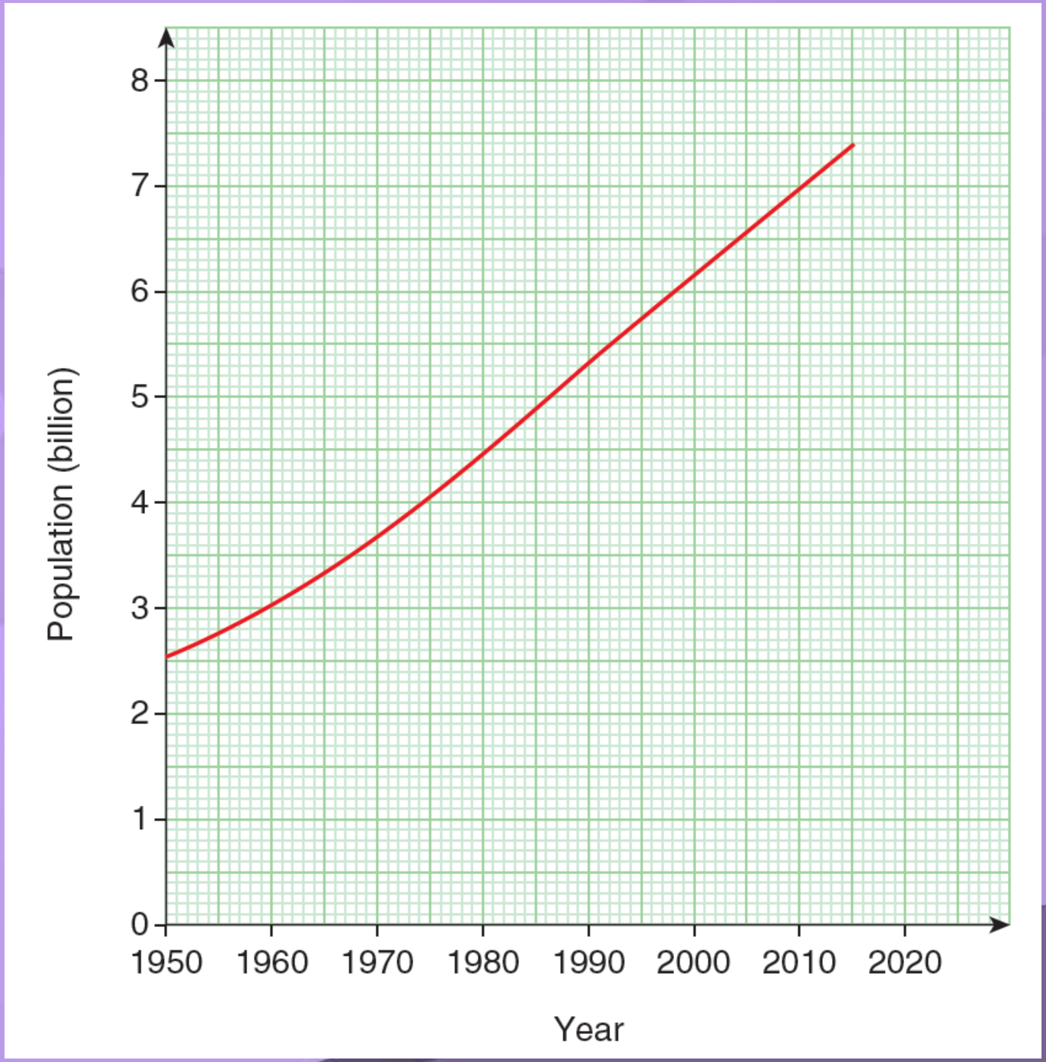
Content

45.1 The world's growing population (p.86)

- The world population has been increasing rapidly after the industrial revolution. The United Nations projects the world's population to reach 10 billion in 2056.
- How can food production be increased without encroaching on the world's remaining forests and wildernesses? It might be done by making the most efficient use of existing agricultural land—particularly by improving crop varieties and planting techniques, and making sensible use of added plant nutrients and pesticides.

45.1 The world's growing population (p.86)

The global population and predicted population growth



45.2 Essential elements for plant growth (p.87)

- Nitrogen, phosphorus, and potassium are three of the essential elements needed by plants. Plants do not grow well if these elements are in limited supply in the soil.

Table 45.1 Mineral deficiencies in plants

Element	Typical symptoms of deficiency
Nitrogen, N	poor growth, yellow leaves
Phosphorus, P	poor root growth, discoloured leaves
Potassium, K	poor fruit growth, discoloured leaves (Fig. 45.2)

45.2 Essential elements for plant growth (p.87)

Leaves from this palm discoloured, showing a potassium deficiency

- All these elements are absorbed from the soil naturally in the form of inorganic compounds. These elements get used up and have to be replaced by fertilisers.

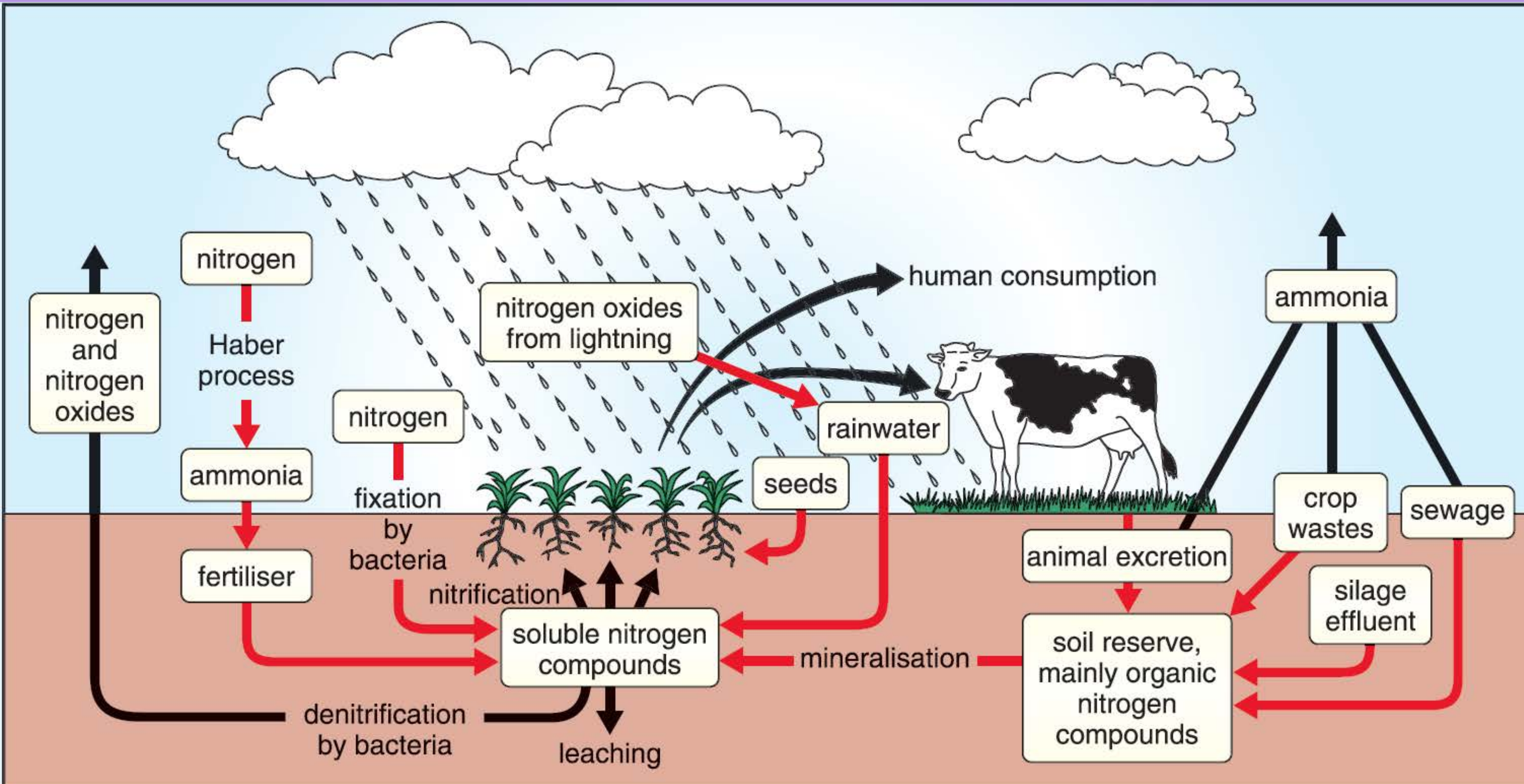
45.2 Essential elements for plant growth (p.87)

- Fertilisers are substances added to the soil to make it more fertile. Plant roots can only absorb the essential elements if they are in a water-soluble form. For example,

  - nitrogen in nitrate ion (NO_3^-) or ammonium ion (NH_4^+);
  - phosphorus in hydrogenphosphate ion (HPO_4^{2-});
  - potassium as potassium ion (K^+).

- Animal manure is a natural fertiliser. Synthetic fertilisers are made in factories, and sprinkled or sprayed on fields.

45.2 Essential elements for plant growth (p.87)



Nitrogen cycle *Ref.*

45.3 Nitrogen fixation processes (p.89)

- **Nitrogen fixation (固氮作用)** is a process by which atmospheric nitrogen is converted into important nitrogen compounds.
- The nitrogen and oxygen in the atmosphere react together during thunderstorms. Lightning provides the activation energy needed to start the reaction: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

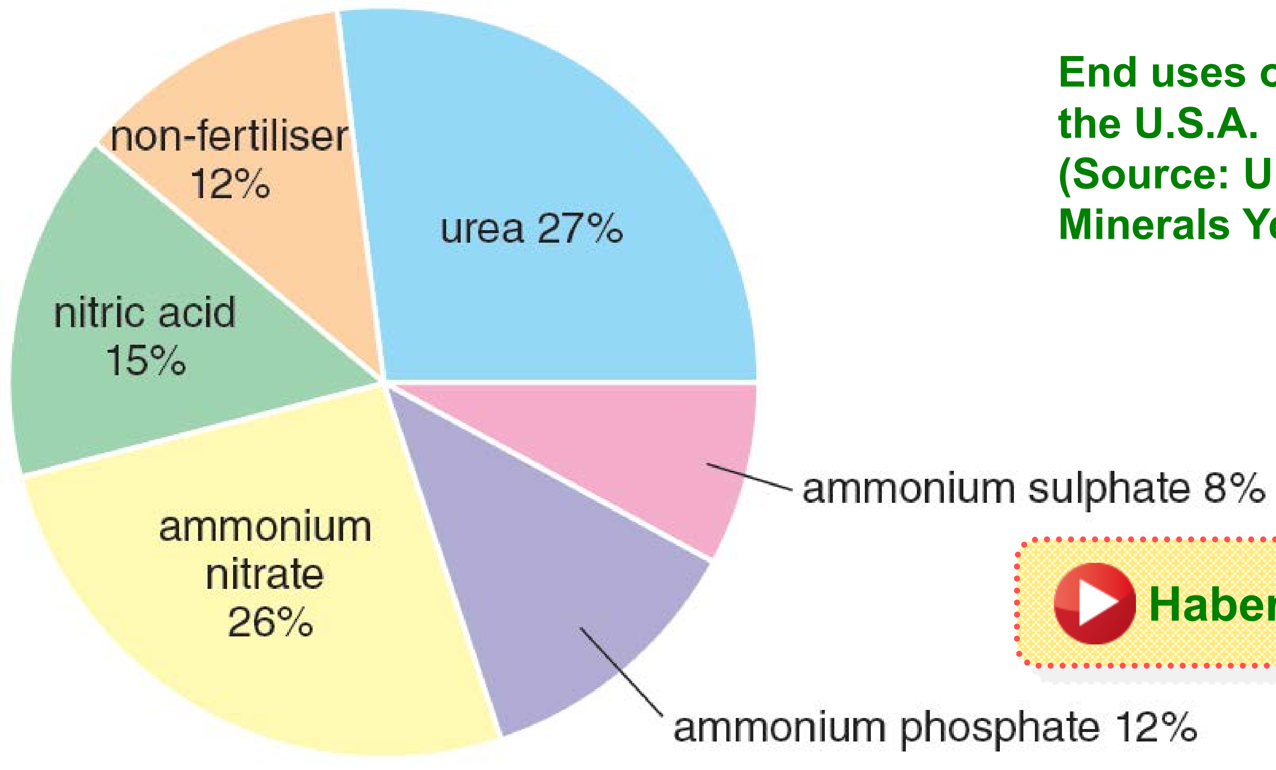
45.3 Nitrogen fixation processes (p.89)

- The nitrogen monoxide formed is further oxidised by oxygen in the air to give nitrogen dioxide. Nitrogen dioxide dissolves in water droplets and forms nitric acid, which falls to the Earth as rain.
- Some plants, such as peas and clovers, are able to convert atmospheric nitrogen into ammonium ion by the action of bacteria found in root nodules. The ammonium ion may be oxidised by nitrifying bacteria to give nitrate ion.
- Nitrogen is also taken from the atmosphere when ammonia is made by the Haber process.

45.4 The Haber process (p.90)

- Over 150 million tonnes of ammonia are manufactured in the world each year. In most countries, more than 70% of the ammonia produced is used to produce fertilisers.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$



End uses of ammonia produced in the U.S.A.
(Source: U.S. Geological Survey Minerals Yearbook 2015)

Haber process ***Ref.***

45.4 The Haber process (p.90)

Feedstocks

- The raw materials for the Haber process are air, natural gas and steam.

- Nitrogen and hydrogen are the feedstocks for the Haber process.
- Nitrogen is obtained by the fractional distillation of liquefied air.
- Hydrogen is manufactured by reacting natural gas (mostly methane) with steam. Methane reacts with steam in the presence of a nickel catalyst to form hydrogen.

$$CH_4(g) + H_2O(g) \xrightarrow{Ni(s)} CO(g) + 3H_2(g)$$

- Sulphur compounds must be removed to prevent severe catalyst poisoning.

45.4 The Haber process (p.90)

The choice of operation conditions in the Haber process

- The operation conditions used in the Haber process are arrived at by consideration of both the equilibrium position and reaction rate.
- In order to maximise profits, the major problems confronting chemists are to convert the reactants into the product
  - as quickly as possible;
  - as completely as possible.
- In reality, for economic reasons, it is the rate to attain equilibrium that proves the determining factor, rather than simply the percentage of ammonia present at equilibrium.

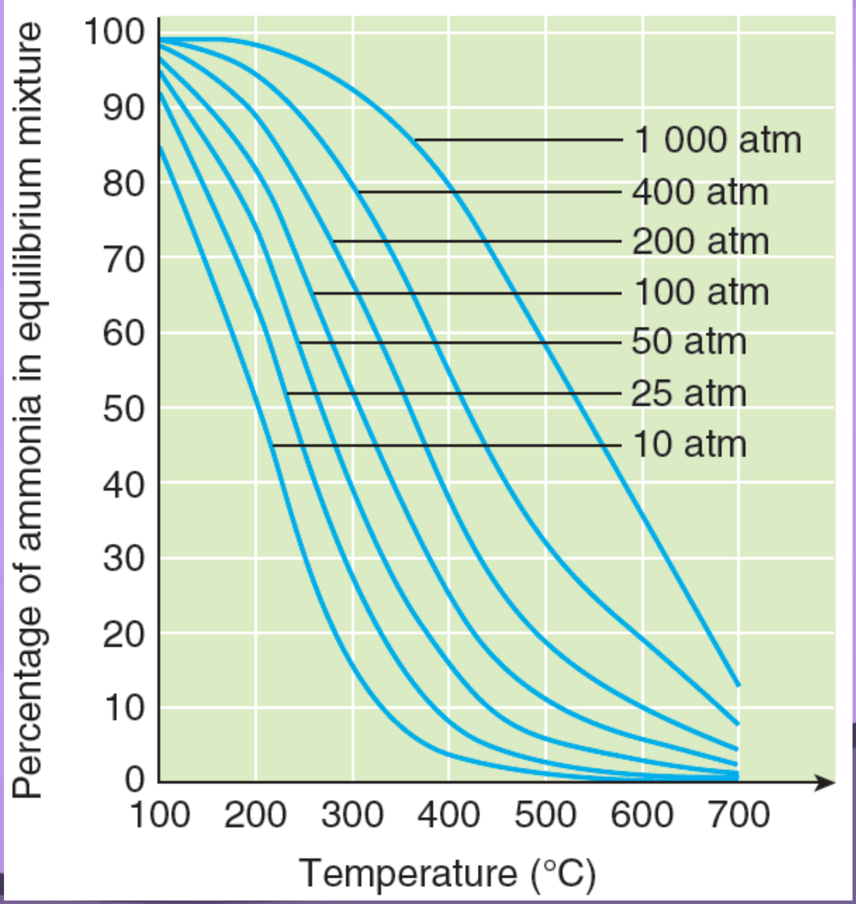
45.4 The Haber process (p.90)

The choice of temperature

- In the Haber process, the forward reaction is exothermic ($\Delta H^{\ominus} = -92$ kJ mol^{-1}). This means that the production of ammonia will be favoured by lower temperatures.
- Higher temperatures will result in less ammonia in the equilibrium mixture. By this consideration, it would follow that the Haber process should be carried out at low temperatures.
- However, at low temperatures the reaction is very slow and would take a long time to reach equilibrium.

45.4 The Haber process (p.90)

- In practice, chemists choose a compromise temperature — one that gives a reasonable equilibrium yield while attaining equilibrium at a fast enough speed.



45.4 The Haber process (p.90)

The choice of pressure

- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- High pressures will cause the position of equilibrium to shift to the right, producing more ammonia gas.
- Moreover, high pressure causes the molecules closer together, increasing the concentration and hence the rate of reaction. Less time is required to attain equilibrium.
- However, the use of high pressures need expensive equipment to compress the gases, a lot of energy to run, and tough reaction vessels to withstand the pressure.

45.4 The Haber process (p.90)

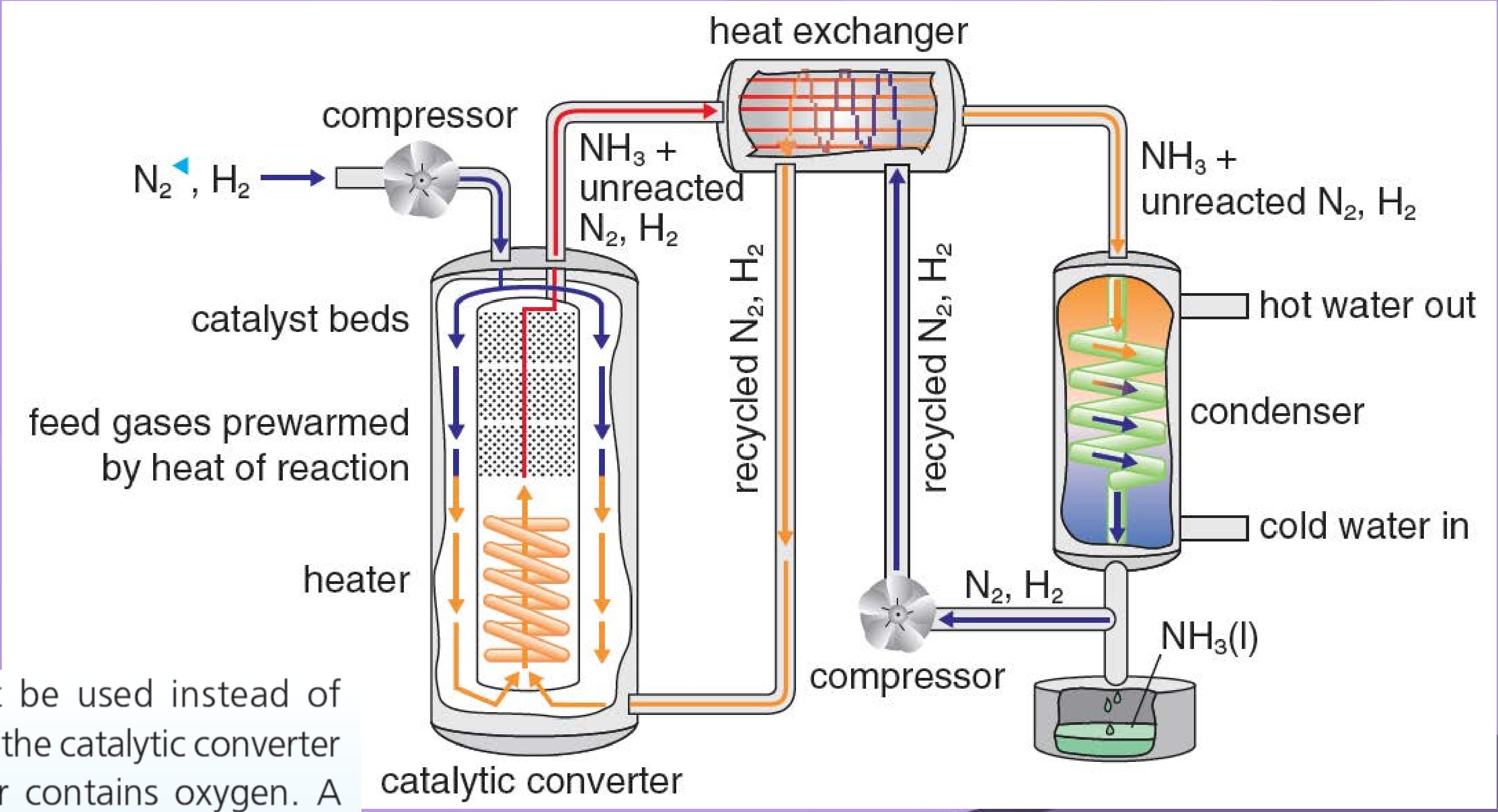
- Safety is also a concern.
- In practice, chemists choose a compromise pressure — one that is high enough to achieve a reasonable equilibrium yield, but not so high to avoid high cost and hazards.

Catalyst

- An iron catalyst is added to speed up the reaction, allowing the equilibrium to be attained faster and lower temperatures to be used.
- As the reaction takes place on the surface of a catalyst, the iron used is finely divided so as to make the surface area as large as possible. This arrangement makes the catalyst more effective.

45.5 The modern ammonia plant (p.93)

- The figure outlines the processes that occur in an ammonia plant.



Air cannot be used instead of nitrogen in the catalytic converter because air contains oxygen. A mixture of oxygen and hydrogen is explosive.

45.5 The modern ammonia plant (p.93)

- Thorough purification of both nitrogen and hydrogen is necessary. Impurities would poison the catalyst in the converter. The nitrogen and hydrogen are fed into the catalytic converter in the ratio of 1 : 3 by volume.

- The operation conditions chosen are usually
  - a temperature of 450 °C;
  - a pressure of 250 atmospheres;
  - finely divided iron as catalyst.

45.5 The modern ammonia plant (p.93)

- This process produces an actual conversion to ammonia of about 15%. Hot product gases are used to warm up the nitrogen and hydrogen in a heat exchanger before they enter the catalytic converter. Efficient use of energy not only saves energy, but also has less environmental impact.
- In the condenser, the gaseous mixture is cooled and ammonia condensed to liquid form. The unreacted gases are recycled through the catalytic converter. This reycling process improves the overall yield to around 97%.
- The iron catalyst lasts about five years before it becomes poisoned by impurities in the gas stream, such as sulphur compounds, and has to be replaced.

45.5 The modern ammonia plant (p.93)

Q (Example 45.1)

The synthesis of sulphuric acid is carried out by the Contact process. The key step in the process is the conversion of sulphur dioxide to sulphur trioxide in the presence of avanadium(V) oxide catalyst.

$$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5(s)} 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$

45.5 The modern ammonia plant (p.93)

The operation conditions are set at 450 ^{o}C and 1 atm to achieve a 96% conversion.

a) i) Explain how a temperature decrease would affect the conversion percentage.

ii) Explain why a temperature of 450 ^{o}C is used rather than a much higher or lower temperature.

b) i) Explain how a pressure increase would affect the conversion percentage.

ii) Explain why a pressure of 1 atm is used rather than a higher pressure.

c) In order to increase the conversion percentage, a slight excess of O_2(g) is used in the reacting gas mixture.
Why is O_2(g), rather than SO_2(g), used in slight excess?

45.5 The modern ammonia plant (p.93)

A

a) i) The forward reaction is exothermic. A temperature decrease will cause the position of equilibrium to shift to the right, increasing the conversion percentage.

ii) A higher temperature gives a lower conversion percentage as the forward reation is exothermic.
However, at low temperatures the rate is too low.
450 °C is a compromise between conversion percentage and rate.

b) i) In the equation, the number of moles of gas on the product side is smaller than that on the reactant side. A pressure increase will cause the position of equilibrium to shift to the right, increasing the conversion percentage.

ii) The conversion percentage is already very high. Increasing the pressure can only lead to a small increase in the conversion percentage.
However, a very high cost is needed for applying a higher pressure.

c) O_2(g) is more readily available.

45.5 The modern ammonia plant (p.93)

Practice 45.1

1 Ethanoic acid can be made from the reaction between carbon monoxide and methanol: $CO(g) + CH_3OH(g) \rightleftharpoons CH_3COOH(g)$ $\Delta H < 0$
In a simulation study of the reaction, identical mixtures of $CO(g) + CH_3OH(g)$ were allowed to attain equilibrium under different reaction conditions. The percentage of $CH_3COOH(g)$ in each equilibrium mixture was recorded. The table below lists the results obtained. (No catalysts were used in *Trials 4* and *5*.)

Trial	Operation conditions			Percentage of $CH_3COOH(g)$ in equilibrium mixture (%)
	Temperature (°C)	Pressure (atm)	Catalyst	
1	100	40	rhodium / iodide ion	80
2	100	80	rhodium / iodide ion	96
3	500	40	rhodium / iodide ion	*x*
4	500	80	—	*y*
5	100	40	—	*z*

45.5 The modern ammonia plant (p.93)

a) In which TWO trials are the percentages of CH_3COOH(g) in equilibrium mixtures the same? Explain your answer.

Trials 1 and *5*

For identical mixtures, the position of equilibrium is affected by temperature and pressure only.

In *Trials 1* and *5*, both the temperature and pressure are the same, thus they have the same percentage of CH_3COOH(g) in equilibrium mixture.

45.5 The modern ammonia plant (p.93)

b) In which trial is the percentage of $CH_3COOH(g)$ in the equilibrium mixture the highest? Explain your answer.

Trial 2

The forward reaction is exothermic. A temperature decrease shifts the position of the equilibrium to the right, increasing the percentage of $CH_3COOH(g)$ in the equilibrium mixture.

Number of moles of gaseous product is less than that of gaseous reactants. A pressure increase shifts the position of equilibrium to the right, increasing the percentage of $CH_3COOH(g)$ in the equilibrium mixture.

In *Trial 2*, the temperature is the lowest while the pressure is the highest.

45.5 The modern ammonia plant (p.93)

c) Typical operation conditions used for the reaction are as follows:
Temperature 200 °C
Pressure 60 atm
Catalyst rhodium / iodide ion
Explain why this set of operation conditions is used.

The temperature at 200 °C is high enough to increase the rate of the reaction but low enough to give a reasonable yield.

The pressure at 60 atm is high enough to increase both the rate of reaction and the yield of $CH_3COOH(g)$ but just low enough to minimise the maintenance cost of pipelines (the cost of building and running the plant is not high).

Rhodium / iodide ion catalyses the reaction / speeds up the reaction.

45.5 The modern ammonia plant (p.93)

2 Catalysts are not consumed in reactions. Suggest why it is still necessary to replace the used catalysts from time to time in industrial processes.

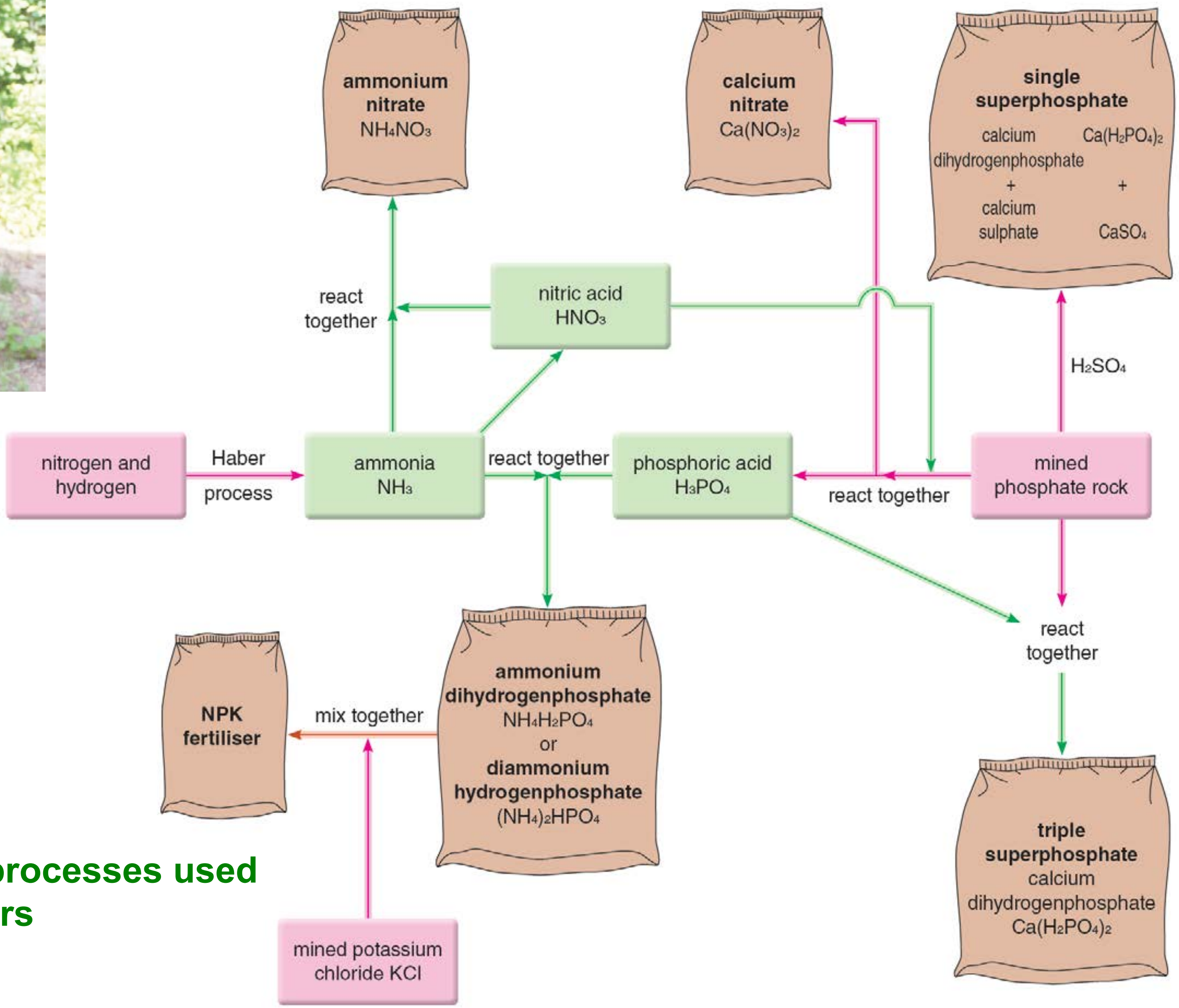
Catalysts can be poisoned.

45.6 Making fertilisers in industry (p.97)

A modern fertiliser factory will produce two main types of products:

- straight N fertilisers
  - solid nitrogen-containing fertilisers sold in pellet form
  - *e.g.* NH_4NO_3, $(NH_4)_2SO_4$ and urea ($CO(NH_2)_2$
- NPK compound fertilisers
  - mixtures that supply the three most essential elements (N, P and K) lost from the soil by extensive use
  - usually a mixture of NH_4NO_3, ammonium phosphate and KCl in different proportions to suit different conditions

A bag of fertiliser; note the three key numbers (N:P:K) on the fertiliser bag are mass percentages of N, P and K respectively



The integrated processes used to make fertilisers

45.6 Making fertilisers in industry (p.97)

- Ammonium nitrate (Nitram®) is probably the most widely used nitrogenous fertiliser. It is manufactured by reacting ammonia gas and nitric acid: $NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$
- The ammonium nitrate can be crystallised into pellet form suitable for spreading on the land.
- Some of the ammonia made in the Haber process is converted into nitric acid. Then the nitric acid can react with ammonia to make ammonium nitrate.

45.6 Making fertilisers in industry (p.97)

Ammonium nitrate is spread as pellets onto the soil

45.6 Making fertilisers in industry (p.97)

- The sources of phosphorus are deposits of phosphate-containing rock, which is dug or mined from the ground. Phosphate rock is treated:
  - with nitric acid to produce phosphoric acid and calcium nitrate. Then the phosphoric acid is neutralised with ammonia to produce phosphates.
  - with sulphuric acid to produce single superphosphate, a mixture of calcium dihydrogenphosphate and calcium sulphate.
  - with phosphoric acid to produce triple superphosphate, which is calcium dihydrogenphosphate.

45.6 Making fertilisers in industry (p.97)

Manufacture of nitric acid from ammonia

- *Stage 1* NH_3 is oxidised by O_2 to NO.

7 atm, 900 °C

$$4NH_3(aq) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \quad \Delta H = -910 \text{ kJ mol}^{-1}$$

Pt-Rh catalyst

- *Stage 2* NO is further oxidised to NO_2.

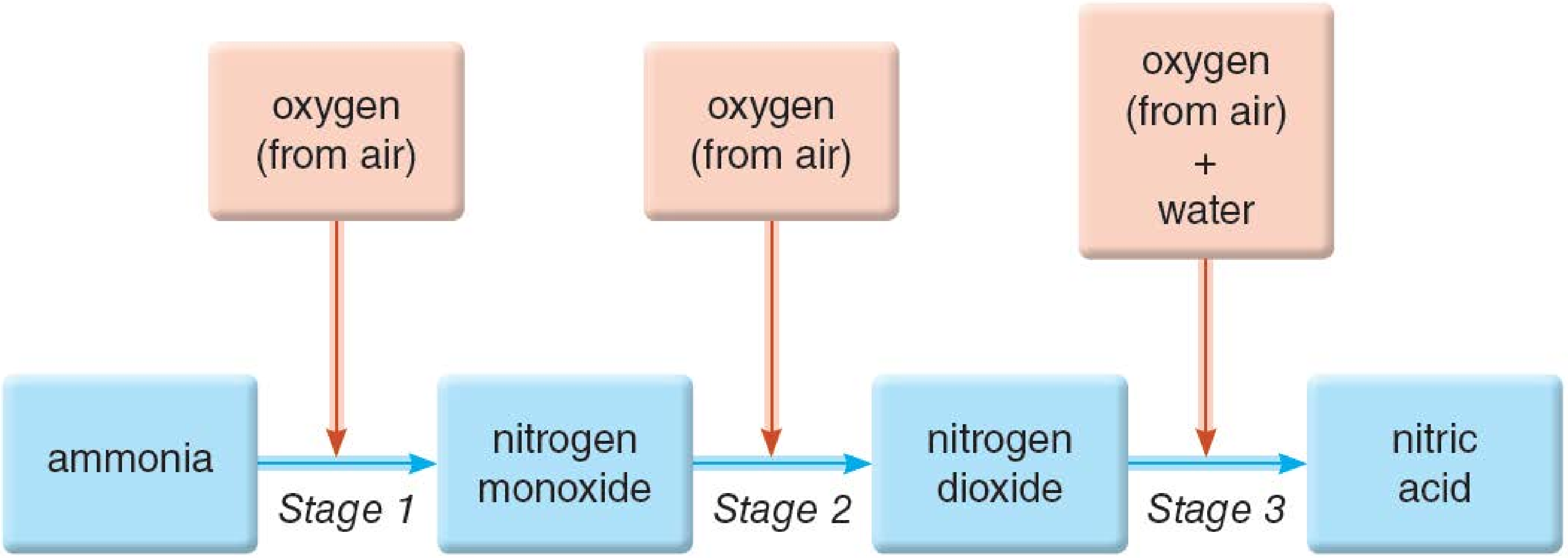
7–12 atm, 40 °C

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -115 \text{ kJ mol}^{-1}$$

- *Stage 3* NO_2 reacts with O_2 and H_2O to make HNO_3.

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightleftharpoons 4HNO_3(aq)$$

45.6 Making fertilisers in industry (p.97)



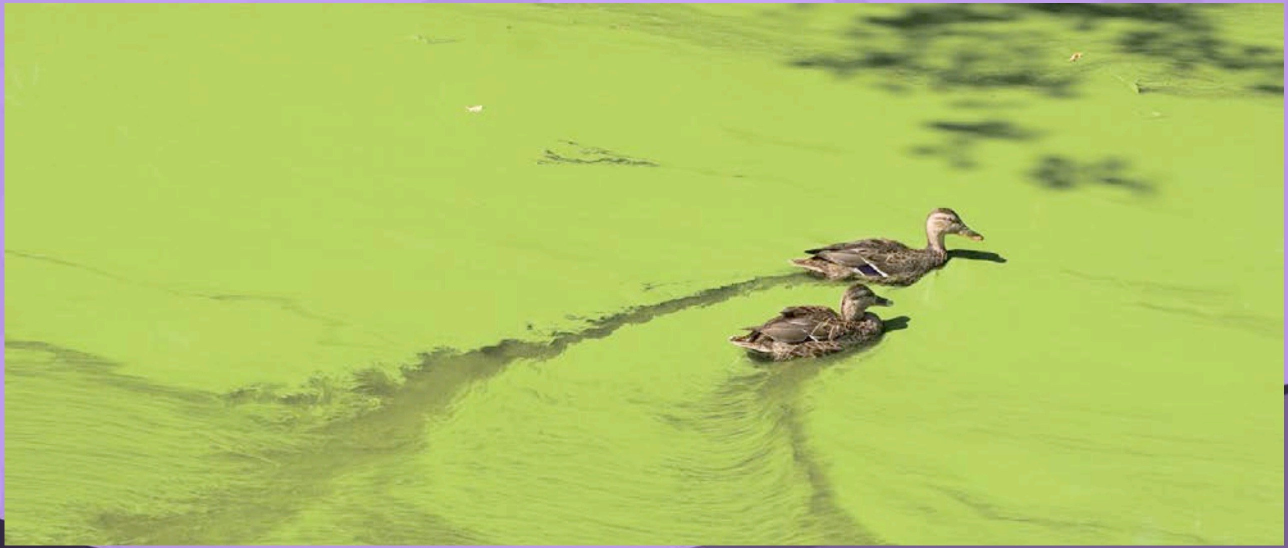
45.7 Synthetic fertilisers: benefits and costs (p.101)

- Farmers could not grow enough crops to support the world's growing population without these fertilisers.
- However, the excessive use of synthetic fertilisers has an impact on the environment.

45.7 Synthetic fertilisers: benefits and costs (p.101)

In rivers

- Fertilisers can seep into rivers from farmland. Nitrates and, to a greater extent, phosphates help the growth of algae.
- A bloom of algae can spread across the water surface blocking out sunlight for other plants in the water.



45.7 Synthetic fertilisers: benefits and costs (p.101)

- These plants cannot carry out photosynthesis and die. Bacteria in the water feed on the decaying plant materials and use up the oxygen dissolved in the water. So fish *suffocate*. This process is known as **eutrophication (富營養化)**.

Eutrophication *Ref.*

45.7 Synthetic fertilisers: benefits and costs (p.101)

In water supply

- The nitrates from fertilisers entering rivers can end up in the water supply system and consumed by humans. The nitrates are converted to nitrites in the human bodies and oxidise the haemoglobin in blood to form *methemoglobin*.
- As a result, the blood carries less oxygen around the body. This may cause the skin of infants (especially 6-month old or younger) to take on a blue tinge. This is known as the **blue baby syndrome (藍嬰症)**.
- People are also worried that nitrates may cause stomach cancer. But others argue that the links between nitrates and diseases have not been proven.

45.8 The chloroalkali industry (p.102)

- The **chloroalkali industry (氯鹼工業)** is a major branch of the chemical industry.
- It is the industry that produces Cl_2 and NaOH by the electrolysis of conc. NaCl (brine).
- NaCl can be obtained from sea water or from underground salt mines.
- Three very important substances are produced in the electrolytic process — Cl_2, NaOH and H_2.
- The process is a very expensive one, requiring a vast amount of electricity. It is economical only because all three products have a large number of uses.

Table 45.2 Principle uses of the products of the chloroalkali industry

Product of the chloroalkali industry	Uses
Sodium hydroxide	making soaps and detergents
	making paper
	for treatment of acidic effluent
Hydrogen	making ammonia
	in welding using an oxy-hydrogen flame
	for hydrogenation of oils to make margarine
	as a rocket fuel
	making hydrochloric acid
Chlorine	for sterilisation and bleaching
	making insecticides
	making solvents such as dichloromethane and tetrachloromethane
	making polyvinyl chloride

45.8 The chloroalkali industry (p.102)

- It is vital that these three products are not allowed to mix during the electrolytic process, otherwise unwanted side-reactions occur and lower the yield.
- Thus, a requirement of a commercial electrolytic cell for the electrolysis of brine is that the three products are separated effectively.
- There are different types of cells that can be used for the electrolysis of brine. Two types of such cells are the flowing mercury electrolytic cell and the membrane electrolytic cell.

45.8 The chloroalkali industry (p.102)

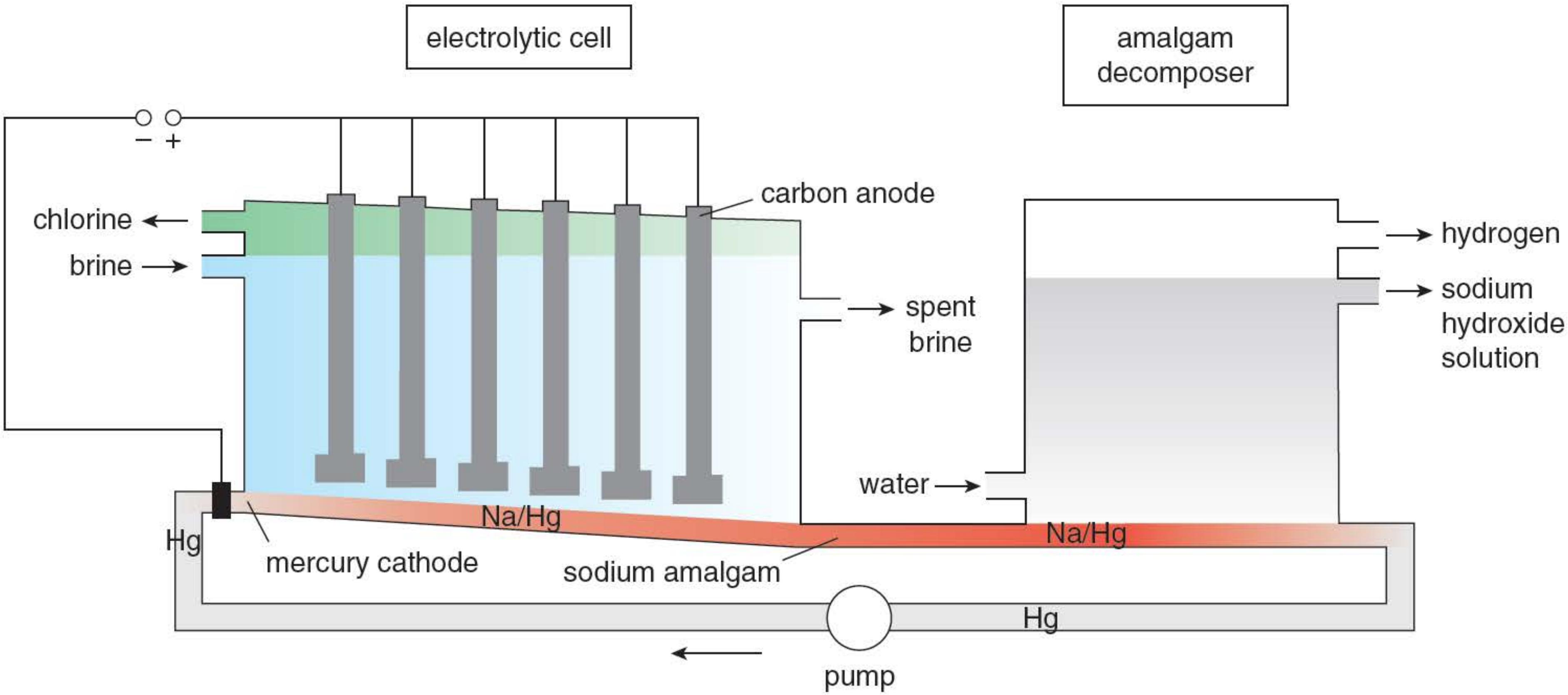
Flowing mercury electrolytic cell

- Carbon anodes in conc. NaCl(aq); a layer of Hg(l) at the bottom
- At the **C anodes**, Cl_2(g) is produced.

  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
- Na^+(aq) is a weaker oxidising agent than a H^+(aq).
  - With **Hg cathode**, Na^+(aq) ions are preferentially discharged to form Na.

    $Na^+(aq) + e^- + Hg(l) \rightarrow Na/Hg(l)$
  - Na is soluble in mercury and the two combine to form sodium **amalgam (汞齊)**.

45.8 The chloroalkali industry (p.102)



45.8 The chloroalkali industry (p.102)

- The sodium amalgam flows into a decomposer where it reacts with water, forming H_2(g) and NaOH(aq).

$$2Na/Hg(l) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + 2Hg(l)$$

- Hydrogen and sodium hydroxide solution are collected separately.
- The mercury is pumped back to the main part for continuous operation.
- The ~50% NaOH(aq) produced is converted to solid flakes by evaporation.
- Overall: $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$

45.8 The chloroalkali industry (p.102)

Pros

- Excellent separation among the sat. NaCl(aq), Cl_2 and NaOH(aq) / the level of impurities is low

Cons

- Hg used is highly toxic; Hg vapour would build up in buildings or escape to the environment

Despite the drawbacks, the flowing mercury electrolytic cell is still a highly effective way of producing chlorine, hydrogen and high quality sodium hydroxide.

45.8 The chloroalkali industry (p.102)

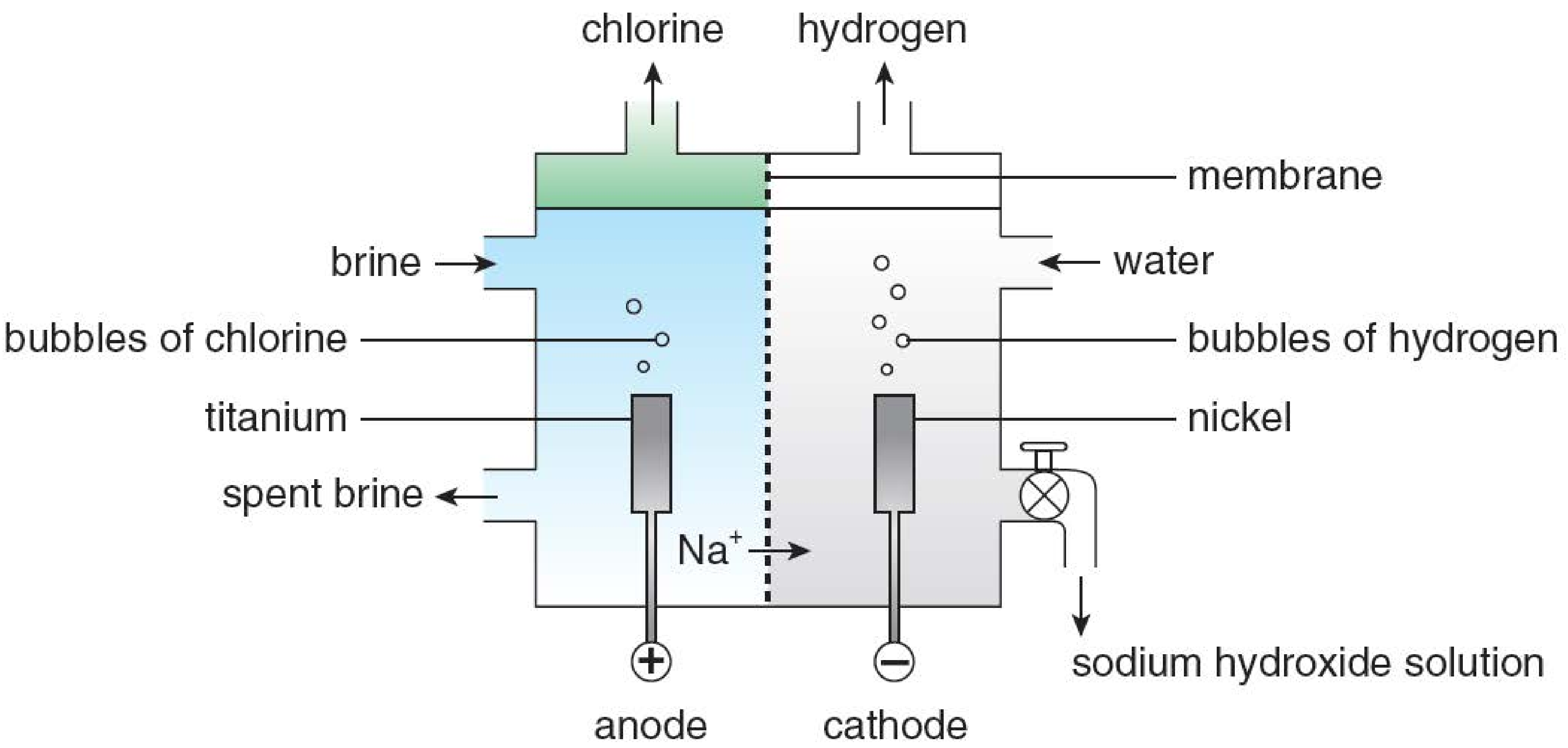
Membrane electrolytic cell

- Less costly and less damaging to the environment than the flowing mercury electrolytic cell; preferred for new plants
- Ti anode (not attacked by chlorine) and Ni cathode, with the two compartments separated by a membrane
- The membrane allows only sodium ions to pass through. In this way, the chlorine liberated at the anode is separated from the sodium hydroxide and hydrogen produced at the cathode.

45.8 The chloroalkali industry (p.102)

The membrane electrolytic cell in a chloroalkali plant in Ludwigshafen am Rhein in Germany

45.8 The chloroalkali industry (p.102)



45.8 The chloroalkali industry (p.102)

- Anode compartment: filled continuously with brine
  Cathode compartment: filled continuously with water

- At the **Ti anode**, $Cl^-(aq)$ ions are oxidised to $Cl_2(g)$.

  $$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

  Leaves a high concentration of $Na^+(aq)$ around the anode.

- At the **Ni cathode**, $H^+(aq)$ ions are reduced to $H_2(g)$.

  $$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

  Water dissociates continuously to replace $H^+(aq)$ reduced.
  Leaves a high concentration of $OH^-(aq)$ around the cathode.

45.8 The chloroalkali industry (p.102)

- The sodium ions flow through the membrane, where they combine with the hydroxide ions to form sodium hydroxide solution.
- Overall: $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$
- The ~30% NaOH(aq) is converted to solid NaOH flakes by evaporation.
- The membrane does not allow hydroxide ions to enter the anode compartment, thus minimising the loss of chlorine as hypochlorite.

45.8 The chloroalkali industry (p.102)

Practice 45.2

Chlorine and hydrogen are manufactured in the chloroalkali industry. The electrolysis involved in the chloroalkali industry can be performed in a mercury electrolytic cell or a membrane electrolytic cell.

a) In both these cells, chlorine is produced at one electrode.

i) Write the half equation for the production of chlorine at this electrode.

$2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$

45.8 The chloroalkali industry (p.102)

ii) Give TWO large-scale uses of the chlorine formed.

Any two of the following:

- Bleach
- Disinfectant / sterilising
- Extraction of bromine
- Water treatment
- PVC
- Solvents
- Hydrochloric acid
- Making medicines
- Making pesticides
- Making CFCs / HCFCs / chloroalkanes

45.8 The chloroalkali industry (p.102)

b) Write the overall equation for the electrolysis involved.

$2NaCl(aq) + 2H_2O \rightarrow 2NaOH(aq) + Cl_2(aq) + H_2(g)$

c) Explain why flowing mercury electrolytic cells have been gradually phased out.

Mercury is poisonous.

45.8 The chloroalkali industry (p.102)

d) Sodium chloride is highly abundant and hydrogen is a non-polluting fuel. A student gives the following comment:

'Electrolysis of brine can be used in large-scale production of hydrogen and this helps to reduce air pollution problems.'

Do you agree with the student? Explain.

'Yes' answers:

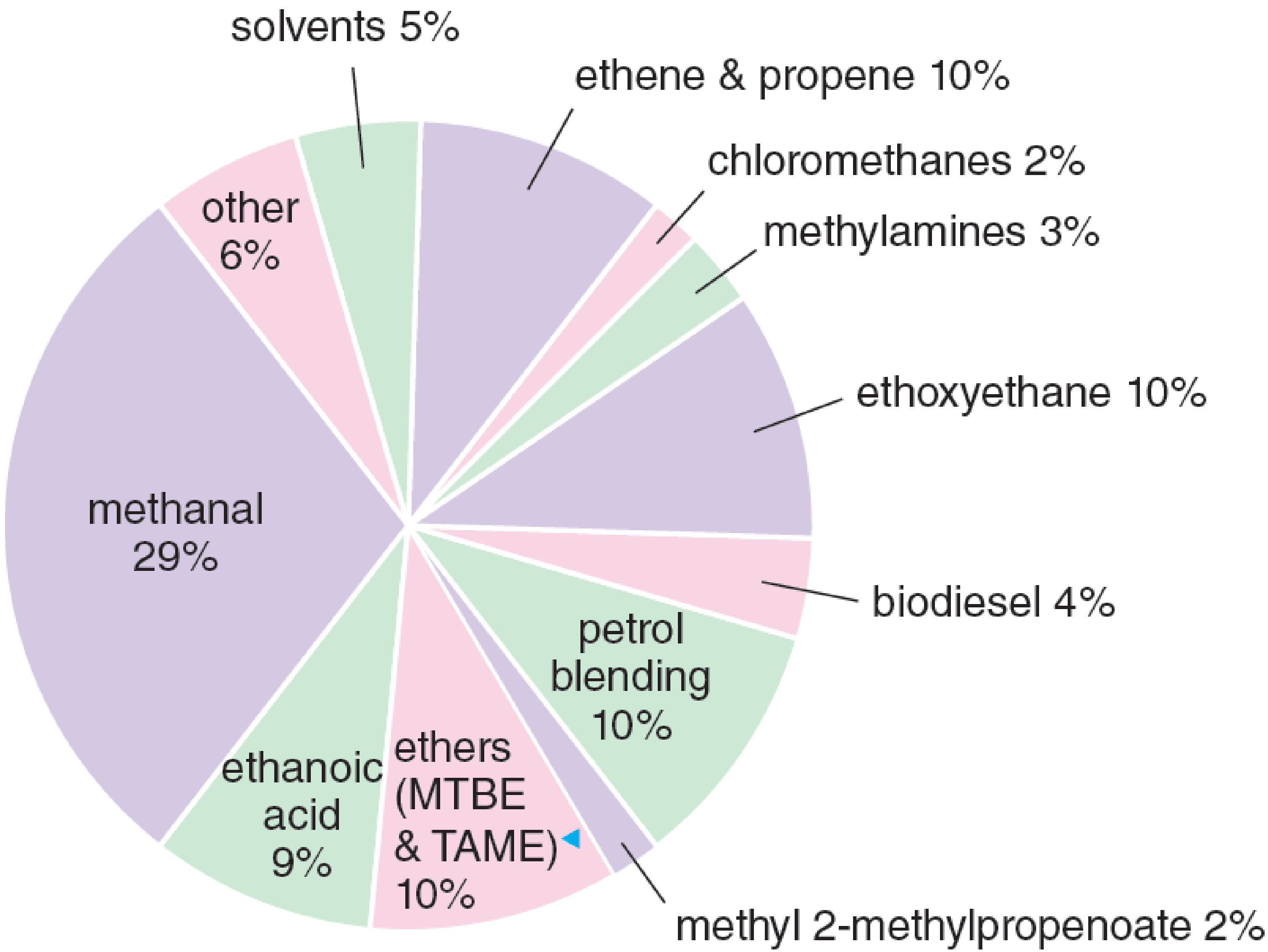
- Burning of hydrogen produces water only.
- Electrolysis of brine for producing hydrogen can help reduce air pollution problems if there is a cheap source of electricity (e.g. photovoltaic cell).

'No' answers:

- The production of hydrogen by electrolysis of brine requires the use of electricity, which is commonly generated by burning of fossil fuels. Burning of fossil fuels is a major source of air pollutants.
- Chlorine is a main product of the electrolysis of brine. Large scale production of hydrogen will yield surplus chlorine. The disposal of unused chlorine is costly and may cause air pollution problems.

45.9 Uses of methanol (p.109)

- One of the most important feedstocks used in the chemical industry is methanol.
- A molecule of methanol contains one single carbon atom. Thus, methanol can act as a starting material to make compounds with molecules having a larger number of carbon atoms.
- The largest use of methanol is as a feedstock for the manufacture of synthetic polymers. It is used to make methanal and hence a variety of synthetic polymers. Methanol is also the principal source for the manufacture of ethanoic acid.



Uses of methanol
(Source: IHS Markit, 2015)

45.9 Uses of methanol (p.109)

- Methanol is also used directly as a fuel or fuel supplement for cars.
- In China, petrol is mixed with methanol (15%) without the need for engines to be redesigned. With some redesigning, more methanol (up to 85%) can be used to mix with petrol.
- The use of methanol as a fuel is expected to increase in the coming years.

45.9 Uses of methanol (p.109)

M-85 is a blend of 85% methanol and 15% petrol; this can be used in vehicles with modified engines

45.10 Manufacture of methanol (p.110)

- Methanol is manufactured from **syngas (合成氣)**, which is a mixture of carbon monoxide and hydrogen.

Production of syngas

- Currently, the only large-scale process for the production of syngas is **steam reforming of natural gas (水蒸汽-天然氣重整)**.

$$CH_4(g) + H_2O(g) \xrightleftharpoons[\text{nickel oxide catalyst}]{\text{30 atm, 730 }^{o}\text{C}} CO(g) + 3H_2(g) \quad \Delta H = +206 \text{ kJ mol}^{-1}$$

45.10 Manufacture of methanol (p.110)

Methanol synthesis

- The synthesis of methanol from syngas:

$$CO(g) + 2H_2(g) \underset{\text{copper and zinc oxide catalyst}}{\overset{\text{50–100 atm, 200–300 °C}}{\rightleftharpoons}} CH_3OH(g) \quad \Delta H = -91 \text{ kJ mol}^{-1}$$

- Conversion of carbon monoxide to methanol is normally 16–40%.
- The crude methanol produced contains both water and low levels of by-products. Pure methanol is obtained by fractional distillation.

45.10 Manufacture of methanol (p.110)

A converter in which methanol is being produced from syngas

45.10 Manufacture of methanol (p.110)

What operation conditions favour the production of methanol?

- Theoretically, the maximum yield of methanol would be obtained
  - at a low temperature (because the forward reaction is exothermic); and
  - at a high pressure (because the number of moles of gas on the product side is smaller than that on the reactant side).
- A high pressure also increases the concentrations of the gases and thus increases the reaction rate and decreases the time required to attain equilibrium.

45.10 Manufacture of methanol (p.110)

- However, there are drawbacks in fulfilling these theoretical conditions.
  - The reaction would be very slow when using a low temperature.
  - When using a high pressure, a lot of energy is required to compress the gases. The equipment needed to withstand high pressures is very expensive. There are also safety implications.

- In practice, a compromise is made between yield, reaction rate and production cost. A temperatre of 200–300 °C and a pressure of 50–100 atmospheres are used.

45.10 Manufacture of methanol (p.110)

Advancements of methanol production technology

- Any solid biomass, such as agricultural, city and industrial waste, can be used to make syngas for methanol production. This conversion process uses renewable feedstocks.
- Carbon dioxide in flue gas can also be used in methanol production. Carbon dioxide and hydrogen (from syngas) react to produce methanol according to the equation below:

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \quad \Delta H = -49 \text{ kJ mol}^{-1}$$

This conversion process may help reducing the release of carbon dioxide to the atmosphere.

Key terms (p.113)

nitrogen fixation	固氮作用	amalgam	汞齊
eutrophication	富營養化	syngas	合成氣
blue baby syndrome	藍嬰症	steam reforming of natural gas	水蒸汽-天然氣重整
chloroalkali industry	氯鹼工業		

Summary (p.114)

1 a) In the Haber process, nitrogen and hydrogen react according to the equation below.

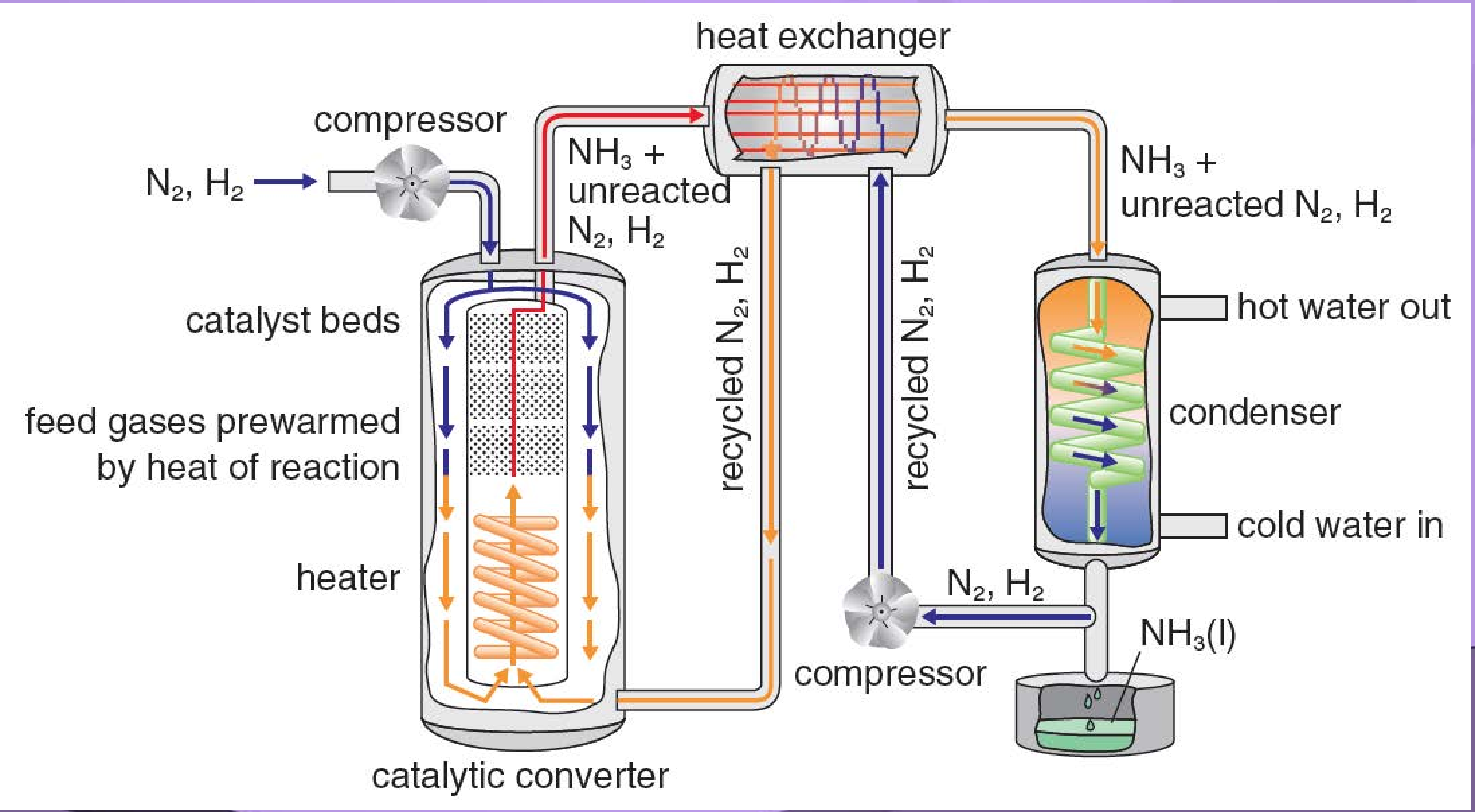
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

b) The operation conditions for the production of ammonia by the Haber process are usually

- a temperature of 450 °C;
- a pressure of 250 atm;
- finely divided iron as catalyst.

Summary (p.114)

c) The following diagram outlines the Haber process that occurs in an ammonia production plant.



Summary (p.114)

2 a) The chloroalkali industry produces chlorine, hydrogen and sodium hydroxide by the electrolysis of concentrated sodium chloride solution (brine).

b) The two main types of cell used for the electrolysis of concentrated sodium chloride solution are:
- flowing mercury cell;
- membrane cell.

c) The electrolystic process can be represented by the overall equation below:

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$$

Summary (p.114)

3 Methanol is produced from syngas (a mixture of carbon monoxide and hydrogen) obtained from natural gas (methane).

a) Production of syngas — steam reforming of natural gas

$$CH_4(g) + H_2O(g) \underset{730\ °C,\ 30\ atmospheres}{\overset{nickel\ oxide\ catalyst}{\rightleftharpoons}} CO(g) + 3H_2(g)$$

b) Methanol synthesis

$$CO(g) + 2H_2(g) \underset{200–300\ °C,\ 50–100\ atmospheres}{\overset{copper\ and\ zinc\ oxide\ catalyst}{\rightleftharpoons}} CH_3OH(g)$$

Unit Exercise (p. 116)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

question targeted at level 3 and above;

question targeted at level 4 and above;

question targeted at level 5.

‘ * ’ indicates 1 mark is given for effective communication.

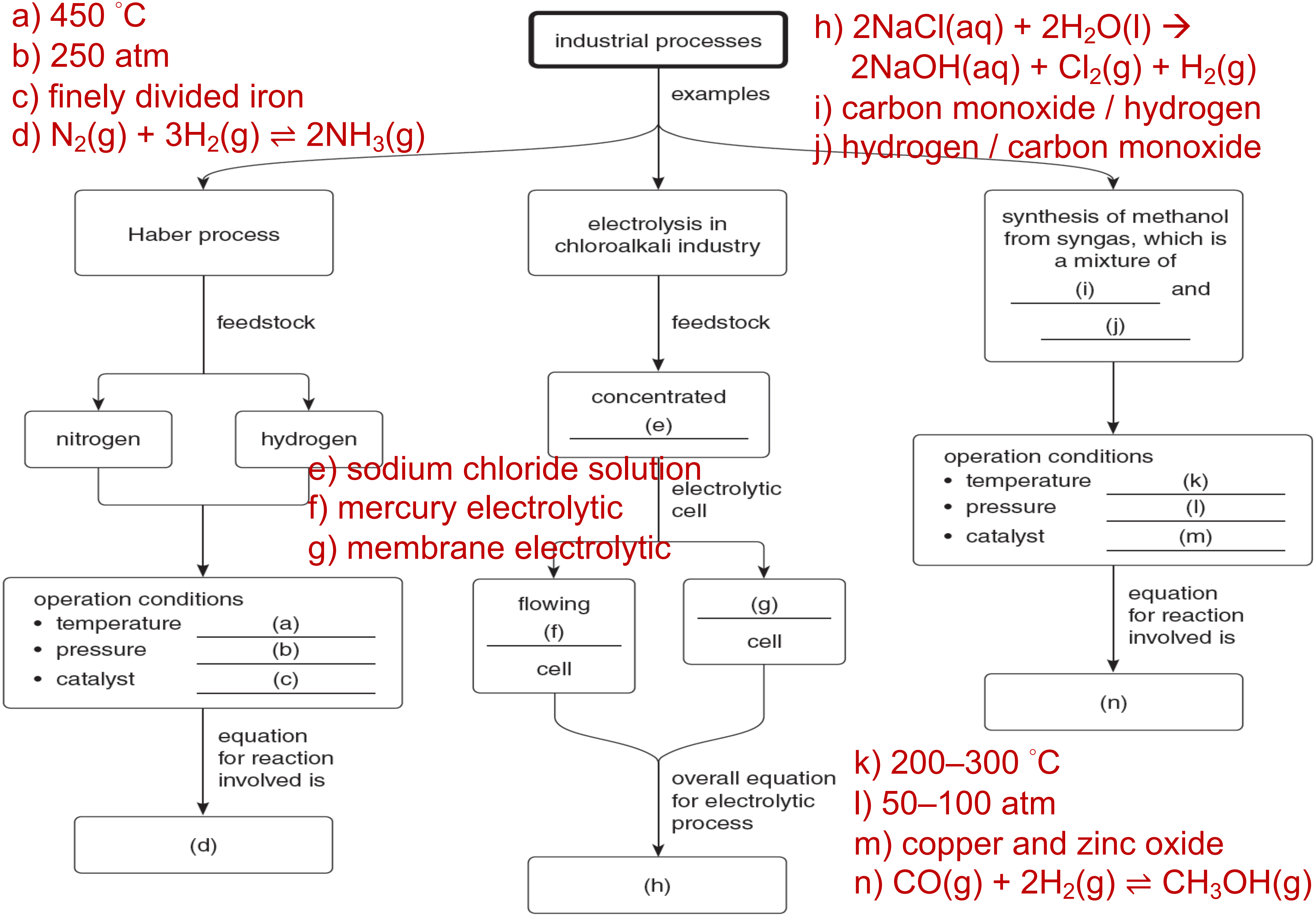
Unit Exercise (p. 116)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.

a) 450 °C
b) 250 atm
c) finely divided iron
d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

h) $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$
i) carbon monoxide / hydrogen
j) hydrogen / carbon monoxide



e) sodium chloride solution
f) mercury electrolytic
g) membrane electrolytic

k) 200–300 °C
l) 50–100 atm
m) copper and zinc oxide
n) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Unit Exercise (p. 116)

PART II MULTIPLE CHOICE QUESTIONS

Directions: Questions 2 and 3 refer to the reaction below.

The reaction between carbon monoxide and steam is used to produce hydrogen.

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad \Delta H = -40 \text{ kJ mol}^{-1}$$

What effect would the following changes have on the rate of reaction and the yield of hydrogen?

Answer: B

2 Increase in temperature

	Rate	Yield of H_2
A	increases	increases
B	increases	decreases
C	increases	no change
D	no change	decreases

Explanation:
The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the yield of $H_2(g)$.

Unit Exercise (p. 116)

3 Increase in pressure

	Rate	Yield of H_2
A	increases	increases
B	increases	decreases
C	increases	no change
D	no change	no change

Answer: C

Explanation:
A pressure increase has NO effect on the yield of $H_2(g)$ as there is no change in the number of moles of gas during the course of the reaction.

Unit Exercise (p. 116)

Directions: Questions 4–6 refer to the reaction below.

The first stage in the manufacture of nitric acid is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -906 \text{ kJ mol}^{-1}$$

4 In modern industrial plants this reaction is carried out at a pressure of around 3 atm. Which of the following statements is INCORRECT? The raised pressure

Answer: B

A helps push the reactants through the reactor.
B shifts the position of equilibrium to the right.
C increases the cost of the reactor.
D increases the energy cost of this part of the process.

Explanation:
The raised pressure shifts the position of equilibrium to the left, the side with fewer number of moles of gas.

Unit Exercise (p. 116)

5 A platinum-rhodium alloy catalyst is used in this reaction.
Which of the following statements is INCORRECT?
The catalyst

A lowers the activation energy of the reaction.
B has no effects on the equilibrium constant for the reaction.
C alters the enthalpy change of the reaction.
D reduces the energy cost of this part of the process.

Answer: C

Explanation:
A catalyst has NO effect on the enthalpy change of a reaction.

Unit Exercise (p. 116)

6 The operating temperature of this reaction is about 900 °C. The use of a high temperature

A increases the rate of the reaction and the equilibrium yield.
B increases the rate of the reaction and decreases the equilibrium yield.
C decreases the rate of the reaction and the equilibrium yield.
D decreases the rate of the reaction and increases the equilibrium yield.

(Edexcel Advanced GCE, Unit 4, Jun. 2013, 5)

Answer: B

Explanation:
The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the equilibrium yield.

Unit Exercise (p. 116)

7 Methanol is manufactured via the following reaction in the presence of a catalyst.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H < 0$$

Which of the following combinations describes the effect of increasing the pressure of the system?

	Yield of $CH_3OH(g)$	Reaction rate
A	decreases	increases
B	decreases	decreases
C	increases	increases
D	increases	decreases

Answer: C

Explanation:

Number of moles of gaseous product is less than that of gaseous reactants.

A pressure increase shifts the position of equilibrium to the right, increasing the yield of $CH_3OH(g)$.

Unit Exercise (p. 116)

Directions: Questions 8 and 9 refer to the following information:

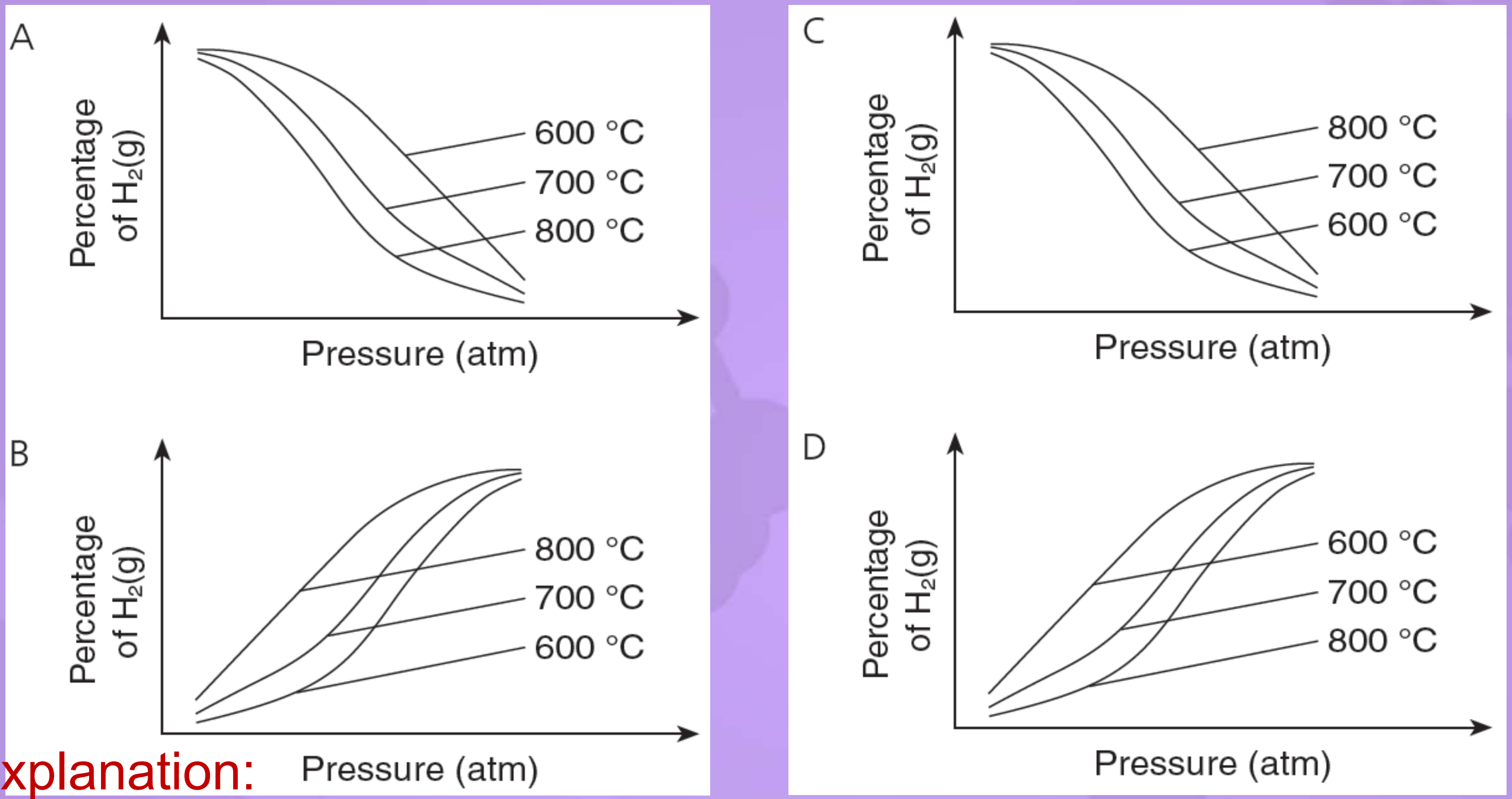
Hydrogen is produced in industry from the reaction between methane and steam in the presence of a catalyst.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

8 Which of the following graphs describes the effect of pressure and temperature on the percentage of hydrogen in the equilibrium mixture?

Unit Exercise (p. 116)

Answer: C



Explanation:

The forward reaction is endothermic. A temperature increase shifts the position of equilibrium to the right, increasing the yield of $H_2(g)$.

Number of moles of gaseous products is more than that of gaseous reactants. A pressure increase shifts the position of equilibrium to the left, decreasing the yield of $H_2(g)$.

Unit Exercise (p. 116)

9 Which of the following combinations describes the effect of removing the catalyst from the system?

	Yield of products	Reaction rate
A	decreases	decreases
B	no change	decreases
C	no change	no change
D	decreases	no change

Answer: B

Unit Exercise (p. 116)

10 Which of the following products is / are obtained from the chloroalkali industry?

(1) Oxygen
(2) Sodium hypochlorite
(3) Sodium hydroxide

A (1) only
B (2) only
C (1) and (3) only
D (2) and (3) only

Answer: D

Unit Exercise (p. 116)

PART III STRUCTURED QUESTIONS

11 Many catalysts are very expensive but their use does allow the chemical industry to operate more profitably. Explain why the use of catalysts provides economic and environmental benefits.

(WJEC CBAC Advanced Subsidary / Advanced GCE, CH1, Jan. 2014, 9(e))

Any THREE of the following:

- Lower temperature can be used. (1)
- Energy costs are saved. (1)
- More product can be made in a given time. (1)
- Enable reactions that would otherwise be impossible to take place. (1)
- Less fossil fuels are burnt to provide energy, so less carbon dioxide would form. (1)

Unit Exercise (p. 116)

12 Consider the Haber process.

a) Write the chemical equation for the reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (1)

b) Air and natural gas are the raw materials used in the Haber process. Explain why these raw materials are required with the help of appropriate equation(s).

Nitrogen is obtained by the fractional distillation of liquid air. (1)

Methane in natural gas reacts with steam to form hydrogen gas. (1)

$CH4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$ (1)

Unit Exercise (p. 116)

c) Iron in highly porous form is used as a catalyst in the process.

i) Explain why a catalyst can increase the rate of a reaction.

A catalyst provides an alternative reaction pathway with a lower activation energy. (1)

ii) Explain why making the catalyst in highly porous form can increase the efficiency of the catalyst.

The reaction takes place on the surface of the catalyst.
The catalyst in highly porous form increases the contact surface area for reactants and thus increases the efficiency of the catalyst. (1)

d) Scientists think that the Haber process is one of the most important chemical reactions.

Explain the importance of the Haber Process in agriculture.

There is endless supply of the starting materials.
Ammonia is used to make fertilisers, which increase crop yield. (1)

Unit Exercise (p. 116)

13 Ammonia can be manufactured in the Haber process. The equation below represents the reaction involved.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

a) Explain why the reactants are purified before passing into the reaction chamber containing the catalyst.

Impurities in the reaction mixture may poison the catalyst. (1)

Unit Exercise (p. 116)

b) You are given that for the formation of NH_3(g) from N_2(g) and H_2(g) at 350 °C and 600 atm, the yield of NH_3(g) at equilibrium is about 60%. However, the operation conditions of the Haber process in industry are set at about 450 °C and 250 atm with the yield of NH_3(g) at equilibrium of about 25%. With reference to the given information, explain why such operation conditions are chosen in industry.

The higher temperature is used to speed up the reaction. (1)
Not a very high pressure is used in consideration of mechanical design and safety concerns. (1)

c) Suggest how ammonia can be separated from the reaction mixture obtained.

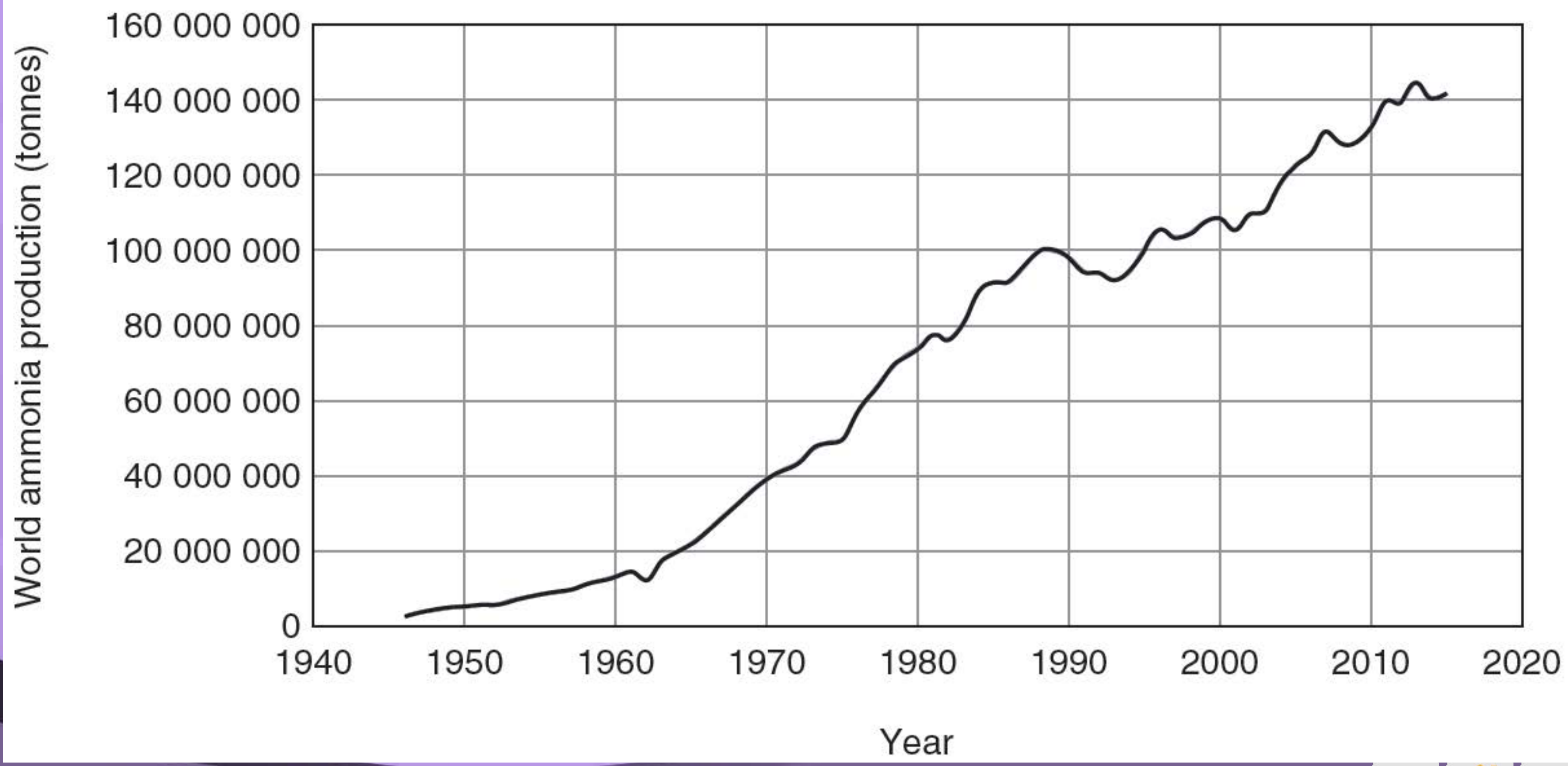
The reaction mixture is cooled to condense ammonia to liquid. (1)

d) Explain why unreacted nitrogen and hydrogen are recycled.

To reduce cost. / To increase the yield of ammonia. (1)

Unit Exercise (p. 116)

14 The graph below shows the world production of ammonia from 1945–2015. The main use of ammonia is to make fertilisers. Large-scale use of fertilisers made from ammonia causes environmental problems. Write about these problems, and explain why they have got worse over the last 70 years.



Unit Exercise (p. 116)

Production of ammonia has increased. / Use of fertilisers has increased. (1)

Fertilisers can seep into rivers from farmland. Nitrates and phosphates help the growth of algae. (1)

A bloom of algae can spread across the water surface, blocking out sunlight for other plants in the water. These plants cannot carry out photosynthesis and die. (1)

Bacteria in the water feed on the decaying plant materials and use up the oxygen dissolved in the water. So fish suffocate. This process is known as eutrophication. (1)

Unit Exercise (p. 116)

15 Consider the manufacture of ammonia by the Haber process in a chemical plant.

a) Suggest how nitrogen gas can be obtained in industry.

b) Explain why there is a need to install a heat exchanger in the chemical plant.

c) If 420 kg of nitrogen and 96 kg of hydrogen are introduced into the reaction chamber, and with the yield of ammonia of 15%, calculate the mass of ammonia produced.

d) Nitric acid can also be produced in the chemical plant. Firstly, ammonia is oxidised to give nitrogen monoxide, and nitrogen monoxide is further oxidised to nitrogen dioxide. Finally, oxidation of nitrogen dioxide gives nitric acid. Write the chemical equation for each of the following reactions:

i) Oxidising ammonia to give nitrogen monoxide

ii) Oxidising nitrogen dioxide to give nitric acid

(HKDSE, Paper 2, 2016, 1(b))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Unit Exercise (p. 116)

16 Nitric acid is made from ammonia. The ammonia is first converted to nitrogen monoxide, which is then reacted with air.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -115 \text{ kJ mol}^{-1}$$

a) Explain the effect of increasing the temperature on the rate of reaction between NO(g) and $O_2(g)$.

The rate of reaction increases.

A temperature rise

- increases the average kinetic energy of the molecules, causing the collision frequency to increase, and hence effective collisions among molecules occur more frequently. (1)
- increases the fraction of molecules with kinetic energy equal to or greater than the activation energy, and hence a higher percentage of molecules with sufficient energy to collide and react. (1)

Unit Exercise (p. 116)

b) Explain the effect of increasing the temperature on the yield of NO_2(g).

The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the yield of NO_2(g). (1)

c) In view of your answers to (i) and (ii), suggest why a temperature of 40 °C is used for the reaction between NO(g) and O_2(g).

A low temperature is required for a high yield of NO_2(g).
However, the reaction may proceed too slowly if the temperature is too low. (1)
40 °C is a compromise between rate and yield. (1)

Unit Exercise (p. 116)

17 The manufacture of nitric acid from ammonia involves several stages. The first stage is the oxidation of ammonia to nitrogen monoxide.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \quad \Delta H = -910 \text{ kJ mol}^{-1}$$

The catalyst for this reaction is a platinum-rhodium alloy in the form of a gauze. This catalyst gauze is heated initially but then remains hot during the reaction.

a) Suggest a reason why the catalyst must be hot.

To overcome the activation energy. / To provide the minimum energy to make the reaction start. (1)

b) Suggest a reason why the catalyst remains hot during the reaction.

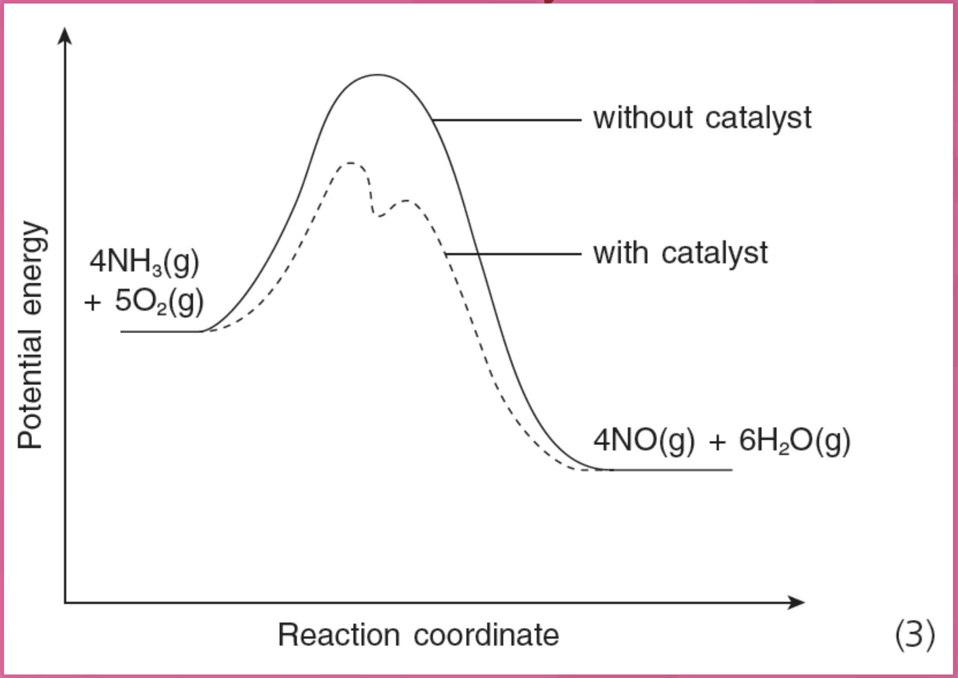
The reaction is exothermic. (1)

c) Explain how a catalyst increases the rate of a reaction.

A catalyst provides an alternative reaction pathway with a lower activation energy. (1)

Unit Exercise (p. 116)

d) Draw, in the same sketch, TWO labelled potential energy profiles for the above conversion: one with the catalyst and the other one without the catalyst.



e) Suggest why the used catalyst is replaced from time to time.

The catalyst can be poisoned. (1)

f) Suggest ONE use of the nitric acid made in the process.

To produce ammonium nitrate which is used as a fertiliser. (1)

Unit Exercise (p. 116)

18 The manufacture of sulphuric acid involves the following conversion of SO_2(g) to SO_3(g): $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -197 \text{ kJ mol}^{-1}$

Nowadays in industry, a solid catalyst vanadium(V) oxide is used for the conversion of SO_2(g) to SO_3(g).

a) The reactants need to be purified before passing into the reaction chamber containing the catalyst. Why?

b) The operation conditions are set at 450 °C and 1 atm to achieve a 96% conversion. Suggest why it is NOT preferable to further increase the conversion percentage by each of the following methods:

i) Lowering the temperature of the reaction system

ii) Increasing the pressure of the reaction system

c) In order to increase the conversion percentage, one of the reactants used is in slight excess. From the perspective of feedstock, which of SO_2(g) or O_2(g) would be in slight excess? Explain your answer.

(HKDSE, Paper 2, 2017, 1(b)(ii))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Unit Exercise (p. 116)

19 Propenenitrile (CH_2CHCN) is used to make polypropenenitrile. Propenenitrile is manufactured from propene as shown in the equation.

$$C_3H_6(g) + NH_3(g) + \frac{3}{2}O_2(g) \rightleftharpoons CH_2CHCN(g) + 3H_2O(g) \quad \Delta H = -540 \text{ kJ mol}^{-1}$$

The operation conditions used are 450 °C and 2.5 atmospheres in the presence of a catalyst.
Justify why this set of operation conditions is used with reference to position of equilibrium and reaction rate.

A higher temperature increases the rate of reaction. (1)
The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the yield of $CH_2CHCN(g)$. (1)
The operation temperature of 450 °C is a compromise between rate and yield.
The number of moles of gaseous products is more than that of gaseous reactants. A pressure increase shifts the position of equilibrium to the left, decreasing the yield of $CH_2CHCN(g)$. (1)
A low pressure keeps the yield of $CH_2CHCN(g)$ high, and decreases building / running costs. (1)

Unit Exercise (p. 116)

20 Chlorine can be produced by the flowing mercury cell process.

a) Write the half equation for the change occurring at the anode.

b) Write the half equation for the change occurring at the cathode.

c) Explain why the flowing mercury cell process has been gradually phased out.

(HKDSE, Paper 2, 2017, 1(c)(ii))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Unit Exercise (p. 116)

21 Chlorine is one of the products manufactured in the chloroalkali industry. The electrolysis involved in the chloroalkali industry can be performed in a mercury electrolytic cell or a membrane electrolytic cell.

a) State the feedstock used in the chloroalkali industry.

Concentrated sodium chloride solution / brine (1)

b) Write the overall equation for the electrolysis involved in the chloroalkali industry.

$2NaCl(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$ (1)

c) The chloroalkali industry can also manufacture chlorine bleach. Write an equation for the reaction involved.

$Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$ (1)

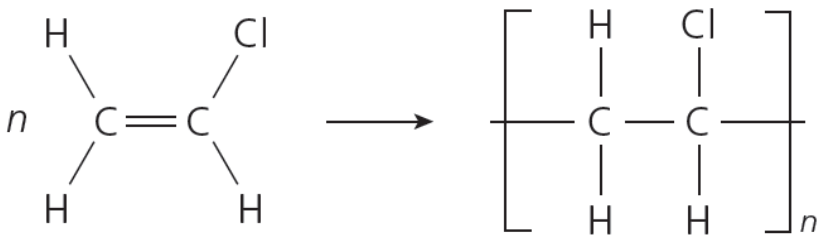
Unit Exercise (p. 116)

d) Besides chlorine bleach, chlorine is used to make a useful synthetic polymer.

i) Name a synthetic polymer that is made from chlorine.

To make polyvinyl chloride. (1)

ii) Write the chemical equation for the formation of the synthetic polymer and state ONE use of it.



(1)

It is used in making pipes / used in wire and cable insulation. (1)

Unit Exercise (p. 116)

e) State TWO environmental problems associated with the chloroalkali industry.

Any two of the following:

- The chloroalkali industry uses large amounts of electrical energy, much of which is derived from fossil fuels.
  Burning of fossil fuels releases carbon dioxide / sulphur dioxide into the atmosphere. This leads to environmental problems.
  (Carbon dioxide is a greenhouse gas which contributes to global warming and climate change. Sulphur dioxide increases the acidity of rivers and lakes, affecting ecosystems.) (1)
- Mercury electrolytic cells use toxic mercury which may threat our health when discharged to the environment. (1)
- Electrolysis of brine produces chlorine gas. Chlorine is highly toxic and may threaten the environment if leaked out. (1)

Unit Exercise (p. 116)

22 Methanol is made by reacting carbon monoxide with hydrogen. The equation for this reaction is:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91 \text{ kJ mol}^{-1}$$

a) Explain why the maximum equilibrium yield of methanol would be obtained by low temperature and high pressure.

The forward reaction is exothermic. A temperature decrease shifts the position of equilibrium to the right. (1)
Thus, a low temperature favours the formation of methanol.
The number of moles of gaseous product is less than that of gaseous reactants. A pressure increase shifts the position of equilibrium to the right. (1)
Thus, a high pressure favours the formation of methanol.

b) What effect, other than on the yield, does the use of a high pressure have on the reaction?

Increase the rate of reaction. (1)

Unit Exercise (p. 116)

c) State the operation conditions used for the production of methanol in industry.

Temperature: 200–300 °C

Pressure: 50–100 atm

Catalyst: copper and zinc oxide (1)

d) A catalyst of copper and zinc oxide is used in this process. The catalyst is coated on an inert alumina support.

Why is the catalyst spread as a thin layer on the alumina?

To maximise the surface area. / Less catalyst can be used. (1)

e) Which of the following hazard warning labels should be displayed on a container of methanol?

Unit Exercise (p. 116)

23 Methanol is produced from syngas made from natural gas.

a) Why is methanol an important compound in the chemical industry?

A molecule of methanol contains one single carbon atom. Thus, methanol can act as a starting material to make compounds with molecules having a larger number of carbon atoms. (1)

b) State the TWO major constituent gases in syngas.

Carbon monoxide and hydrogen (1)

c) Name the process for making syngas from natural gas. Write the chemical equation for the reaction involved.

Steam reforming of natural gas (1)

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ (1)

d) Write the chemical equation for the reaction in the production of methanol from syngas.

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ (1)

Unit Exercise (p. 116)

e) The table below lists the operation conditions of two methods for making methanol from syngas.

	Catalyst used	Temperature used (°C)	Pressure (atm)
Method 1	a mixture of zinc oxide and chromium(III) oxide	400	300
Method 2	copper based substance	250	70

Making methanol using *Method 2* is cheaper than using *Method 1*. Explain why.

Any two of the following:
- Lower temperature (1)
- Lower pressure (1)
- Use less energy (1)

Unit Exercise (p. 116)

f) People dealing with a leak during this synthesis would need to wear protective equipment.
State ONE piece of protective equipment that would be worn and state why it is needed.

Any one of the following:

- Breathing equipment / gas mask / respirator / oxygen mask
  because CO / CH_3OH / reaction mixture is toxic. (1)
- Fire-proof clothing
  because CO / H_2 / CH_3OH / reaction mixture is flammable. (1)
- Gloves / protective clothing
  because CH_3OH can be absorbed through the skin. (1)
- Eye protection
  because CH_3OH damages eyes / irritates eyes / causes blindness. (1)
- Flak jacket
  because hydrogen is explosive. (1)

Unit Exercise (p.116)

24 Ethanol is an important industrial compound.

Ethanol can be produced by the hydration of ethene.

The equation for the equilibrium that is established is

$$H_2C{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \qquad \Delta H = -42 \text{ kJ mol}^{-1}$$

The operating conditions for the process are a temperature of 300 °C and a pressure of 7 MPa.

Under these conditions, the conversion of ethene into ethanol is 5%.

a) Deduce how an overall yield of 95% is achieved in this process without changing the operating conditions.

Recycle unreacted ethene and steam. (1)

b) Use your knowledge of equilibrium reactions to explain why a manufacturer might consider using an excess of steam in this process, under the same operating conditions.

(AQA GCE, Unit 2, Jun. 2013, 10(a))

The position of equilibrium shifts to the right so as to decrease the amount of steam. (1)

Thus, the yield of ethanol increases.