Mastering Chemistry

- Book 6
- Topic 13 Industrial Chemistry

Content

Continued on next page

Content

- Key terms
- Summary
- Unit Exercise
- Topic Exercise

46.1 Green chemistry (p.124)

- Economic growth is often linked to environmental pollution and resource depletion. The challenge is to develop in a way that meets the needs of the present generation without compromising the ability of future generations to meet their own needs.

46.1 Green chemistry (p.124)

- This type of development is called '**sustainable development (可持續發展)**' and it will be more and more critical as the population of the world increases.

46.1 Green chemistry (p.124)

Historically, chemical plants have had considerable environmental impacts:

- they occupy large areas of land, often near the coast, and can be highly visually intrusive;
- there can be effluent emissions of vapour or waste liquids into the air or sea / rivers;

46.1 Green chemistry (p.124)

- solid waste may need to be stored on site in waste lagoons (e.g. *fuel ash lagoons* in electric plants);
- hot water from cooling systems may be released into rivers or the sea.

46.1 Green chemistry (p.124)

One of the ways in which the chemical industry is working towards sustainable development is by using '**Green chemistry (綠色化學)**'. Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. It achieves sustainability through:

- the development of economical renewable energy sources;
- the use of reagents derived from renewable materials; and
- replacing pollution-generating technologies with clean alternatives.

46.1 Green chemistry (p.124)

- There are twelve key principles of green chemistry. It follows that in any chemical process the key factors to consider are cost, impact on the environment, and health and safety.

Table 46.1 Green chemistry's 12 principles

1	Prevent waste handling	Design chemical syntheses requiring least waste handling. Leave no waste to treat or clean up.
2	Maximise atom economy	Design syntheses that maximise the incorporation of the feedstock into the final product.
3	Design less hazardous chemical syntheses	Design syntheses that use or generate substances with little or no toxicity to either humans or the environment.
4	Design safer chemicals and products	Design chemical products that are fully effective yet have little or no toxicity.

46.1 Green chemistry (p.124)

5	Use safer solvents and auxiliary substances	Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.
6	Increase energy efficiency	Run chemical reactions at room temperature and pressure whenever possible.
7	Use renewable feedstocks	Use feedstocks that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products; the source of depletable feedstocks is often fossil fuels or mining operations.
8	Avoid using chemical derivatives	Avoid using blocking groups or any temporary modifications if possible. Derivatives use additional reagent and generate waste.

46.1 Green chemistry (p.124)

9	Use catalysts	Catalysts generally reduce energy usage and side-products as waste.
10	Design chemicals and products to degrade after use	Design chemical products that break down to innocuous substances after use.
11	Analyse in real time to prevent pollution	Include in-process, real-time monitoring and control during syntheses to minimise or eliminate the formation of waste products.
12	Minimise the potential for accidents	Design chemicals and their physical forms (solid, liquid, or gas) that minimise the potential for chemical accidents including explosion, fire and release to the environment.

46.2 Atom economy (p.127)

- Most of the chemical industry is concerned with turning reactant(s) into the desired product.
- All industrial chemists want to make the maximum amount of product from the given reactant(s).
- It is possible to check how efficient a chemical process is by using the idea of percentage yield.

$$\text{Percentage yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100\%$$

46.2 Atom economy (p.127)

Practice 46.1

In a chemical synthesis of calcium oxide, calcium carbonate is roasted in an oven. The equation of the reaction is:

	$CaCO_3(s) \rightarrow$	$CaO(s) +$	$CO_2(g)$
relative molecular mass or formula mass	100.1	56.1	44.0

500 kg calcium carbonate are used and 210 kg calcium oxide are obtained. Calculate the percentage yield of calcium oxide.

$$\text{Theoretical yield of CaO} = 500\text{ kg} \times \frac{56.1}{100.1} = 280\text{ kg}$$

$$\text{Percentage yield of CaO} = \frac{210\text{ kg}}{280\text{ kg}} \times 100\% = 75.0\%$$

46.2 Atom economy (p.127)

- The idea of percentage yield is useful, but from a green chemistry perspective, it cannot provide the full picture. A reaction can have a high percentage yield but also make a lot of by-products as waste.
- One of the key principles of green chemistry is that processes should be designed to maximise the incorporation of the feedstock into the desired product and, at the same time, produce a minimum mass of waste.

46.2 Atom economy (p.127)

- When deciding which reactions to use in a chemical plant, the percentage of mass of the reactant atoms ending up in the desired product is one factor that is taken into consideration. This percentage is called the **atom economy (原子經濟)**. The greater the atom economy, the less is the waste.

Atom economy (%)

$$= \frac{\text{the sum of relative molecular mass or formula mass of product(s)}}{\text{the sum of relavtive molecular mass or formula mass of reactants}} \times 100\%$$

46.2 Atom economy (p.127)

- Consider again the synthesis of calcium oxide:

	$CaCO_3(s)$ →	$CaO(s)$ +	$CO_2(g)$
relative molecular mass or formula mass	100.1	56.1	44.0

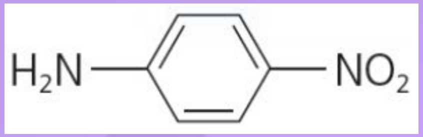
- Atom economy of the reaction $= \frac{56.1}{100.1} \times 100\% = 56.0\%$

- Thus, even for 100% yield, only over half of the mass of the reactant will be incorporated into the desired product while the rest will be wasted. This is not a green process.

46.2 Atom economy (p.127)

Practice 46.2

Synthetic dyes can be manufactured starting from compounds such as

4-nitrophenylamine ().

A synthesis of 4-nitrophenylamine from phenylamine involves the following reaction: $2C_6H_5NH_2 + CH_3COCl \rightarrow C_6H_5NHCOCH_3 + C_6H_5NH_3Cl$

phenylamine *N*-phenylethanamide

N-phenylethanamide is used to make 4-nitrophenylamine.

(Relative atomic masses: H = 1.0, C = 12.0, N = 14.0, O = 16.0, Cl = 35.5)

a) Calculate the atom economy for the production of *N*-phenylethanamide from phenylamine.

b) In a process where 100.0 kg of phenylamine are used, 55.2 kg of *N*-phenylethanamide are obtained.
Calculate the percentage yield of *N*-phenylethanamide.

c) Comment on your answers to (a) and (b) with reference to the commercial viability of the process.

46.2 Atom economy (p.127)

$$2C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NHCOCH_3 + C_6H_5NH_3Cl$$

	$2C_6H_5NH_2$	CH_3COCl	$C_6H_5NHCOCH_3$	$C_6H_5NH_3Cl$
Relative molecular mass or formula mass	93.0	78.5	135.0	

a) Atom economy for production of *N*-phenylethanamide $= \dfrac{135.0}{2 \times 93.0 + 78.5} \times 100\%$

$= 51.0\%$

b) Theoretical yield of *N*-phenylethanamide $= 100.0\ \text{kg} \times \dfrac{135.0}{2 \times 93.0}$

$= 72.6\ \text{kg}$

Percentage yield of *N*-phenylethanamide $= \dfrac{55.2\ \text{kg}}{72.6\ \text{kg}} \times 100\%$

$= 76.0\%$

c) Although the yield is satisfactory (76.0%), the atom economy is only 51.0%. Nearly half of the material produced is waste and must be disposed of.

46.3 How green is a process (p.129)

- An overall environmental impact analysis should take into account not only the chemical reactions, but also the hazards and consequences of acquiring and transporting the feedstocks.
- Besides, the overall energy demand should also be considered. A reaction can have 100% atom economy, yet still be problematic because of hazardous feedstocks.
- The Haber process is an energy-intensive process, as a large amount of energy is required for attaining the high temperature and pressure for accomplishing the reaction.

46.3 How green is a process (p.129)

- However, the Haber process can be considered as an example of green chemistry because
  - the reaction has 100% atom economy;
  - the reactants (N_2 and H_2) are non-toxic and pose no harm to the environment;
  - the reaction takes place in gas phase (no solvents are used);
  - the product is separated by cooling to become a liquid (no separating agents are used);
  - the raw material (N_2) is available in large amount in the atmosphere (depletion is not a problem);
  - the reaction does not require the use of any derivatives;
  - a catalyst is used in the process.

46.3 How green is a process (p.129)

Q (Example 46.1)

It is important for manufactures to use chemical processes having both high percentage yield and high atom economy. Explain why each of these is important.

A

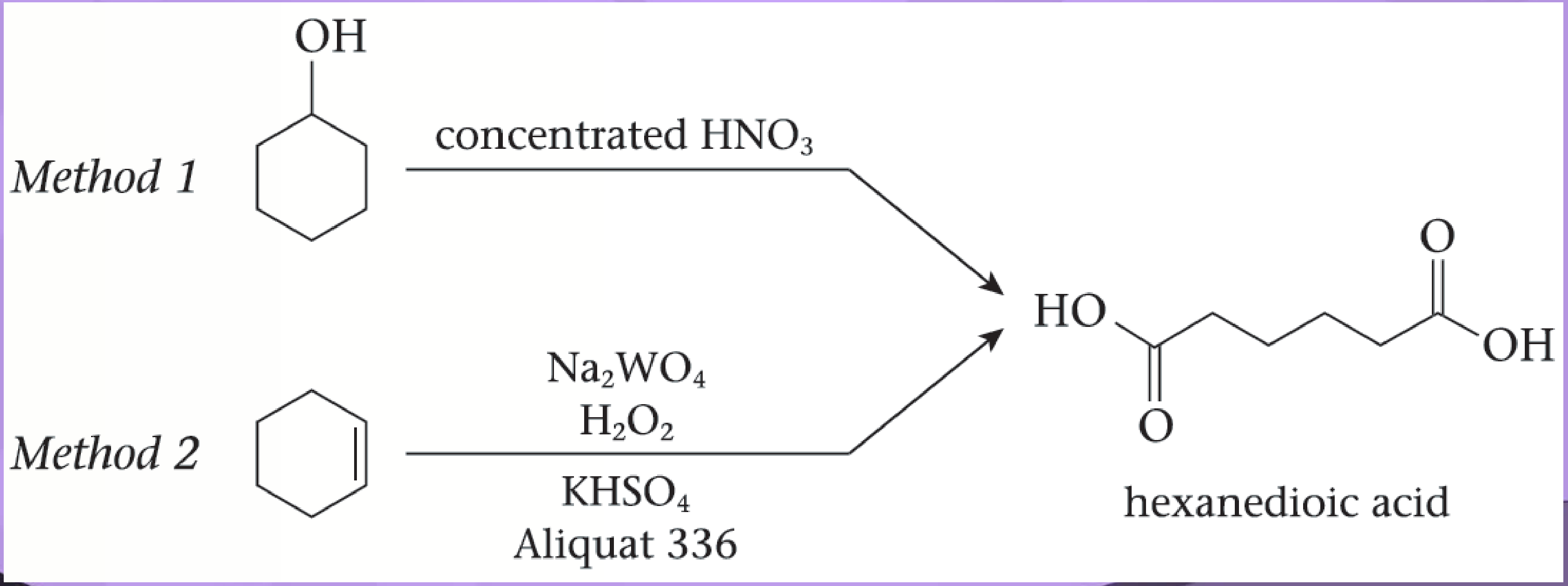
A chemical process with a high percentage yield helps reduce the cost by not wasting feedstock / by reducing the need to recycle unreacted reactants.

A chemical process with a high atom economy reduces the processing of waste and this makes the process greener.

46.3 How green is a process (p.129)

Q (Example 46.2)

Hexanedioic acid is an industrially important compound. It is the monomer used in the manufacture of nylon-6,6. Two methods that can produce hexanedioic acid is shown below:



46.3 How green is a process (p.129)

Method 1 involves the oxidation of cyclohexanol by concentrated nitric acid. The by-products are oxides of nitrogen. The yield of the reaction is 93%.

Method 2 involves the oxidation of cyclohexene with 30% H_2O_2(aq) in the presence of small amounts of Na_2WO_4 (sodium tungstate) and Aliquat 336 (methyltrioctylammonium chloride) which act as the catalysts. The only by-product is H_2O. The yield of the reaction is 90%.

a) *Method 2* is considered to be greener than *Method 1*.
Suggest TWO reasons.

b) In what aspect are both methods considered as NOT green?

46.3 How green is a process (p.129)

A

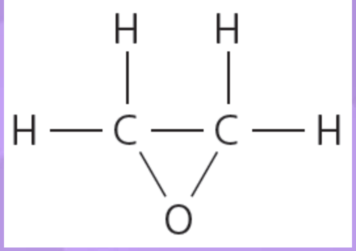
a) The by-products (oxides of nitrogen) in Method 1 is toxic, but the by-product (H_2O) in *Method 2* is harmless.
Catalysts are used in *Method 2* but not in *Method 1*.

b) The starting materials of the two methods are possibly obtained from non-renewable resources.

46.3 How green is a process (p.129)

Practice 46.3

Epoxyethane ($(CH_2)_2O$) is an intermediate in the production of car anti-freeze. It is also used to sterilise medical supplies.



epoxyethane

The feedstock used to make epoxyethane is ethene obtained via the cracking of hydrocarbons from petroleum.

Epoxyethane can be made by two different methods. The overall equation for each method is shown below.

Method 1 $C_2H_4(g) + Cl_2(aq) + Ca(OH)_2(s) \rightarrow (CH_2)_2O(g) + CaCl_2(aq) + H_2O(l)$

Method 2 $2C_2H_4(g) + O_2(g) \xrightleftharpoons{\text{catalyst}} 2(CH_2)_2O(g)$

46.3 How green is a process (p.129)

a) Calculate the atom economy of *Method 1*.

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0, Cl = 35.5, Ca = 40.1)

	$C_2H_4(g)$ +	$Cl_2(aq)$ +	$Ca(OH)_2(s)$ ⟶	$(CH_2)_2O(g)$ +	$CaCl_2(aq)$ +	$H_2O(l)$
Relative molecular mass or formula mass	28.0	71.0	74.1	44.0		

Atom economy of *Method 1* $= \dfrac{44.0}{28.0 + 71.0 + 74.1} \times 100\%$

$= 25.4\%$

b) Discuss, from TWO different perspectives, whether *Method 1* or *Method 2* is greener.

Method 2 is greener.

Any two of the following:

- *Method 2* has a higher atom economy.
- A catalyst is used in *Method 2*.
- *Method 2* uses less hazardous chemicals. / *Method 1* uses toxic chlorine.

46.4 Catalyst in industry (p.133)

- If catalysts did not exist, many chemical processes would go very slowly and some reactions would need much higher temperatures and pressures to proceed at a reasonable rate. Using high temperatures and pressures often involves burning fossil fuels. So the use of catalysts can reduce the overall costs of chemical processes.
- Research into new catalysts is an important area of scientific work. This is shown by the industrial manufacture of ethanoic acid.

46.4 Catalyst in industry (p.133)

Greening the manufacture of ethanoic acid

Oxidation of butane or naphtha

- Until the 1970s, the main method of making ethanoic acid was to oxidise butane or naphtha from petroleum. Butane was heated in air, using a catalyst of manganese, cobalt or chromium ion, at 150 °C and 55–60 atmospheres.

$$2C_4H_{10}(g) + 5O_2(g) \rightarrow 4CH_3COOH(l) + 2H_2O(l)$$

- This process produces a large amount of by-products, such as propanone, methanoic acid and so on. About 65 tonnes of by-products are produced for every 100 tonnes of ethanoic acid. Ethanoic acid must be separated by fractional distillation.

46.4 Catalyst in industry (p.133)

The Monsanto process

- Methanol is a cheaper feedstock when compared with butane or naphtha.
- This BASF process in 1960 used a catalyst of cobalt and iodide ion, running at 300 °C and at a pressure of 700 atmospheres.
- However, at 700 atmospheres, safety was a serious concern and there were high energy costs for generating the high temperature and pressure.
- The company Monsanto developed the **Monsanto process (孟山都法)** using the same reaction but a new catalyst system made of rhodium metal and iodide ion.

46.4 Catalyst in industry (p.133)

$$CH_3OH(l) + CO(g) \xrightarrow[200\ ^\circ C,\ 30\text{–}60\ atm]{rhodium\ /\ iodide\ ion} CH_3COOH(l)$$

- This is a very efficient process to produce ethanoic acid with a high yield of about 90% and an atom economy of 100%. Much less energy is needed. The reaction is fast and the catalyst has a long life.

46.4 Catalyst in industry (p.133)

- However, there are disadvantages with this process, including:
  - rhodium is very expensive;
  - rhodium and iodide ions form insoluble salts and so the water content (~10% water) in the reaction vessel has to be kept relatively high to prevent this;
  - a final distillation step is required to remove water, as the product mixture contains a relatively high content of water. This increases the energy and cost demand;
  - rhodium also catalyses side reactions (such as production of propanoic acid).

46.4 Catalyst in industry (p.133)

The Cativa process

- In 1986, the oil company British Petroleum bought all the rights of the Monsanto process. The company devises a new process called the Cativa process. This process uses the same reaction of methanol with carbon monoxide but changes the catalysts to iridium metal and iodide ion.
- The Cativa process has several advantages over the Monsanto process:
  - iridium is much cheaper than rhodium;
  - the process is much faster (up to 150 times faster than the Monsanto process), so a large amount of product can be made without increasing the size of the plant;

46.4 Catalyst in industry (p.133)

- the catalysts are more selective in producing ethanoic acid, so the propanoic acid content in the product is much less than that in the Monsanto process and less energy is needed to purify the product;
- the catalysts are poisoned less easily, so they last longer;
- the water content in the production process is lower (as 5%), so less energy is needed to dry the product.

The Cativa process has superseded the Monsanto process.

Key terms (p.136)

sustainable development	可持續發展	Monsanto process	孟山都法
green chemistry	綠色化學	Cativa process	卡遜瓦法
atom economy	原子經濟		

Summary (p.137)

1 Sustainable development is 'a development that meets the needs of the present generation without compromising the ability of future generations to meet their needs'.

2 Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Summary (p.137)

3 Atom economy **(%)**

$$= \frac{\text{the sum of relative molecular mass or formula mass of product(s)}}{\text{the sum of relavtive molecular mass or formula mass of reactants}} \times 100\%$$

4 Research into new catalysts in the industrial manufacture of ethanoic acid can be shown by the following processes:

a) oxidation of butane or naphtha;

b) the Monsanto process;

c) the Cativa process.

Unit Exercise (p. 138)

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. 138)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.

- green chemistry
  - principles
    - prevent ____(a)____ handling
    - maximise ____(b)____ economy
      - formula: $= \frac{(l)}{(m)} \times 100\%$
    - design less ____(c)____ chemical syntheses
    - design ____(d)____ chemicals and products
    - use ____(e)____ solvent and auxiliary substances
    - increase ____(f)____ efficiency
    - use ____(g)____ feedstocks
    - avoid using chemical ____(h)____
    - use catalysts
    - design chemicals and products to ____(i)____ after use
    - analyse in real time to prevent ____(j)____
    - minimise the potential for ____(k)____

a) waste
b) atom
c) hazardous
d) safer
e) safer
f) energy
g) renewable
h) derivatives
i) degrade
j) pollution
k) accidents
l) the sum of relative molecular mass or formula mass of desired product(s)
m) the sum of relative molecular mass or formula mass of reactants

Unit Exercise (p. 138)

PART II MULTIPLE CHOICE QUESTIONS

2 A ‘greener’ chemical process will be one that

A uses energy less efficiently.
B forms a non-polluting waste product.
C produces significant amounts of waste.
D makes use of non-renewable resources.

(Edexcel Advanced Subsidiary GCE, Unit 2R, Jun. 2013,13)

Answer: B

Unit Exercise (p. 138)

3 Which of the following is the greenest solvent?

A Methanol
B Benzene
C Ethanol
D Water

Answer: D

Unit Exercise (p. 138)

4 Green chemists look for renewable feedstocks to make products. Which of the following is NOT a renewable feedstock?

A Biomass
B Corn
C Natural gas
D Starch

Answer: C

Unit Exercise (p. 138)

5 Chloromethane (CH_3Cl) is made by reacting methane with chlorine.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

What is the atom economy of the reaction?
(Relative atomic masses: H = 1.0, C = 12.0, Cl = 35.5)

A 100.0%
B 58.0%
C 42.0%
D 32.0%

Answer: C

	$CH_4(g)$	+ $Cl_2(g)$	$\longrightarrow$ $CH_3Cl(g)$	+ $HCl(g)$
Relative molecular mass or formula mass	16.0	71.0	50.5	

$$\text{Atom economy of reaction} = \frac{50.5}{16.0 + 71.0} \times 100\% = 58.0\%$$

Unit Exercise (p. 138)

6 The Haber process is an example of green chemistry because

(1) the reaction has 100% atom economy.
(2) the reaction is exothermic.
(3) no solvent is required in the process.

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

Answer: B

Unit Exercise (p. 138)

7 Which of the following is / are the advantage(s) for a reaction to have a high percentage yield of product?

(1) It reduces the waste of reactants.
(2) It attains equilibrium quickly.
(3) It must be a 'green' process.

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

Answer: A

Unit Exercise (p. 138)

8 Which of the following are environmental benefits of green chemistry?

(1) Fewer raw materials and natural resources used.
(2) Cleaner production technologies and reduce emissions.
(3) Smaller quantities of hazardous waste to be treated and disposed of.

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

Answer: D

Unit Exercise (p. 138)

PART III STRUCTURED QUESTIONS

9 Magnesium sulphate can be used as a fertiliser. It is manufactured by a neutralisation reaction.

$$H_2SO_4(aq) + MgO(s) \rightarrow MgSO_4(aq) + H_2O(l)$$

a) Calculate the atom economy of the reaction.
(Relative atomic masses: H = 1.0, O = 16.0, Mg = 24.3, S = 32.1)

	$H_2SO_4(aq)$ +	$MgO(s)$ ⟶	$MgSO_4(aq)$ +	$H_2O(l)$
Relative molecular mass or formula mass	98.1	40.3	120.4	

$$\text{Atom economy of reaction} = \frac{120.4}{98.1 + 40.3} \times 100\%$$

$$= 87.0\%$$ (1)

Unit Exercise (p. 138)

b) Industrial chemical processes should have as high an atom economy as possible. Explain why.

Reduces the production of unwanted products / Reduces the amount of waste products. (1)

c) Write down ONE reason for and ONE reason against the use of synthetic fertilisers.

For

World population is rising / production of more food is needed (1)

Against

Any one of the following:

- Eutrophication or death of aquatic organisms (from excessive use of fertilisers) (1)
- Idea of pollution of water supplies (from excessive use of fertilisers) (1)

Unit Exercise (p. 138)

10 Bromine can be extracted from potassium bromide by the following two processes.

Process 1 Solid potassium bromide reacts with concentrated sulphuric acid.

$$2KBr + 2H_2SO4 \rightarrow K_2SO_4 + Br_2 + SO_2 + 2H_2O$$

Process 2 Aqueous solution of potassium bromide reacts with chlorine gas.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

Unit Exercise (p. 138)

a) i) Calculate the atom economy of *Process 1*.

	$2KBr$	+	$2H_2SO_4$	$\longrightarrow$	K_2SO_4	+	Br_2	+	SO_2	+	$2H_2O$
Relative molecular mass or formula mass	119.0		98.1				159.8				

$$\text{Atom economy of } \textit{Process 1} = \frac{159.8}{2 \times 119.0 + 2 \times 98.1} \times 100\%$$

$= 36.8\%$ (1)

ii) Calculate the atom economy of *Process 2*.

(Relative atomic masses: H = 1.0, O = 16.0, S = 32.1, Cl = 35.5, K = 39.1, Br = 79.9)

	$2KBr$	+	Cl_2	$\longrightarrow$	$2KCl$	+	Br_2
Relative molecular mass or formula mass	119.0		71.0				159.8

$$\text{Atom economy of } \textit{Process 2} = \frac{159.8}{2 \times 119.0 + 71.0} \times 100\%$$

$= 51.7\%$ (1)

Unit Exercise (p. 138)

b) Which is a greener process, *Process 1* or *Process 2*? Give TWO reasons to support your answer.

Process 2 is a greener process.

Any two of the following:

- *Process 2* has a higher atom economy. (1)
- Aqueous KBr / Br^- is easily obtained from seawater. (1)
- *Process 2* does not produce sulphur dioxide, which is a toxic gas. (1)
- *Process 2* does not use concentrated sulphuric acid, which is highly corrosive. (1)

c) What is the disadvantage of *Process 2* from the viewpoint of green chemistry?

Process 2 uses toxic chlorine gas. (1)

d) Suggest ONE source for the chlorine used in *Process 2*.

Chlorine gas can be obtained from the electrolysis of brine. (1)

Unit Exercise (p. 138)

11 Hydrogen peroxide can be manufactured by two different routes.

Route 1 Reacting barium peroxide with ice-cold dilute sulphuric acid.

$$BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

Route 2 Reacting hydrogen and oxygen from the air in the presence of a catalyst.

$$H_2(g) + O_2(g) \rightarrow H_2O_2(aq)$$

Unit Exercise (p. 138)

a) Calculate the atom economy of *Route 1*.
(Relative atomic masses: H = 1.0, O = 16.0, S = 32.1, Ba = 137.3)

	$BaO_2(s)$ +	$H_2SO_4(aq)$ ⟶	$BaSO_4(s)$ +	$H_2O_2(aq)$
Relative molecular mass or formula mass	169.3	98.1	233.4	

$$\text{Atom economy of } \textit{Route 1} = \frac{233.4}{169.3 + 98.1} \times 100\%$$

$$= 87.3\% \quad (1)$$

b) Suggest THREE reasons why *Route 2* is considered a greener process.

Any three of the following:

- Oxygen comes from air. Depletion is not an issue. (1)
- No toxic material is formed. (1)
- The atom economy is 100%. (1)
- A catalyst is used. (1)

Unit Exercise (p. 138)

12 The chemical industry uses catalysts for many of its reactions.

a) State an example of a catalyst used by the chemical industry and write the equation for the reaction that is catalysed. Any one of the following:

Catalyst	Reaction
Iron	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Vanadium(V) oxide	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Copper and zinc oxide	$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

(Any other example is also acceptable.)

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

A catalyst increases the rate of a chemical reaction by providing an alternative reaction pathway of lower activation energy. (1)

c) State how the use of catalysts helps chemical companies to make their processes greener.

- Low temperatures / lower pressures can be used. Less energy demand / less fossil fuels used / carbon dioxide emission reduced (1)
- Different reactions with greater atom economy can be used. Less waste is produced. / Enzymes generate specific products. (1)

Unit Exercise (p. 138)

13 Ethanoic acid, CH3COOH, can be made by several different processes. Three of these are *Process R*, *Process S* and *Process T*.

a) In *Process R*, methanol reacts with carbon monoxide.

$CH_3OH + CO \rightarrow CH_3COOH$

Process R has 100% atom economy.

Explain how you can tell this from the simple equation.

No waste products made / All the atoms that react end up in the product. / Only one product made (1)

Unit Exercise (p. 138)

b) In *Process S*, sodium ethanoate, CH_3COONa, reacts with sulphuric acid.

$$2CH_3COONa + H_2SO_4 \rightarrow Na_2SO_4 + 2CH_3COOH$$

Look at the table of relative molecular masses / formula masses, M_r.

Substance	Relative molecular mass / formula mass
CH_3COONa	82
H_2SO_4	98
Na_2SO_4	142
CH_3COOH	60

i) A mass of 8.2 g of sodium ethanoate reacts with excess sulphuric acid. What mass of ethanoic acid, CH_3COOH, can be made?

ii) Calculate the atom economy for *Process S*. Sodium sulphate, Na_2SO_4, is a waste product.

Unit Exercise (p. 138)

b) i)

Mass of CH_3COOH made $= 8.2 \text{ g} \times \frac{60}{82}$

$= 6.0 \text{ g}$ (1)

ii)

$2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2CH_3COOH$

Atom economy of *Process S* $= \frac{2 \times 60}{2 \times 82 + 98} \times 100\%$

$= 46\%$ (1)

Unit Exercise (p. 138)

c) In Process T, hydrocarbons are oxidised to make ethanoic acid.
Mike predicts that 5.2 tonnes of ethanoic acid should be made. The factory actually makes 2.4 tonnes of ethanoic acid.

i) Calculate the percentage yield of ethanoic acid. Write your answer to two significant figures.

$$\text{Percentage yield of } CH_3COOH = \frac{2.4}{5.2} \times 100\%$$

$$= 46\% \qquad (1)$$

ii) Describe ONE disadvantage of having a percentage yield of this value.
Waste a lot of reactants. (1)

(OCR GCSE (Higher Tier), Chem. B (Gateway Science), B741/02, Jun. 2014, 13)

Unit Exercise (p. 138)

14 Petrol sold in some countries now contains at least 5% ethanol. The production of ethanol, for use as a fuel, is being increased.
Ethanol can be produced by two methods.

Method 1 Reaction of ethene (from petroleum) and steam
Method 2 Fermentation of sugar from food crops

a) Ethene reacts with steam to produce ethanol according to the equation:

$$C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \qquad \Delta H = -45 \text{ kJ mol}^{-1}$$

The operation conditions used are 300 °C and 65 atmospheres in the presence of a catalyst.
Justify why this set of operation conditions is used with reference to the position of equilibrium and reaction rate.

Unit Exercise (p. 138)

The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the yield of $CH_3CH_2OH(g)$. (1)
However, the reaction may proceed too slowly if the temperature is too low. (1)
300 °C is a compromise between rate and yield.

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 $CH_3CH_2OH(g)$. (1)
Not very high pressure is used in consideration of mechanical design and safety concerns. (1)

Unit Exercise (p. 138)

b) Describe how ethanol can be produced from sugar by fermentation.

Dissolve sugar in water. (1)

Add yeast. (1)

Warm / any temperature between 15 °C to 40 °C. (1)

No air / oxygen can enter the apparatus. (1)

Unit Exercise (p. 138)

c) Evaluate whether more of this ethanol should be produced from food crops or from petroleum.

Crops	Petroleum	
Advantages:	*Disadvantages*:	
• Renewable resource	• Non-renewable resource	(1)
• Less energy / fuel needed / lower temperature	• More energy / fuel needed / higher temperature	(1)
• Can use waste crop material	• —	(1)
• Carbon neutral	• Not carbon neutral	(1)
• Low safety risk	• High safety risk	(1)
• Low technology	• High technology	(1)
	• Can be used to make other products	(1)
Disadvantages:	*Advantages*:	
• Process is slow	• Process is fast	(1)
• Many steps in the process	• Few steps in the process	(1)
• Ethanol is impure / may contain water	• Ethanol is pure	(1)
• Food shortages	• 'Conserves' food	(1)
• Very large areas of arable land needed to grow crops } reverse arguments acceptable		(1)
• Destruction of habitat } reverse arguments acceptable		(1)
• Slow growth of crops } reverse arguments acceptable		(1)
• Labour intensive } reverse arguments acceptable		(1)
A final conclusion based on advantages and disadvantages		

Unit Exercise (p. 138)

15 Phosgene ($COCl_2$) is an important chemical. It can be produced from the reaction of CO(g) with Cl_2(g): CO(g) + Cl_2(g) → $COCl_2$(g)

a) Write a chemical equation to show how CO(g) can be obtained from natural gas.

b) At a certain temperature, if the concentration of CO(g) is doubled while the concentration of Cl_2(g) is kept unchanged, the new rate of reaction will become 2.83 times the original rate. Deduce the order of reaction with respect to CO(g).
(Note: The order of a reaction may NOT be an integar.)

c) Explain separately why the above process of producing $COCl_2$(g) can be considered
i) green, or
ii) NOT green.

(HKDSE, Paper 2, 2017, 1(c)(i),(iii),(iv))

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

Unit Exercise (p. 138)

16 The hydrolysis of sucrose can be represented by the following equation:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{HCl(aq)} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

a) Three trials of an experiment were performed under the same experimental conditions to study the kinetics of the hydrolysis. The table below shows the data obtained:

	Initial concentration of $C_{12}H_{22}O_{11}(aq)$ (mol dm^{-3})	Initial concentration of HCl(aq) (mol dm^{-3})	Initial rate of disappearance of $C_{12}H_{22}O_{11}(aq)$ (mol dm^{-3} s^{-1})
Trial 1	0.010	0.10	6.0×10^{-7}
Trial 2	0.020	0.20	2.4×10^{-6}
Trial 3	0.010	0.30	1.8×10^{-6}

Unit Exercise (p. 138)

i) Given that the order of reaction with respect to $H_2O(l)$ is zero, deduce the order of reaction with respect to $C_{12}H_{22}O_{11}(aq)$ and that to HCl(aq).

ii) State the rate equation for the reaction.

iii) Based on the result in *Trial 1*, calculate the rate constant under the experimental conditions.

b) The hydrolysis of sucrose can also be performed by the action of a certain enzyme. Suggest the function of the enzyme in the hydrolysis.

c) Enzymatic hydrolysis of starch eventually gives glucose as the only product. According to the principles of green chemistry, suggest TWO reasons why starch is considered to be more suitable than sucrose as a source of glucose.

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

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

Unit Exercise (p. 138)

17 Hydrogen is produced in industry from methane and steam in a two-stage process.

The overall reaction can be represented by the equation below.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$$

The table shows some information about the process.

Temperature needed	700–1 000 °C
Energy source	burning some of the methane gas
Waste product	carbon dioxide gas

Unit Exercise (p. 138)

a) Calculate of the atom economy of the overall reaction.
(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

	$CH_4(g)$	+ $2H_2O(g)$	$\rightleftharpoons$ $CO_2(g)$	+ $4H_2(g)$
Relative molecular mass or formula mass	16.0	18.0		2.0

$$\text{Atom economy of overall reaction} = \frac{4 \times 2.0}{16.0 + 2 \times 18.0} \times 100\%$$

$= 15.4\%$ (1)

b) Explain why this process can be considered NOT green.

Methane comes from a fossil fuel. It is in finite supply / non-renewable. (1)
The high temperature uses a lot of fossil fuels. (1)
The waste product, carbon dioxide, is a greenhouse gas. It causes climate change. (1)
The reaction has a low atom economy. (1)

Unit Exercise (p. 138)

18 *Reaction I* below shows a process of producing methanol using catalyst at 100 atm and 250 °C in industry:

Reaction I $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

a) i) Suggest a suitable catalyst for the reaction.

ii) Suggest why the reaction would proceed slowly in the absence of a catalyst.

iii) Explain why the operation pressure in industry for the reaction is set at 100 atm but not at atmospheric pressure.

Unit Exercise (p. 138)

b) Methanol can also be produced from carbon dioxide, a side product of some industrial processes, using another catalyst as shown in *Reaction II* below:

Reaction II $CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$

Based on the given information:

i) Suggest one reason why *Reaction II* can be considered as greener than *Reaction I*.

ii) Suggest a potential benefit of *Reaction II* to the environment.

c) One of the industrial applications of methanol is to produce ethanoic acid. Write a chemical equation for the reaction involved.

(HKDSE, Paper 2, 2018, 1(b))

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

Topic Exercise (p.145)

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.

Topic Exercise (p.145)

PART I MULTIPLE CHOICE QUESTIONS

1 The decomposition of ammonia is represented by the equation below.

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

The activation energy for the forward reaction is 342 kJ mol^{-1}.

What is the activation energy for the backward reaction?

Answer: C

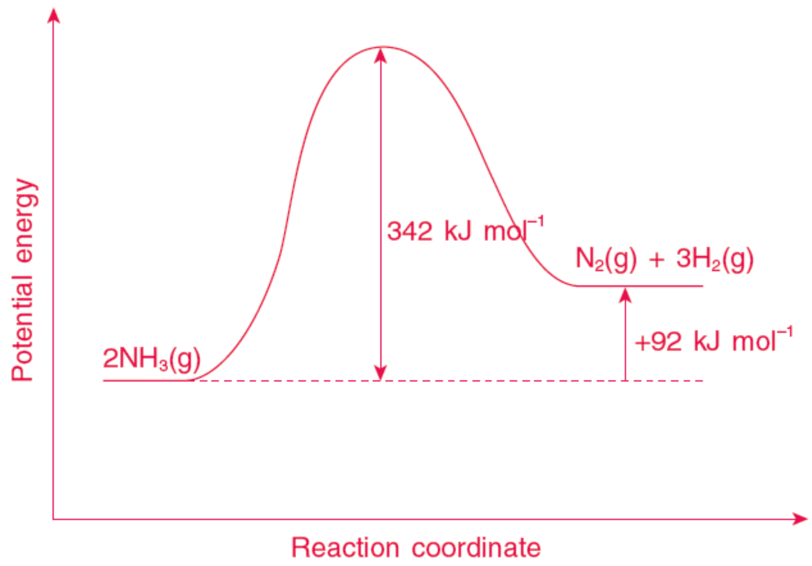
A 92 kJ mol^{-1}

B 184 kJ mol^{-1}

C 250 kJ mol^{-1}

D 434 kJ mol^{-1}

The potential energy profile for the decomposition of ammonia is shown below.



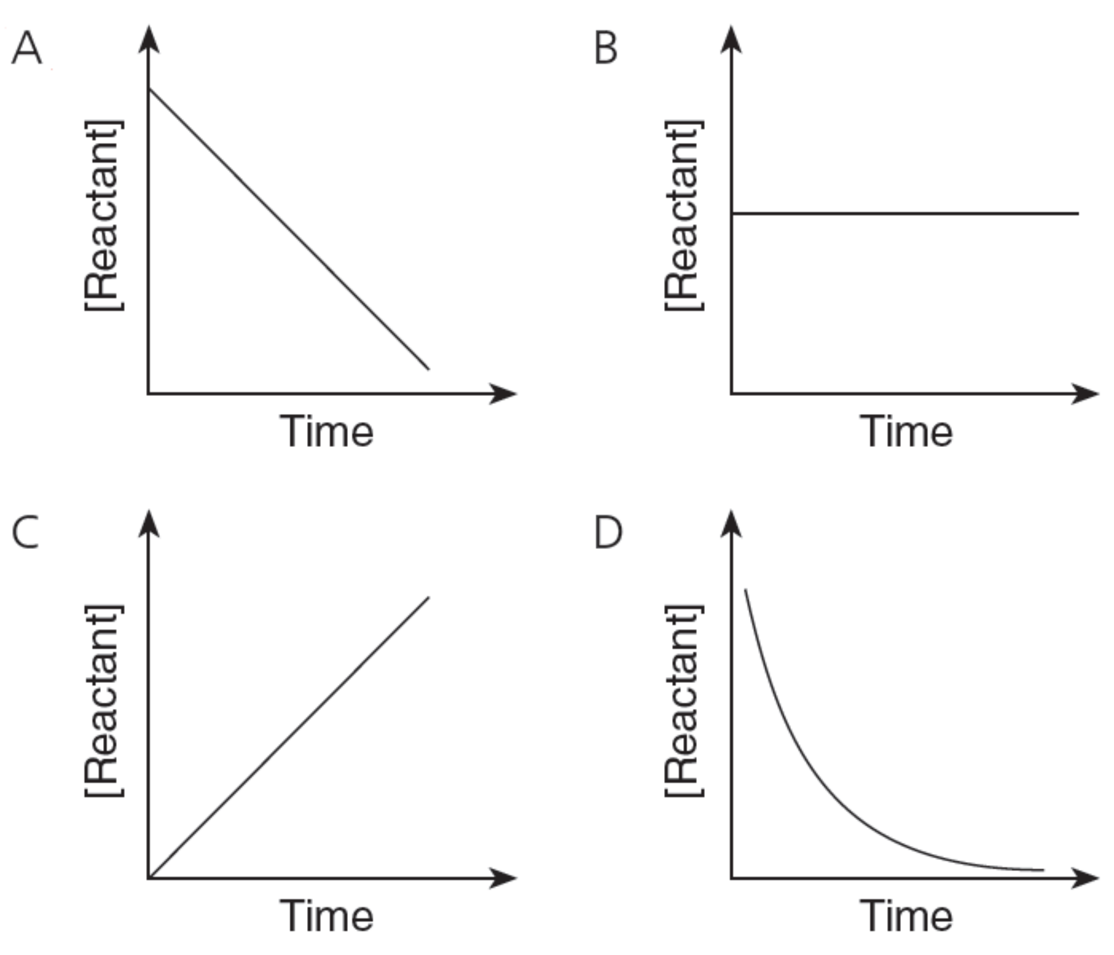
Activation energy for the backward reaction = (342 – 92) kJ mol^{-1}

= 250 kJ mol^{-1}

Topic Exercise (p.145)

2 Which of the following graphs shows the concentration of a reactant, on the vertical axis, against time for a zero order reaction?

(HKDSE, Paper 1A, 2014, 1)



Answer: A

Topic Exercise (p.145)

3 The rate constant of a reaction has the same units as the rate of reaction. What is the overall order of the reaction?

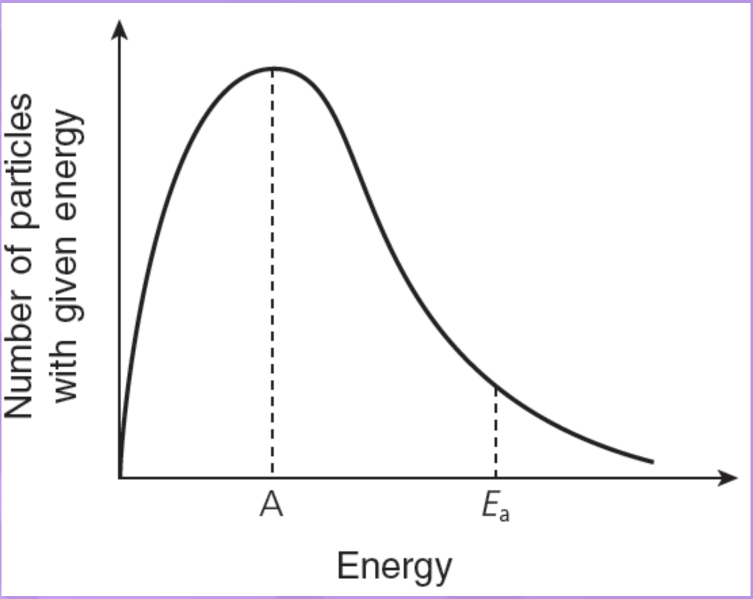
A Zero
B First
C Second
D Third

Answer: A

Explanation:
For a zero-order reaction:
rate = k[reactant]^0 = k
The units of k are the same as those of rate, i.e. mol dm^{-3} s^{-1}.

Topic Exercise (p.145)

4 The following figure shows a typical energy distribution for particles of a gas in a sealed container at a fixed temperature.



Answer: C

Which of the following statements is correct?

A Position A represents the mean energy of a molecule in the container.

B Addition of a catalyst moves the position of E_a to the right.

C The area under the curve to the right of E_a represents the number of molecules with enough energy to react.

D The position of the peak of the curve at a higher temperature is further away from both axes.

(AQA AS Level, Paper 2, Jun. 2016, 16)

Topic Exercise (p.145)

5 The activation energy, of a reaction can be obtained from the rate constant, *k*, and the absolute temperature, *T*. Which graph of these quantities produces a straight line?

Answer: D

A *k* against *T*

B *k* against $\frac{1}{T}$

C log *k* against *T*

D log *k* against $\frac{1}{T}$

Topic Exercise (p.145)

6 An important step in the production of sulphuric acid is the oxidation of sulphur dioxide.

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

Which of the conditions below is best suited to produce a high yield of sulphur trioxide, SO_3?

A 1 atm pressure and 800 °C
B 2 atm pressure and 800 °C
C 1 atm pressure and 400 °C
D 2 atm pressure and 400 °C

(Edexcel Advanced GCE, Unit 4R, Jun. 2013, 1)

Answer: D

Explanation:
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.
Thus, a higher pressure favours the formation of SO_3(g).
The forward reaction is exothermic. A temperature decrease shifts the position of equilibrium to the right.
Thus, a lower temperature favours the formation of SO_3(g).

Topic Exercise (p.145)

7 Ethanol can be produced by the hydration of ethene according to the equation shown below.

$$H_2C{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \quad \Delta H = -45 \text{ kJ mol}^{-1}$$

Which of the following methods can increase the yield of ethanol?

(1) Increasing the pressure
(2) Increasing the temperature
(3) Recycling the unreacted ethene and steam

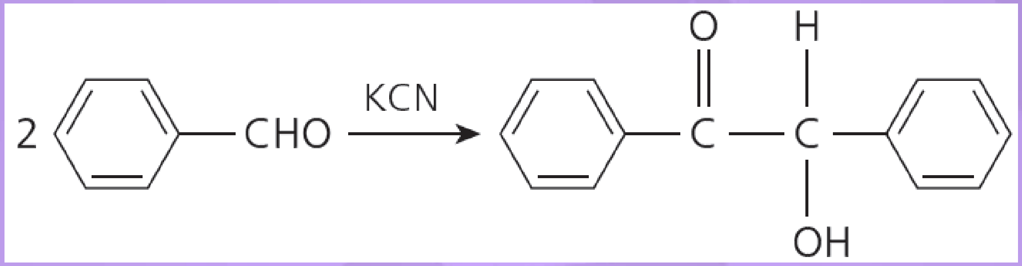
A (1) and (2) only
B (1) and (3) only
C (2) and (3) only
D (1), (2) and (3)

Answer: B

Explanation:
(1) 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, increasing the yield of ethanol.
(2) The forward reaction is exothermic. A temperature increase shifts the position of equilibrium to the left, decreasing the yield of ethanol.

Topic Exercise (p.145)

8 Compound B can be obtained from compound A by heating with potassium cyanide in a solvent-free condition.



compound A compound B

This reaction is an example of green chemistry because

(1) the reaction has a high atom economy.

(2) no catalyst is used.

(3) no solvent is required.

A (1) only

B (2) only

C (1) and (3) only

D (2) and (3) only

Answer: C

Topic Exercise (p.145)

Directions : Each question (Questions 9–10) consists of two separate statements. Decide whether each of the two statements is true or false; if both are true, then decide whether or not the second statement is a correct explanation of the first statement. Then select one option from A to D according to the following table :

A Both statements are true and the 2nd statement is a correct explanation of the 1st statement.

B Both statements are true but the 2nd statement is NOT a correct explanation of the 1st statement.

C The 1st statement is false but the 2nd statement is true.

D Both statements are false.

Topic Exercise (p.145)

1st statement	2nd statement
9 Fermentation of sucrose solution can produce a very concentrated ethanol solution.	The concentration of ethanol can be increased by adding more yeast to the sucrose solution during fermentation.

Answer: D

Explanation: Fermentation stops when the ethanol concentration reaches about 15%. Above this concentration, the yeast cells die.

1st statement	2nd statement
10 In the Haber process, the reaction between nitrogen and hydrogen goes to completion.	The atom economy of the reaction between nitrogen and hydrogen to give ammonia is 100%.

Answer: C

Topic Exercise (p.145)

PART II STRUCTURED QUESTIONS

11 The reaction between propanone and iodine in the presence of hydrochloric acid was studied at a constant temperature.

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{HCl(aq)} CH_3COCH_2I(aq) + HI(aq)$$

The following rate equation was deduced.

$$\text{rate} = k[CH_3COCH_3(aq)][H^+(aq)]$$

a) The order of reaction with respect to iodine is zero. State the effect, if any, of a change in the concentration of iodine in the reaction mixture on the rate of the reaction, when concentrations of other substances are kept constant.

No effect (1)

Topic Exercise (p.145)

b) In an experiment, the initial concentrations of propanone, iodine and hydrochloric acid were 5.20×10^{-2} mol dm^{-3}, 1.75×10^{-3} mol dm^{-3} and 4.45×10^{-1} mol dm^{-3} respectively. The initial rate of reaction was 7.22×10^{-7} mol dm^{-3} s$_{-1}$.

Calculate the rate constant at this temperature. Give units with your answer.

7.22×10^{-7} mol dm^{-3} s^{-1} = k(5.20×10^{-2} mol dm^{-3})(4.45×10^{-1} mol dm^{-3})

$k = 3.12 \times 10^{-5}$ dm^{3} mol^{-1} s^{-1} (1)

Topic Exercise (p.145)

12 The chemical kinetics of the following reaction at a certain temperature were studied:

$$BrO_3^-(aq) + 6I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + Br^-(aq) + 3H_2O(l)$$

a) Suggest how you could follow the progress of formation of I_2(aq).

Any one of the following:

- Change in concentration of iodine (1)
  by titration with standard sodium thiosulphate solution (1)
- Change in colour / absorbance of iodine in the reaction mixture (1)
  by colorimetry (1)
- Change in acidity / pH of reaction mixture due to hydrogen ions (1)
  by using a pH meter / titration with a standard alkali. (1)

Topic Exercise (p.145)

b) A student studied the rate of this reaction and obtained the results shown in the table.

Trial	Initial concentration (mol dm^{-3})			Initial rate of formation of $I_2(aq)$ (mol dm^{-3} s^{-1})
	$BrO_3^-(aq)$	$I^-(aq)$	$H^+(aq)$	
1	0.10	0.10	0.30	8.12×10^{-3}
2	0.20	0.15	0.30	2.44×10^{-2}
3	0.20	0.20	0.60	1.30×10^{-1}

Given that the order of reaction with respect to $BrO_3^-(aq)$ ion is 1, deduce the order of reaction respect to $I^-(aq)$ ion and that to $H^+(aq)$ ion.

Topic Exercise (p.145)

Suppose the order of reaction with respect to $I^-(aq)$ ion is *p* and that respect to $H^+(aq)$ ion is *q*. The rate equation for the reaction is of the form:

$$\text{rate} = k[BrO_3^-(aq)][Br^-(aq)]^p[H^+(aq)]^q$$

From *Trials 1* and 2,

$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{(0.10)(0.10)^p(0.30)^q}{(0.20)(0.15)^p(0.30)^q} = \frac{8.12 \times 10^{-3}}{2.44 \times 10^{-2}}$$

$$p = 1$$

From *Trials 2* and *3*,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{(0.20)(0.15)(0.30)^q}{(0.20)(0.20)(0.60)^q} = \frac{2.44 \times 10^{-2}}{1.30 \times 10^{-1}}$$

$$q = 2$$

∴ the order of reaction with respect to $I^-(aq)$ ion is 1 and that with respect to $H^+(aq)$ ion is 2.

Topic Exercise (p.145)

c) Based on *Trial 1*, deduce the initial rate of reaction with respect to BrO_3^-(aq) ion.

Initial rate of reaction with respect to BrO_3^-(aq) ion =
$\frac{1}{3}$ x 8.12 x 10^{-3} mol dm^{-3} s^{-1}
= 2.71 x 10^{-3} mol dm^{-3} s^{-1} (1)

d) The rates of formation of I_2(aq) were measured when the amount of reactants used up were small in comparison to the total quantities of reactants present. Explain why it was necessary to do this.

The rate measured would be for the initial concentrations. (1)

Topic Exercise (p.145)

13 Glucose can be oxidised using acidified potassium permanganate solution. The kinetics of the reaction can be studied using the procedure outlined below.

1 Measured volumes of glucose solution, sulphuric acid and water were added to a conical flask.
2 A measured volume of potassium permanganate solution was added to the flask. The mixture was gently swirled and a stopwatch started.
3 The time taken for the mixture in the flask to change colour was recorded and the initial rate of the reaction was then calculated.
4 The experiment was repeated using different volumes of the solutions. The results of the trials are shown in the table below.

Trial	Glucose (cm^3)	Sulphuric acid (cm^3)	Potassium permanganate (cm^3)	Water (cm^3)	Initial rate ($mol\ dm^{-3}\ s^{-1}$)
A	20.0	20.0	10.0	0.0	1.0×10^{-5}
B	20.0	20.0	5.0	5.0	5.0×10^{-6}
C	10.0	20.0	10.0	10.0	9.8×10^{-6}
D	10.0	10.0	10.0	20.0	4.9×10^{-6}

Topic Exercise (p.145)

a) Which piece of equipment should be used to measure the volumes used in each experiment? Justify your choice.

Any one of the following:

- Burette / graduated pipette (1)

Allows accurate measurements. (1)

- Measuring cylinder (1)

Allows doing multiple experiments quickly / accurate enough to determine orders. (1)

b) What colour change would you see in *Step 3*?

From purple to colourless (1)

c) Explain why water was added to the flask in *Trials B*, *C* and *D*?

To keep the total volume constant. / So the concentration of each reactant is proportional to the volume used. (1)

d) Suggest a technique that could be used to continuously monitor the change in concentration of potassium permanganate during the reaction.

By colorimetry (1)

Topic Exercise (p.145)

e) State the order with respect to glucose, sulphuric acid and potassium permanganate and hence write the rate equation for the reaction.

(Edexcel Advanced GCE, Unit 6B, Jun. 2013, 3(a))

Compare *Trials A* and *B*. The volumes of glucose and sulphuric acid remain the same, but the volume of potassium permanganate solution is halved. The initial rate becomes half. Thus, the order of reaction with respect to potassium permanganate is one. (1)

Compare *Trials A* and *C*. The volumes of sulphuric acid and potassium permanganate solution remain the same, but the volume of glucose is halved. The initial rate remains almost the same. Thus, the order of reaction with respect to glucose is zero. (1)

Compare *Trials C* and *D*. The volumes of glucose and potassium permanganate solution remain the same, but the volume of sulphuric acid is halved. The initial rate becomes half. Thus, the order of reaction with respect to sulphuric acid is one. (1)

The rate equation for the reaction is: rate = $k[H^+(aq)][MnO_4^-(aq)]$ (1)

Topic Exercise (p.145)

14 a) Answer the following short questions:

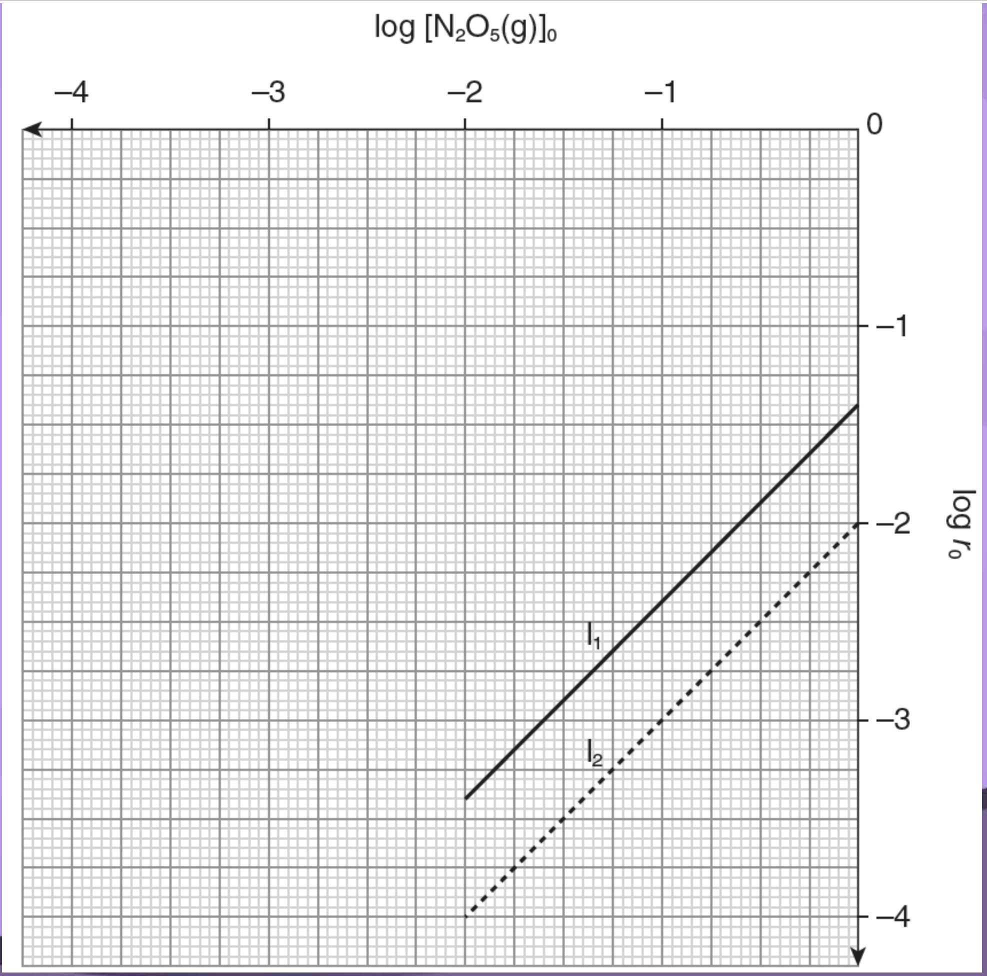
i) Write TWO half equations for the electrolysis of brine using membrane electrolytic cell in chloroalkali industry.

ii) Sketch a labelled diagram for a Maxwell-Boltzmann distribution cuve.

iii) Which one of the following species can be a raw material for manufacturing vitamin C in industry?
acetic acid, acetone, formaldedhyde, glucose

b) Two sets of experiments (one at 360 K; another at 345 K) were performed to study the chemical kinetics of thedecomposition of $N_2O_5(g)$: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
For each set of the experiments, the variation of log r_0 with log $[N_2O_5(g)]_0$ was plotted and both of them got a straight line as shown in the graph below:

	Representing	Unit
$[N_2O_5(g)]_0$	initial concentration of $N_2O_5(g)$	mol dm^{-3}
r_0	initial rate of decomposition of $N_2O_5(g)$	mol dm^{-3} s^{-1}
l_1	straight line obtained at 360 K	–
l_2	straight line obtained at 345 K	–



Topic Exercise (p.145)

It is given that $\log r_0 = \log k + n \log [N_2O_5(g)]_0$, where k is the rate constant and n is the order of reaction with respect to $N_2O_5(g)$.

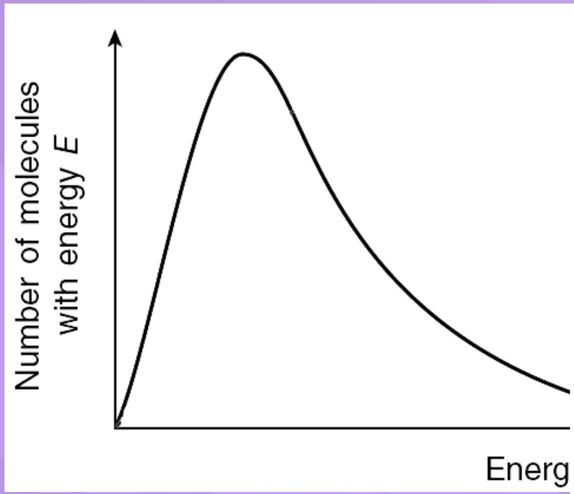
i) Given that l_1 and l_2 have the same slope, what can you deduce in terms of chemical kinetics?
ii) From l_1, deduce the order of reaction with respect to $N_2O_5(g)$.
iii) From l_2, deduce the rate constant for the reaction at 345 K.
iv) According to the relevant information of the graph, calculate the activation energy of the reaction.
(Gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

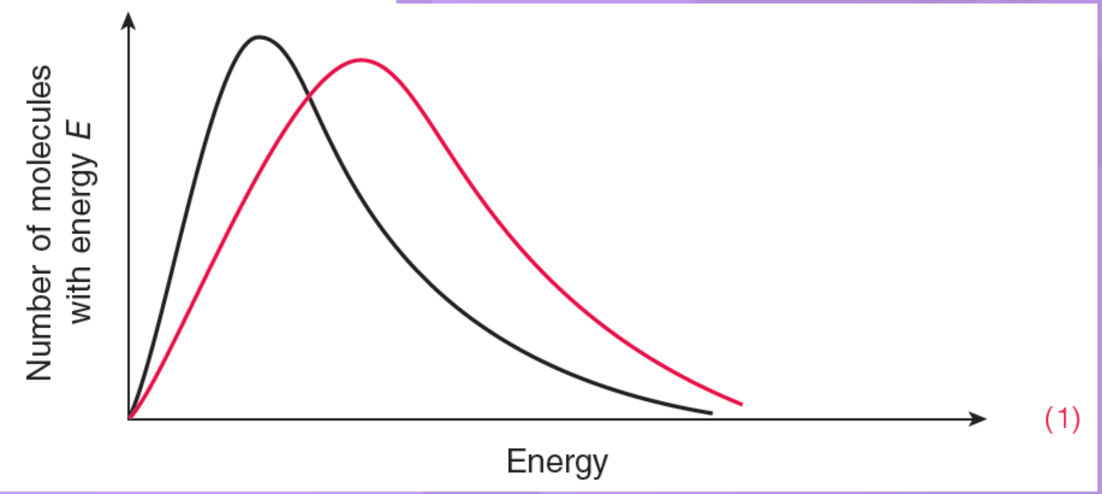
(HKDSE, Paper 2, 2018, 1(a), (c))

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

Topic Exercise (p.145)

15 The graph shows the Maxwell-Boltzmann distribution of molecular energies of a gaseous system.





a) On the graph, draw the Maxwell-Boltzmann distribution for the same system at a higher temperature.

b) Use the graph to explain why a small increase in temperature results in a large increase in the rate of a gaseous reaction.

(Edexcel Advanced Subsidiary GCE, Paper 2, Jun. 2016, 3(b))

Topic Exercise (p.145)

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)

A single activation energy is marked on graph. / A temperature rise increases the fraction of molecules with kinetic energy equal to or greater than the activation energy. (1)

So a higher percentage of molecules with sufficient energy to collide and react. (1)

OR

A single activation energy (E_a) is marked on graph. (1)

At energy beyond E_a, only a small increase in temperature will largely increase that portion of area under the curve, (1)

that is, a significant increase in the number of molecules with sufficient kinetic energy (equal to or greater than E_a) to possibly collide effectively and react. (1)

Topic Exercise (p.145)

16 The rate constant of a certain reaction increases by four times when the temperature is increased from 298 K to 328 K.

Calculate the activation energy of the reaction.
(Gas constant, R = 8.31 J K^{-1} mol^{-1})

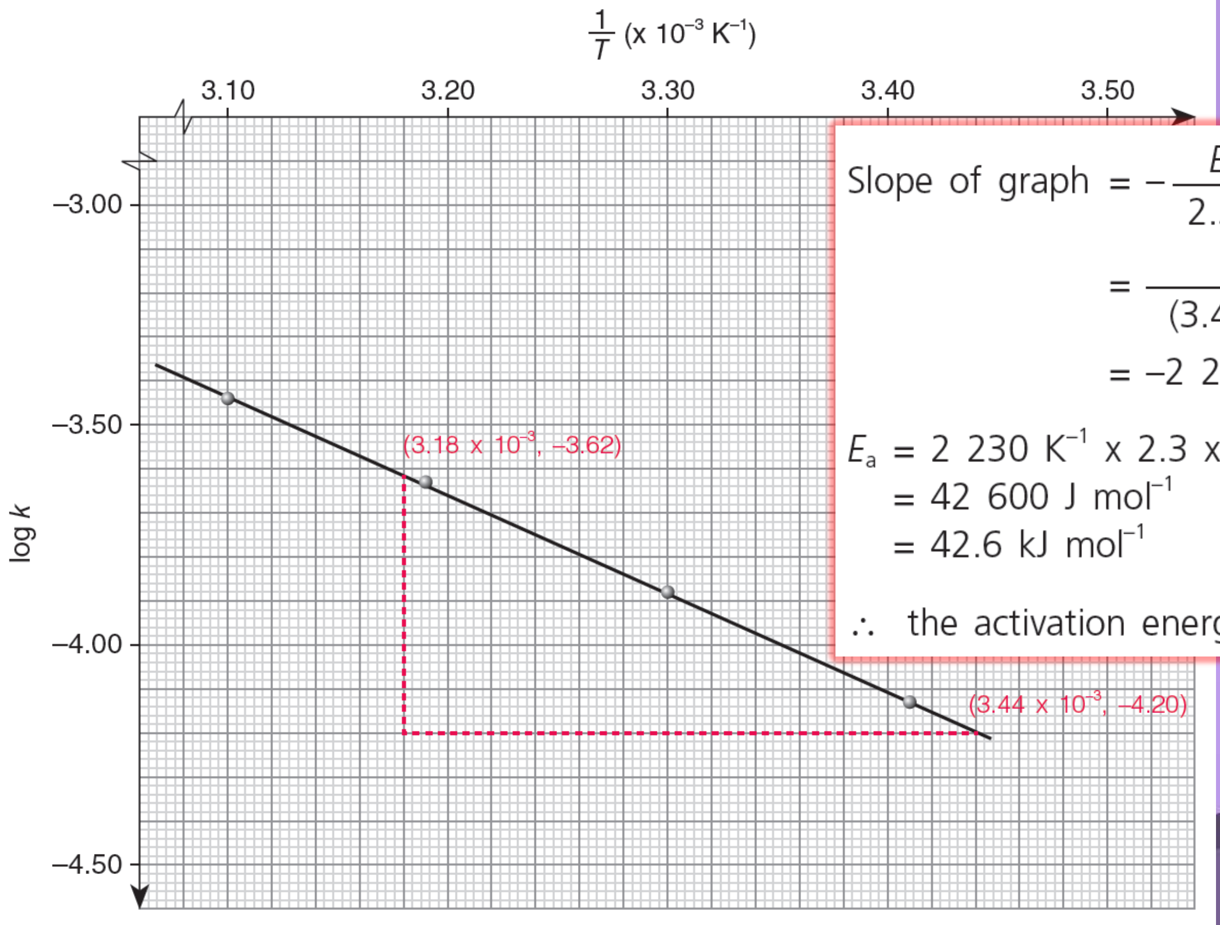
$$\log \frac{k_{328}}{k_{298}} = \log 4 = \frac{E_a}{2.3R}\left(\frac{1}{298} - \frac{1}{328}\right) \quad (1)$$

$$E_a = 37.5 \text{ kJ mol}^{-1} \quad (1)$$

Topic Exercise (p.145)

17 The values of rate constant (k) for a reaction at different temperatures (T) were determined. The graph below shows the plot of log k against $\frac{1}{T}$.

Calculate the activation energy of this reaction. (Gas constant, R = 8.31 J K^{-1} mol^{-1})



$$\text{Slope of graph} = -\frac{E_a}{2.3R}$$

$$= \frac{-4.20 - (-3.62)}{(3.44 - 3.18) \times 10^{-3}\ \text{K}} \quad (1)$$

$$= -2\ 230\ \text{K}^{-1} \quad (1)$$

$$E_a = 2\ 230\ \text{K}^{-1} \times 2.3 \times 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= 42\ 600\ \text{J mol}^{-1}$$

$$= 42.6\ \text{kJ mol}^{-1} \quad (1)$$

∴ the activation energy for the reaction is 42.6 kJ mol^{-1}.

Topic Exercise (p.145)

18 I^-(aq) ion reacts with $S_2O_8^{2-}$(aq) ion as shown in the equation below.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq) \qquad \Delta H < 0$$

A student investigated the rate of this reaction using the initial rate method. The student measured the time *t* taken for a certain amount of iodine to be produced.

The results of three trials of the experiment are listed below:

Trial	Initial concentration (mol dm^{-3})		*t* (s)
	I^-(aq)	$S_2O_8^{2-}$(aq)	
1	0.0500	0.0500	56.0
2	0.100	0.0375	37.0
3	0.100	0.0500	28.0

Topic Exercise (p.145)

a) Deduce from the above information the rate equation for the reaction between I^-(aq) ion and $S_2O_8^{2-}$(aq) ion.

Suppose the order of reaction with respect to I–(aq) ion is *p* and that with respect to $S_2O_8^{2-}$(aq) is *q*. The rate equation for the reaction is of the form:

$$\text{rate} = k[I^-(aq)]^p[S_2O_8^{2-}(aq)]^q$$

Initial rate of reaction ∝ 1/*t*

Compare *Trials 1* and *3*,

$$\frac{\text{initial rate 1}}{\text{initial rate 3}} = \frac{(0.0500)^p(0.0500)^q}{(0.100)^p(0.0500)^q} = \frac{\frac{1}{56.0}}{\frac{1}{28.0}}$$

$p = 1$ (1)

Compare *Trials 2* and *3*,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{(0.100)(0.0375)^q}{(0.100)(0.0500)^q} = \frac{\frac{1}{37.0}}{\frac{1}{28.0}}$$

$q = 1$ (1)

∴ the rate equation for the reaction is:

$$\text{rate} = k[I^-(aq)][S_2O_8^{2-}(aq)] \ (1)$$

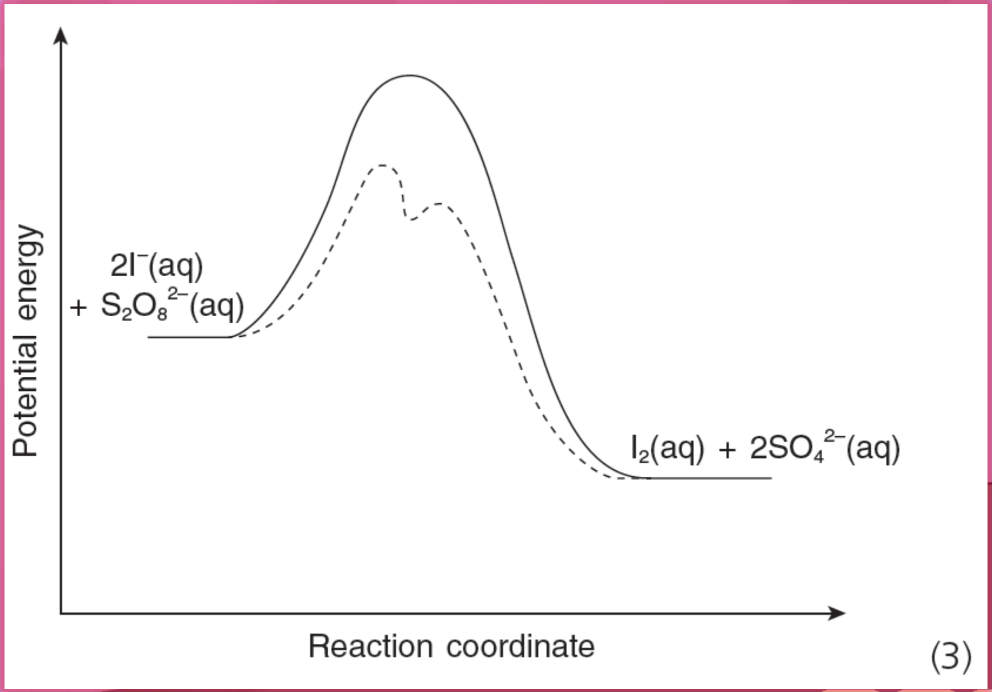
Topic Exercise (p.145)

b) The reaction between I^-(aq) ion and $S_2O_8^{2-}$(aq) ion can be catalysed by Fe^{2+}(aq) ion. The catalytic process is considered to consist of two steps:

$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$$

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

Draw, in the same sketch, TWO labelled potential energy profiles (x-axis: reaction coordinate; y-axis: potential energy) for the above conversion: one with Fe^{2+}(aq) as the catalyst (using dotted line '-----'); the other one without catalyst (using solid line '_____').



Topic Exercise (p.145)

19 Ammonia is manufactured from nitrogen and hydrogen in the Haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92 \text{ kJ mol}^{-1}$

a) As air contains about 78% of nitrogen by volume, can air be used instead of nitrogen in the reaction? Explain.

No

Air contains about 20% oxygen.

A mixture of oxygen and hydrogen is explosive. (1)

b) Explain why the maximum equilibrium yield of ammonia would be obtained by low temperatures and high pressures.

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 ammonia.

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 ammonia.

Topic Exercise (p.145)

c) Explain why the industrial process might NOT use low temperatures and high pressures.

The reaction may proceed too slowly if temperatures are too low. (1) High pressures increase the rate of reaction and yield of ammonia. However, the use of high pressures increases the building / running costs. There is also a safety concern. (1)

d) i) What is the catalyst used in the Haber process?

Finely divided iron (1)

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

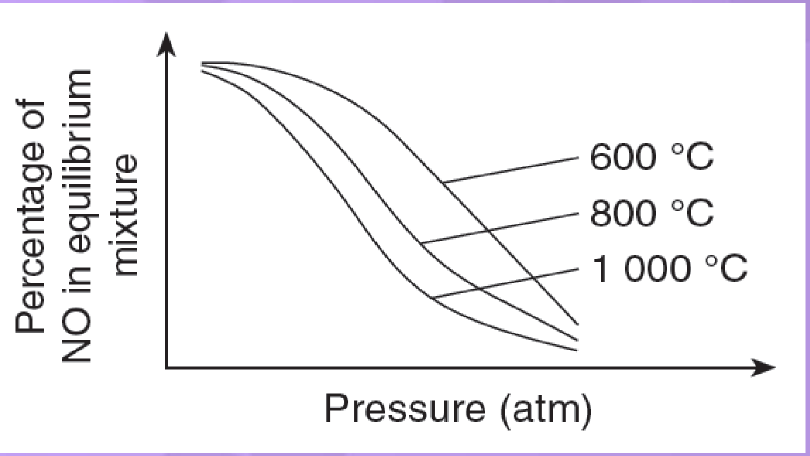
Impurities in the reaction mixture may poison the catalyst. (1)

Topic Exercise (p.145)

20 Nitric acid can be produced from ammonia. The first stage involved the oxidation of ammonia over a catalyst.

ammonia + oxygen ⇌ nitrogen monoxide + steam

The graph shows how the percentage of nitrogen monoxide in the equilibrium mixture is related to both the temperature and the pressure used.



a) Use the graphs to explain whether

i) the synthesis of nitrogen monoxide is exothermic or endothermic;

ii) there are more moles of gaseous products than reactants.

Topic Exercise (p.145)

i) Percentage of nitrogen monoxide in equilibrium mixture decreases with increasing temperature. (1)
This means that the position of equilibrium shifts to the left when the temperature is increased.
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the left. (1)
Thus, the forward reaction, i.e. the synthesis of nitrogen monoxide, should be exothermic.

ii) Percentage of nitrogen monoxide in equilibrium mixture decreases with increasing pressure. (1)
This means that the position of equilibrium shifts to the left when the pressure is increased.
A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the left. (1)
Thus, there are more moles of gaseous products than reactants.

Topic Exercise (p.145)

b) A low pressure of 7 atmospheres and a high temperature of 900 °C are used for the production of nitrogen monoxide. Suggest why.

A high temperature is used to increase the rate of reaction. (1)
A low pressure keeps the percentage yield of nitrogen monoxide high and reduces the building / running costs. (1)

Topic Exercise (p.145)

21 Hydrogen is produced in industry from methane and steam in a two-stage process.

a) In the first stage, carbon monoxide and hydrogen are formed.

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

i) Explain why the maximum equilibrium yield of hydrogen would be obtained by high temperatures and low pressures.

ii) Explain, in terms of the behaviour of particles, why a high operating pressure is used in industry.

iii) A nickel oxide catalyst is used in this stage. Explain why coating the catalyst onto an unreactive honeycomb can increase the efficiency of the catalyst.

Topic Exercise (p.145)

i) The forward reaction is endothermic. A temperature increase shifts the position of equilibrium to the right. (1)
Thus, a high temperature favours the formation of hydrogen.
The number of moles of gaseous products is more than that of gaseous reactants. A pressure decrease shifts the position of equilibrium to the right. (1)
Thus, a low pressure favours the formation of hydrogen.

ii) A high operating pressure increases the rate of reaction / of attainment of equilibrium. (1)
The gas molecules are closer. / The concentrations of all substances increase. (1)
The chance of collision increases, so there are more effective collisions in a unit volume per unit time. (1)

iii) The reaction takes place on the surface of the catalyst.
Coating the catalyst onto an unreactive honeycomb increases the contact surface area for reactants and thus increases the efficiency of the catalyst. (1)

Topic Exercise (p.145)

b) The second stage is carried out in a separate reactor. Carbon monoxide is converted into carbon dioxide and more hydrogen is formed.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

The overall reaction can be represented by the equation below.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$$

i) Calculate the atom economy of the overall reaction.
(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

ii) A new process for making hydrogen is by heating wood from trees. Both processes for making hydrogen also give carbon dioxide. Suggest why this new process might be greener than the old one.

Topic Exercise (p.145)

i) Atom economy of overall reaction = $\frac{4 \times 2 \times 1.0}{(12.0 + 4.0) + 2(2.0 + 16.0)} \times 100\%$

$= 15.4\%$ (1)

ii) Any two of the following:

- Trees are renewable / can plant more trees. (1)
- Trees use carbon dioxide for photosynthesis. / Trees are carbon neutral. / Total carbon dioxide output is zero. (1)
- Methane is a non-renewable energy source. (1)

Topic Exercise (p.145)

22 One of the stages in the production of sulphuric acid from sulphide ores involves the oxidation of sulphur dioxide to sulphur trioxide. The equation for the reaction is $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H_r = -197 \text{ kJ mol}^{-1}$

The conditions used in one industrial process are: 420 °C and a pressure of 1.7 atm together with a vanadium(V) oxide catalyst.

It is proposed to change the conditions to 600 °C and 10 atm pressure, while still using the same catalyst.

a) Evaluate the feasibility of each of these changes in terms of their effect on the rate, yield and economics of the reaction.

Topic Exercise (p.145)

The temperature increase raises 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 $SO_3(g)$. (1)
The temperature increase raises the energy costs. (1)
The pressure increase raises the rate of reaction / of attainment of equilibrium. (1)
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, increasing the yield of $SO_3(g)$. (1)
The pressure increase raises the building and running costs / reduces economic viability. (1)

Topic Exercise (p.145)

b) i) On the axes provided, sketch the energy profiles for the uncatalysed and catalysed reactions.

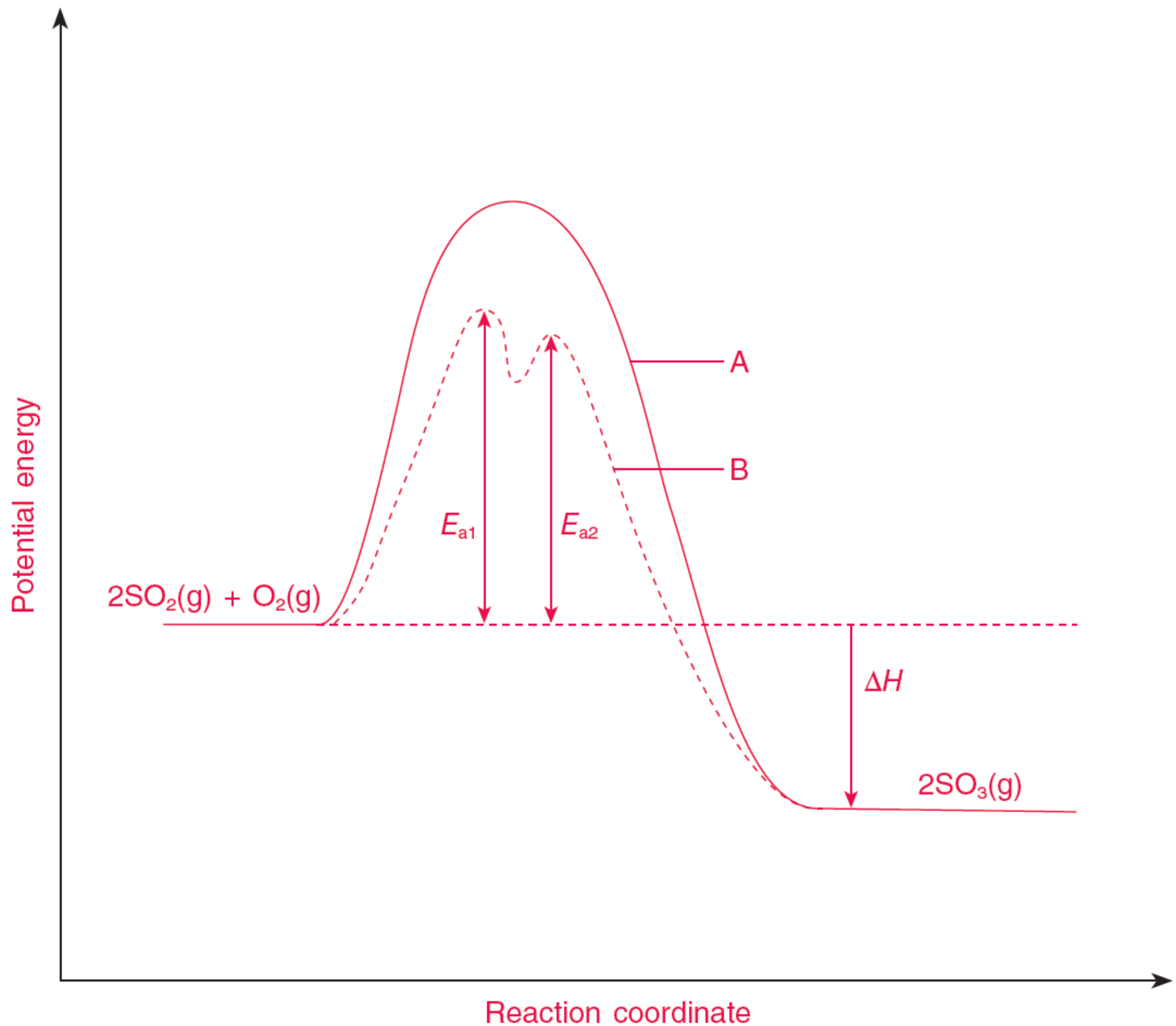
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H_r = -197 \text{ kJ mol}^{-1}$$

Label the uncatalysed reaction, A, and the reaction catalysed by vanadium(V) oxide, B.

ii) On your energy profile, identify and label both the enthalpy change and the activation energy for the catalyzed reaction.

(Edexcel Advanced Subsidiary GCE, Paper 2, Jun. 2017, 6)

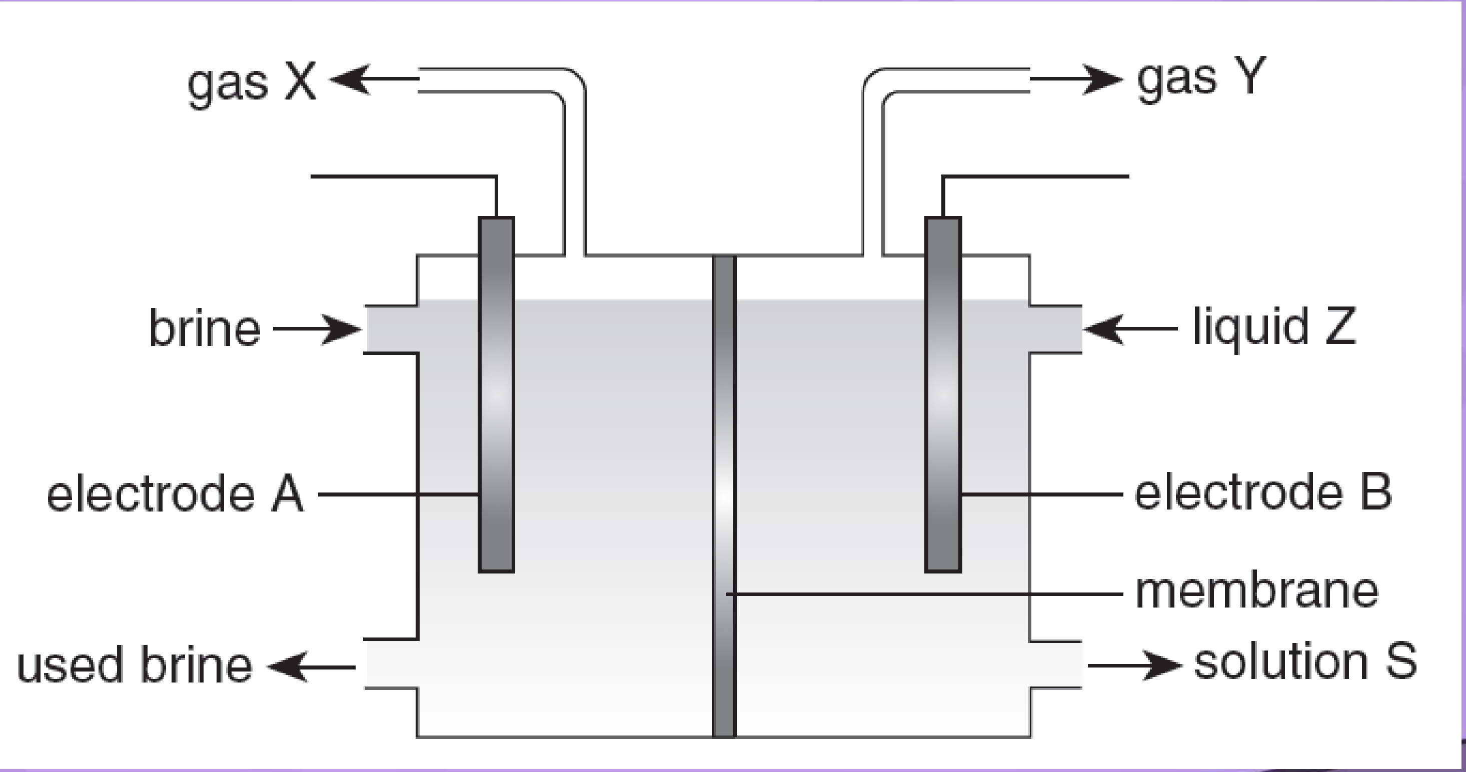
Topic Exercise (p.145)



(3)

Topic Exercise (p.145)

23 The diagram below shows a membrane cell for the production of chlorine, hydrogen and sodium hydroxide solution in the chloroalkali industry.



Topic Exercise (p.145)

a) With the aid of chemical equations, account for the formation of hydrogen, chlorine and sodium hydroxide solution in the membrane cell.

At the anode, chloride ion is preferentially discharged due to its high concentration. (1)
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (1)

At the cathode, hydrogen ion is preferentially discharged because it is a stronger oxidising agent than sodium ion. (1)
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ (1)

As there is a high accumulation of sodium ions in the anode compartment (because anions have been removed), the sodium ions would flow through the membrane to the cathode compartment where they combine with hydroxide ions to form sodium hydroxide solution. (1)

Topic Exercise (p.145)

b) If an accident occurred and caused a release of chlorine, people handling the incident would wear breathing apparatus. Explain why this would be necessary.

Chlorine is a gas.
It is toxic and causes respiratory problems / choking. (1)

Topic Exercise (p.145)

24 Methanol is an important feedstock for the chemical industry.

In the manufacture of methanol, carbon monoxide and hydrogen are reacted together in the reversible reaction shown below.

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

a) Write a chemical equation to show how CO(g) can be obtained from natural gas.

b) You are given that for the formation of methanol from syngas at 200 °C and 150 atm, the yield of methanol at equilibrium is about 95%. However, the operating conditions of the synthesis in a plant are set at 300 °C and 100 atm with the yield of about 40%. With reference to the given information, explain why such operating conditions are chosen.

c) State an advancement of the methanol production technology. Explain why it is considered as an advancement.

Topic Exercise (p.145)

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

b) 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) Any one of the following:

- Use biomass to make syngas for methanol production. (1)
  This conversion uses renewable feedstocks. (1)
- Use carbon dioxide in flue gas for methanol production. (1)
  This helps reduce the release of carbon dioxide to the atmosphere. (1)

Topic Exercise (p.145)

25 Ethanoic acid can be produced by two routes as listed below:

Route 1

$$\text{sugar solution} \xrightarrow{\text{yeast}} CH_3CH_2OH(aq) \xrightarrow[\text{catalyst}]{O_2(g)} CH_3COOH(aq)$$

Route 2

$$CH_3OH(l) + CO(g) \xrightarrow[\text{catalyst}]{180\ ^\circ C;\ 30\ atm} CH_3COOH(l)$$

Topic Exercise (p.145)

a) The reactions in both *Routes 1* and *2* require the use of catalysts.

i) Draw, in the same sketch, TWO labelled energy profiles for a reaction, one with a catalyst and the other one without catalyst.

ii) Theoretically, catalysts are not consumed in reactions. Suggest why it is still necessary to replace the used catalyst from time to time in industrial processes.

b) Suggest TWO reasons why *Route 1* is considered as a green process.

c) Suggest TWO reasons why ethanoic acid used in the plastic industry is manufactured by *Route 2* instead of *Route 1*.

(HKDSE, Paper 2, 2015, 1(b))

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