

CHEMICAL ENERGETICS MCQ PART 1

- 1 Which option involves a positive entropy change?
- A the homolytic fission of gaseous chlorine
 - B the lattice energy of sodium chloride
 - C the contraction of an ideal gas at a constant temperature
 - D cooling a copper strip from 373 K to 273 K

- 2 Which statement regarding catalysts is correct?
- A Catalysts change the ΔH value of a reaction.
 - B Catalysts increase the yield of product in a reaction.
 - C Catalysts provide a different mechanism for a reaction.
 - D Catalysts change the K_c value of a reaction

- 3 *Use of Data Booklet is relevant to this question.*

The $\Delta G^\ominus_{\text{solution}}$ and $\Delta S^\ominus_{\text{solution}}$ for silver chloride, AgCl are $+55.6 \text{ kJ mol}^{-1}$ and $+33.2 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively.

What is the standard enthalpy change (ΔH^\ominus) when 287 g of AgCl is precipitated under the same conditions?

- A +65.5 kJ B -65.5 kJ C +131 kJ D -131 kJ

- 4 30 cm^3 of 0.1 mol dm^{-3} sulfuric acid and 40 cm^3 of 0.2 mol dm^{-3} sodium hydroxide were mixed in a Styrofoam cup.

Assume that the density and specific heat capacity of the final mixture are 1.0 g cm^{-3} and $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ respectively.

What is the temperature change of the solution given that the standard enthalpy change of neutralisation is $-57.3 \text{ kJ mol}^{-1}$?

- A $-1.6 \text{ }^\circ\text{C}$ B $-1.2 \text{ }^\circ\text{C}$ C $+1.2 \text{ }^\circ\text{C}$ D $+1.6 \text{ }^\circ\text{C}$

- 5 Changes in temperature can affect the spontaneity of a reaction.

Which statements are correct?

- 1 If a reaction is endothermic and has a negative entropy change, the reaction is spontaneous at all temperatures.
- 2 If a reaction is exothermic and has a negative entropy change, the reaction is non-spontaneous at all temperatures.
- 3 If a reaction is exothermic and has a positive entropy change, the reaction is spontaneous at all temperatures.

- A 1 and 3 B 1 only C 2 only D 3 only

6 Which equation does **not** correspond to the enthalpy change stated?

- A $\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2\text{K}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $\Delta H_{\text{neutralisation}}^{\oplus}$
- B $\text{Na}^+(\text{g}) + \text{H}^+(\text{g}) + \text{CO}_2^-(\text{g}) \rightarrow \text{NaHCO}_3(\text{s})$ $\Delta H_{\text{lattice energy}}^{\oplus}(\text{NaHCO}_3(\text{s}))$
- C $\text{NaHSO}_4(\text{s}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ $\Delta H_{\text{solution}}^{\oplus}(\text{NaHSO}_4(\text{s}))$
- D $\text{S}(\text{s}) + 4\text{H}_2(\text{g}) + \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})$ $\Delta H_{\text{formation}}^{\oplus}((\text{NH}_4)_2\text{SO}_4(\text{s}))$

7 A 0.483 g sample of glycine ($M_r = 75$) was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.54 °C.

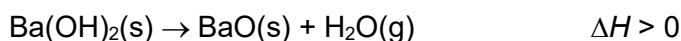
In a separate experiment using the same calorimeter, the combustion of 0.986 g of benzoic acid ($M_r = 122$) gave a temperature rise of 2.14 °C. The enthalpy change of combustion of benzoic acid is $-3054 \text{ kJ mol}^{-1}$.

What is the enthalpy change of combustion, in kJ mol^{-1} , of glycine?

- A -615 B -967 C -2423 D -3812

8 Group 2 hydroxides undergo thermal decomposition in a similar fashion to Group 2 carbonates.

Barium hydroxide undergoes decomposition as shown in the equation below:



Which statements about this reaction are correct?

- 1 The Gibbs free energy change can be positive or negative depending on the temperature.
- 2 The decomposition is spontaneous only at high temperature.
- 3 The entropy change is negative.
- 4 Barium hydroxide decomposes at a lower temperature than magnesium hydroxide.

- A 1 and 2 only B 1 and 3 only
C 2 and 4 only D 1, 2 and 4 only

9 Travellers to countries with cold climate may sometimes use heat packs to keep warm. One example is the sodium ethanoate heat pack. This consists of a supersaturated solution of sodium ethanoate and a small metal disc containing very small crystals of sodium ethanoate. When the disc is broken, the small crystals of sodium ethanoate are released into the solution and act as nucleation sites to catalyse the crystallisation reaction of sodium ethanoate.

Which line gives the signs of ΔH , ΔS and ΔG for the overall process?

	ΔH	ΔS	ΔG
A	-	-	-
B	-	-	+
C	+	+	-
D	+	+	+

- 10 Three experiments were carried out involving acids and alkalis of the same concentration. The temperature changes were recorded as shown in the table below.

Volumes of acids and alkalis added together	$\Delta T / ^\circ\text{C}$
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NaOH(aq)	ΔT_1
50.0 cm ³ of HCl(aq) + 50.0 cm ³ of NaOH(aq)	ΔT_2
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NH ₃ (aq)	ΔT_3

Which row shows the correct relative magnitude of ΔT values?

- A** $\Delta T_2 > \Delta T_3 > T_1$ **B** $\Delta T_1 = \Delta T_2 > \Delta T_3$ **C** $\Delta T_2 = \Delta T_3 > \Delta T_1$ **D** $\Delta T_1 = \Delta T_2 = \Delta T_3$

- 11 Some ΔH values are given below.

	enthalpy change of formation / kJ mol ⁻¹
Fe ₂ O ₃	- 824.2
CO	- 110.5
CO ₂	- 393.5

In the industrial production of iron, iron(III) oxide is reduced by carbon monoxide. What is the enthalpy change of reaction for one mole of iron formed?

- A** - 24.8 kJ mol⁻¹
B + 24.8 kJ mol⁻¹
C - 12.3 kJ mol⁻¹
D + 541.2 kJ mol⁻¹

- 12 Which standard enthalpy change is represented by the correct equation?

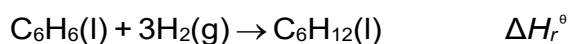
A	$\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	$\Delta H_f^\ominus(\text{CO}_2)$
B	$\text{H}_2\text{SO}_4\text{(aq)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{SO}_4\text{(aq)} + 2\text{H}_2\text{O(l)}$	$\Delta H_{\text{neut}}^\ominus$
C	$\text{K}^+\text{(g)} \rightarrow \text{K}^+\text{(aq)}$	$\Delta H_{\text{sol}}^\ominus(\text{K}^+)$
D	$\text{S(g)} \rightarrow \text{S}^{2-}\text{(g)} + 2\text{e}^-$	$\Delta H_{2^{\text{nd}}\text{EA}}^\ominus(\text{S})$

13 Which of the following processes have different signs for ΔG^\ominus and ΔS^\ominus ?

- 1 $\text{SO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$
2 $\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$
3 $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

14 Cyclohexane, C_6H_{12} , is prepared industrially by the hydrogenation of benzene as shown in the equation below.



Using the data in the table, what is the standard enthalpy change, ΔH_r^\ominus , of this reaction?

compound	standard enthalpy change of combustion / kJ mol^{-1}
$\text{C}_6\text{H}_6(\text{l})$	-3268
$\text{H}_2(\text{g})$	-286
$\text{C}_6\text{H}_{12}(\text{l})$	-3754

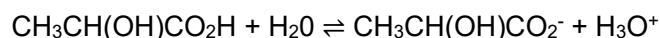
A -372 kJ mol^{-1} **B** -200 kJ mol^{-1} **C** $+200 \text{ kJ mol}^{-1}$ **D** $+372 \text{ kJ mol}^{-1}$

15 Which equation represents the standard enthalpy change stated?

	standard enthalpy change of	equation
A	atomisation of $\text{Cl}_2(\text{g})$	$\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$
B	combustion of $\text{H}_2\text{S}(\text{g})$	$\text{H}_2\text{S}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{SO}_2(\text{g})$
C	formation of $\text{H}_2\text{SO}_4(\text{l})$	$2\text{H}(\text{g}) + 4\text{O}(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{SO}_4(\text{l})$
D	solution of $\text{K}_2\text{SO}_4(\text{s})$	$\text{K}_2\text{SO}_4(\text{s}) \rightarrow 2\text{K}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

CHEMICAL ENERGETICS STRUCTURED QUESTIONS PART 1

- 1 (a) Both lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, and ethanoic acid are colourless liquids at 298 K. Lactic acid dissociates in water to form its conjugate base, lactate ion $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$.



An intramolecular hydrogen bond can be formed in the lactate ion.

- (i) Draw the structure of the lactate ion showing the intramolecular hydrogen bond formed.

[1]

- (ii) Hence, suggest how the K_a of lactic acid would differ from that of ethanoic acid. Explain your answer.

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.....[1]

- (b) Nicotinamide adenine dinucleotide (NAD^+) is a coenzyme responsible for carrying electrons from one reaction to another in living cells.

The electrode potential for the reduction of NAD^+ in a biological system, $E(\text{pH } 7)$, in which the conditions are at 1 mol dm^{-3} , 25°C and $\text{pH } 7$, is as shown. The reduced form of NAD^+ is represented as NADH .



The Nernst equation can be used to calculate the electrode potential of the above system when $[\text{NAD}^+]$ and $[\text{NADH}]$ change.

$$E = E(\text{pH } 7) - \left(\frac{0.0592}{n} \right) \log_{10} \frac{[\text{NADH}]}{[\text{NAD}^+]}$$

where n is the number of moles of electrons transferred in the system.

- (i) Using the Nernst equation given, determine the ratio $\frac{[\text{NADH}]}{[\text{NAD}^]}$ when $E = -0.350 \text{ V}$.

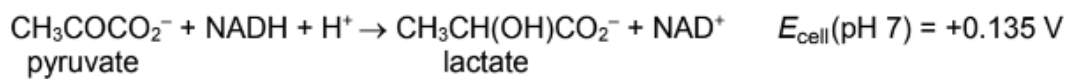
[1]

- (ii) Hence, calculate the percentage of NAD^+ in the NAD^+ – NADH mixture when $E = -0.350 \text{ V}$.

[1]

During intense exercise where there is insufficient supply of oxygen, pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, is converted to lactic acid.

This process involves the conjugate bases of the two acids and the conversion of coenzyme NADH to NAD^+ , as shown below. The standard cell potential of this reaction is measured at 25°C and $\text{pH } 7$.



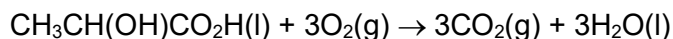
- (iii) Write the half-equation for the reduction of pyruvate to lactate in an acidic condition and calculate its standard electrode potential at 25°C and $\text{pH } 7$.

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.....[2]

- (iv) Calculate ΔG for the anaerobic metabolism of pyruvate at $\text{pH } 7$.

[1]

(c) The standard enthalpy change of combustion of lactic acid can be represented as shown.



(i) What do you understand by the term *standard enthalpy change of combustion of lactic acid*?

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.....[1]

(ii) Using the data in Table 2.1, calculate standard enthalpy change of combustion, ΔH_c^\ominus , of lactic acid.

Table 2.1

Species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}(\text{l})$	-483.2
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8

[1]

(iii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of lactic acid.

[2]

(iv) Apart from average bond energy values found in the *Data Booklet*, suggest one other reason for the difference in your answers in (c)(ii) and (c)(iii).

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.....[1]

[Total: 12]

2 Iron oxides are chemical compounds composed of iron and oxygen. Most iron ores are oxides, making them important precursors to iron metal and its many alloys.

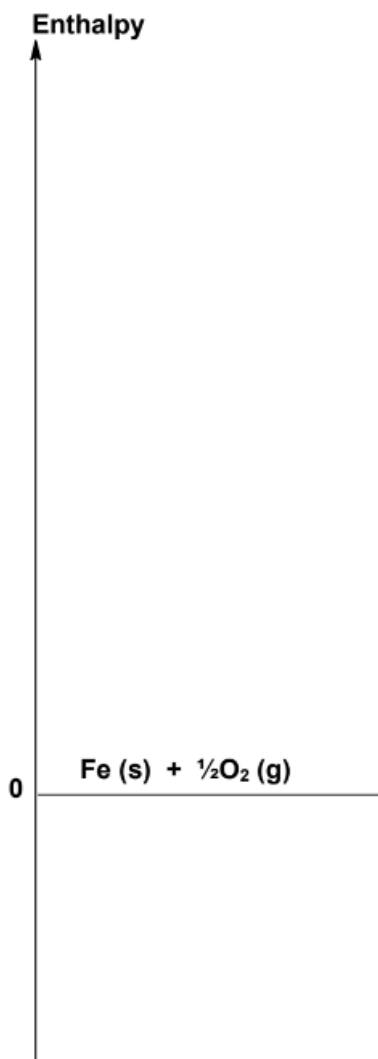
(a) Iron (II) compounds are only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

- (i) Given the following data in Table 2.1 and data from the *Data Booklet*, draw and complete the energy diagram below to calculate the lattice energy of FeO(s) in kJ mol^{-1} .

standard enthalpy change of atomisation of Fe(s)	+416 kJ mol^{-1}
standard enthalpy change of formation of FeO(s)	-272 kJ mol^{-1}
Sum of 1 st and 2 nd electron affinity of oxygen	+157 kJ mol^{-1}

Table 2.1



(ii) Most naturally occurring samples of iron(II) oxides are found as the mineral Wüstite.

Wüstite has the formula Fe_{20}O_x . It contains both Fe^{2+} and Fe^{3+} ions. 90% of the iron is present as Fe^{2+} and the remaining as Fe^{3+} .

By means of calculations, deduce the value of x.

[1]

(iii) State and explain how the lattice energy of FeO compares with the lattice energy of Fe_2O_3 .

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[2]

(b) Another common iron oxide as hematite, Fe_2O_3 is the main source of iron for the steel industry. Fe_2O_3 will readily react with acids to form soluble salts such as the following reaction.



(i) Define standard enthalpy change of solution.

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[1]

- (ii) Use the data in Table 2.2 to calculate the enthalpy change of solution of iron (II) iodide, FeI₂.

$\Delta H_{\text{latt}}(\text{FeI}_2(\text{s}))$	- 2440 kJ mol ⁻¹
$\Delta H_{\text{hyd}}(\text{Fe}^{2+}(\text{g}))$	- 1950 kJ mol ⁻¹
$\Delta H_{\text{hyd}}(\text{I}^{-}(\text{g}))$	- 308 kJ mol ⁻¹

Table 2.2

[1]

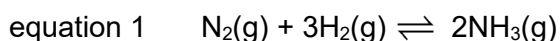
- (iii) A yellow precipitate of PbI₂ forms when 25 cm³ of x mol dm⁻³ Pb²⁺ ions are added to 10 cm³ of 0.100 mol dm⁻³ FeI₂ (aq).

Given that the solubility product, K_{sp} , of PbI₂ = 9.8×10^{-9} mol³ dm⁻⁹, find the minimum value for x , concentration of Pb²⁺ for precipitation to occur.

[2]

[Total: 10]

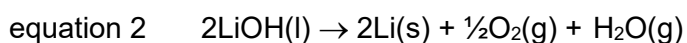
- 3(a) The Haber–Bosch process remains the primary industrial route to synthesise ammonia. It involves the breaking of the triple bond in molecular nitrogen at high pressures and temperatures and the hydrogen gas it requires to turn nitrogen to ammonia comes mainly from natural gas.



This process however is responsible for up to 3% of global CO₂ emissions.

The electrochemical lithium cycling process to make ammonia is a more sustainable approach. It is reported to have achieved an efficiency of 88.5% in lab-scale tests. The process uses electricity, which can have a renewable source, such as wind or solar energy.

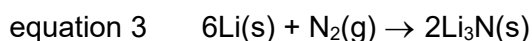
In the first stage, the electrolysis of molten lithium hydroxide produces molten lithium metal at the cathode. Oxygen and steam are formed at the anode.



- (i) Using data from the *Data Booklet*, explain why an aqueous solution of LiOH cannot be used to produce lithium metal by electrolysis.

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..... [1]

The next stage in the process involves gently heating the lithium metal in a stream of nitrogen to produce lithium nitride.



- (ii) Define, with the aid of an equation, lattice energy of lithium nitride.

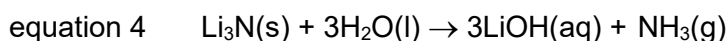
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- (iii) Using the data in Table 4.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the third electron affinity of nitrogen. Show your working clearly.

Table 4.1

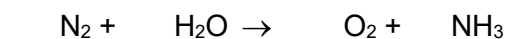
	value / kJ mol ⁻¹
sum of 1 st and 2 nd electron affinity of N	+680
lattice energy of Li ₃ N	-4830
enthalpy change of sublimation of Li: Li(s) → Li(g)	+161
enthalpy change of reaction for the following reaction: 6Li(s) + N ₂ (g) → 2Li ₃ N(s)	-330

The last stage in the process involves reacting lithium nitride with water. A solution containing ammonia and lithium hydroxide is produced.



The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(iv) The following equation represents the overall equation for electrochemical lithium cycling process.



Complete the balancing of the above equation. Show your working clearly.

[1]

The standard Gibbs free energy changes of formation, ΔG_f^\ominus , of several compounds are listed in Table 4.2.

Table 4.2

compound	$\Delta G_f^\ominus / \text{kJ mol}^{-1}$
LiOH(s)	-439
Li ₃ N(s)	-137
H ₂ O(l)	-237
NH ₃ (g)	-17

(iv) Using your equation in **a(iv)**, calculate the standard Gibbs free energy change, ΔG^\ominus , when 2 mol of ammonia are produced.

[1]

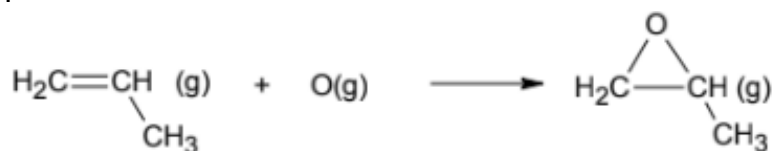
- (v) Calculate the standard Gibbs free energy change, ΔG^\ominus , for the Haber-Bosch process shown in equation 1. By considering the stability of the reactants and products, explain why this value is different from that calculated in a(v).

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 [2]

- (b) An epoxide is a cyclic ether (C–O–C) that is highly reactive. Like all compounds containing a 3-membered ring, the bonds in 1,2-epoxypropane are weaker. This can be illustrated by the following calculation, in which you can assume that the C–H bond energy is the same in propane and 1,2-epoxypropane.

The ΔH^\ominus for the reaction between propene molecules and oxygen atoms has been calculated to be -363 kJ mol^{-1} .



- (i) Use the data from the *Data Booklet* to calculate a theoretical value for the sum of the C–C and $2 \times \text{C–O}$ bond energies in 1,2-epoxypropane.

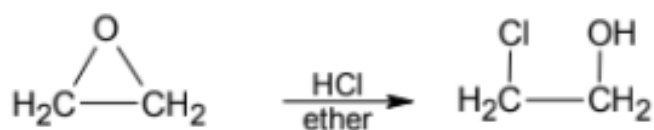
[1]

- (ii) Use the ΔH^\ominus value for the reaction between propene and oxygen atoms given above to calculate the actual value for the sum of the C–C and $2 \times \text{C–O}$ bond energies in 1,2-epoxypropane. Suggest an explanation for the difference between the theoretical and actual values.

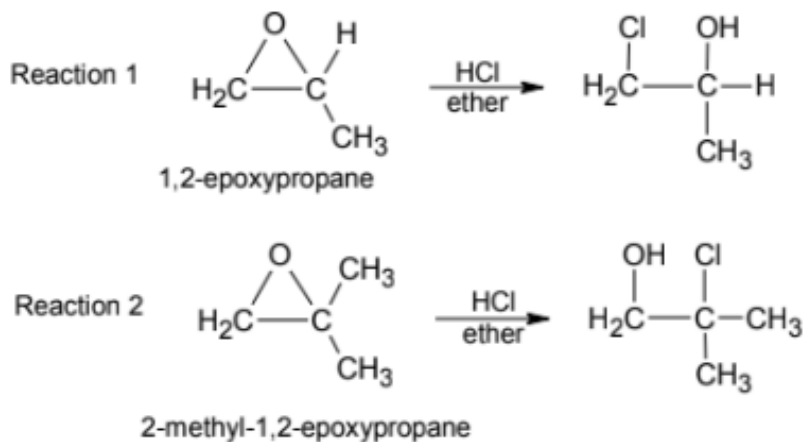
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[2]

- (c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



The ring-opening reaction of epoxides can proceed by either S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane reacts with HCl via different mechanisms to give the following major products.



- (i) Explain why the reaction proceeds via the given predominant mechanism and not the other.

Type of mechanism for reaction 1: S_N2

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Type of mechanism for reaction 2: S_N1

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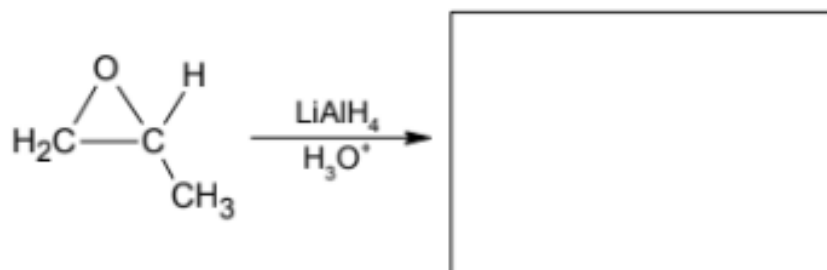
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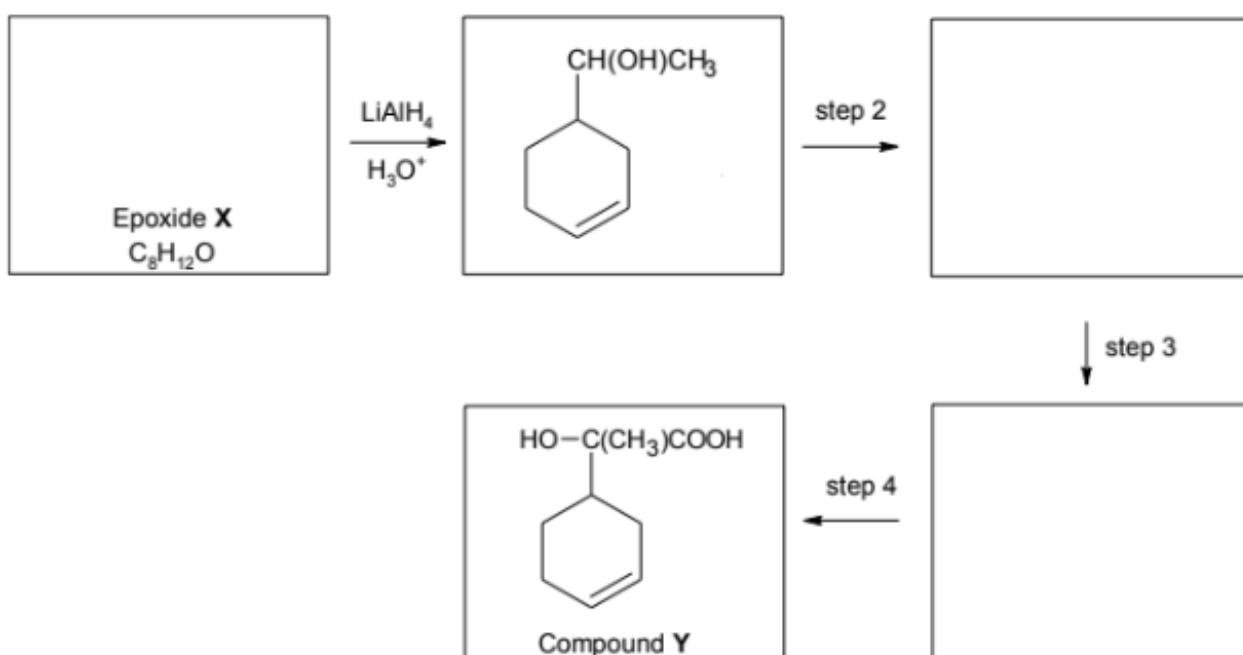
Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides. $\text{S}_{\text{N}}2$ mechanism usually predominates with these reagents.

- (ii) Draw the structural formula of the major product formed when 1,2-epoxypropane reacts with LiAlH_4 .



[1]

- (iii) Compound **Y** can be formed via a four-step synthesis with epoxide **X** as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step.



step 2:

step 3:

step 4:.....[6]

- (iv) A small amount of a sweet-smelling side product, $C_{18}H_{24}O_4$, is formed in step 4. Draw the structure of this side product.

[1]

[Total: 24]

ANSWERS FOR CHEMICAL ENERGETICS MCQ PART 1

1 Which option involves a positive entropy change?

- A the homolytic fission of gaseous chlorine
- B the lattice energy of sodium chloride
- C the contraction of an ideal gas at a constant temperature
- D cooling a copper strip from 373 K to 273 K

A: There is an increase in the number of gaseous particles as the reaction proceeds.
 $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$

B: $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$
There is a decrease in the number of gaseous particles.

C: Gas particles have fewer ways of arrangement with a smaller volume.

D: Cooling a metal results in less disorder as the particles vibrate less. In addition, there are fewer energy quanta available for distribution so there are fewer ways to distribute them in the metal.

2 Which statement regarding catalysts is correct?

- A Catalysts change the ΔH value of a reaction.
- B Catalysts increase the yield of product in a reaction.
- C Catalysts provide a different mechanism for a reaction.
- D Catalysts change the K_c value of a reaction

A: Catalysts do not change the reactants and products of a reaction. Hence the ΔH value remains unchanged.

B: Catalysts do not change in the position of equilibrium in a reaction. Hence the yield of the product does not change.

C: Catalysts reduce the activation energy of a reaction by providing an alternative mechanism for the reaction to proceed by.

D: The rate constant values of both the forward and backward reaction are changed to the same extent by a catalyst. Hence the K_c value of a reaction remains unchanged.

3 *Use of Data Booklet is relevant to this question.*

The $\Delta G^\ominus_{\text{solution}}$ and $\Delta S^\ominus_{\text{solution}}$ for silver chloride, AgCl are $+55.6 \text{ kJ mol}^{-1}$ and $+33.2 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively.

What is the standard enthalpy change (ΔH^\ominus) when 287 g of AgCl is precipitated under the same conditions?

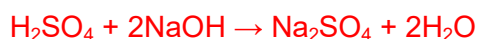
- A +65.5 kJ
- B -65.5 kJ
- C +131 kJ
- D -131 kJ

- 4 30 cm³ of 0.1 mol dm⁻³ sulfuric acid and 40 cm³ of 0.2 mol dm⁻³ sodium hydroxide were mixed in a Styrofoam cup.

Assume that the density and specific heat capacity of the final mixture are 1.0 g cm⁻³ and 4.2 J g⁻¹ K⁻¹ respectively.

What is the temperature change of the solution given that the standard enthalpy change of neutralisation is -57.3 kJ mol⁻¹?

- A -1.6 °C B -1.2 °C **C +1.2 °C** D +1.6 °C



$$n(\text{H}_2\text{SO}_4) = \frac{30}{1000} \times 0.1 = 0.003 \text{ mol}$$

$$n(\text{NaOH}) = \frac{40}{1000} \times 0.2 = 0.008 \text{ mol}$$

H₂SO₄ is the limiting reagent.

$$\begin{aligned} n(\text{H}_2\text{O}) &= 2 \times n(\text{H}_2\text{SO}_4) \\ &= 2 \times 0.003 \\ &= 0.006 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Heat released from the reaction} &= n(\text{H}_2\text{O}) \times |\Delta H_{\text{neu}}| \\ &= 0.006 \times 57.3 \times 1000 \\ &= 343.8 \text{ J} \\ &= \text{heat absorbed by the solution} \end{aligned}$$

$$\begin{aligned} \text{heat absorbed by the solution} &= mc|\Delta T| \\ 343.8 &= 70 \times 1 \times 4.2 \times |\Delta T| \\ |\Delta T| &= 1.2 \text{ °C} \end{aligned}$$

Since heat is absorbed by the solution,

$$\Delta T = +1.2 \text{ °C.}$$

- 5 Changes in temperature can affect the spontaneity of a reaction.

Which statements are correct?

- 1 If a reaction is endothermic and has a negative entropy change, the reaction is spontaneous at all temperatures.
- 2 If a reaction is exothermic and has a negative entropy change, the reaction is non-spontaneous at all temperatures.
- 3 If a reaction is exothermic and has a positive entropy change, the reaction is spontaneous at all temperatures.

- A 1 and 3 B 1 only C 2 only **D 3 only**

$$\Delta G = \Delta H - T\Delta S$$

1 x: $\Delta H > 0, \Delta S < 0, \Delta G > 0$ (non- spontaneous) at all T

2 x: $\Delta H < 0, \Delta S < 0, \Delta G > 0$ (non- spontaneous) when $T > \frac{\Delta H}{\Delta S}$

3 ✓: $\Delta H < 0, \Delta S > 0, \Delta G < 0$ (spontaneous) at all T

6 Which equation does **not** correspond to the enthalpy change stated?

- A $\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2\text{K}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $\Delta H_{\text{neutralisation}}^{\oplus}$
- B** $\text{Na}^+(\text{g}) + \text{H}^+(\text{g}) + \text{CO}_3^{2-}(\text{g}) \rightarrow \text{NaHCO}_3(\text{s})$ $\Delta H_{\text{lattice energy}}(\text{NaHCO}_3(\text{s}))$
- C $\text{NaHSO}_4(\text{s}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ $\Delta H_{\text{solution}}^{\oplus}(\text{NaHSO}_4(\text{s}))$
- D $\text{S}(\text{s}) + 4\text{H}_2(\text{g}) + \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})$ $\Delta H_{\text{formation}}^{\oplus}((\text{NH}_4)_2\text{SO}_4(\text{s}))$

A ✓: 1 mol of H₂O is formed from the reaction of an acid and a base

B x: $\Delta H_{\text{lattice energy}}^{\oplus}(\text{NaHCO}_3(\text{s}))$ is for the reaction $\text{Na}^+(\text{g}) + \text{HCO}_3^-(\text{g}) \rightarrow \text{NaHCO}_3(\text{s})$

C ✓: Being a strong acid, the HSO₄⁻ ion will fully dissociate in water to give H⁺(aq) and SO₄²⁻(aq)

D ✓: $\Delta H_{\text{formation}}^{\oplus}$ involves forming (NH₄)₂SO₄ from the constituent elements, S, H₂, N₂ and O₂ in their standard states

7 A 0.483 g sample of glycine ($M_r = 75$) was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.54 °C.

In a separate experiment using the same calorimeter, the combustion of 0.986 g of benzoic acid ($M_r = 122$) gave a temperature rise of 2.14 °C. The enthalpy change of combustion of benzoic acid is $-3054 \text{ kJ mol}^{-1}$.

What is the enthalpy change of combustion, in kJ mol^{-1} , of glycine?

- A -615 **B -967** C -2423 D -3812

In the experiment with benzoic acid,

No. of moles of benzoic acid combusted = $0.986 / 122 = 0.008082$

$q = -\Delta H_c \times \text{no. of moles of benzoic acid} = 3054 \times 0.008082 = 24.68 \text{ kJ}$

Heat capacity of the bomb calorimeter = $24.68 / 2.14 \text{ kJ } ^\circ\text{C}^{-1}$

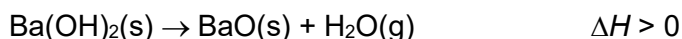
In the experiment with glycine,

No. of moles of glycine combusted = $0.483 / 75 = 0.00644$ $q = (24.68 / 2.14) \times 0.54 = 6.228 \text{ kJ}$

Enthalpy change of combustion of glycine = $-6.228 / 0.00644 = -967 \text{ kJ mol}^{-1}$

- 8 Group 2 hydroxides undergo thermal decomposition in a similar fashion to Group 2 carbonates.

Barium hydroxide undergoes decomposition as shown in the equation below:



Which statements about this reaction are correct?

- 1 The Gibbs free energy change can be positive or negative depending on the temperature.
- 2 The decomposition is spontaneous only at high temperature.
- 3 The entropy change is negative.
- 4 Barium hydroxide decomposes at a lower temperature than magnesium hydroxide.

A 1 and 2 only

B 1 and 3 only

C 2 and 4 only

D 1, 2 and 4 only

This decomposition is endothermic since energy is required for breaking the covalent bonds in the OH^- anion.

ΔS is expected to be positive since there is formation of gaseous H_2O , thus statement 3 is wrong.

ΔG can be positive or negative depending on the temperature.

For reactions to be spontaneous, ΔG needs to be negative. As $\Delta G = \Delta H - T\Delta S$, T has to be high so that $|T\Delta S| > \Delta H$. Thus statement 2 is correct.

Similar to Group 2 carbonates, the thermal decomposition of Group 2 hydroxides is dependent on the charge density of the cation. Since Ba^{2+} is larger in cationic radius as compared to Mg^{2+} , the charge density of Ba^{2+} is smaller. Hence its polarising power is weaker and is less able to distort the electron cloud of the hydroxide ion, weakening the O-H covalent bond to a smaller extent. Thus, barium hydroxide will decompose at a higher temperature than magnesium hydroxide.

- 9 Travellers to countries with cold climate may sometimes use heat packs to keep warm. One example is the sodium ethanoate heat pack. This consists of a supersaturated solution of sodium ethanoate and a small metal disc containing very small crystals of sodium ethanoate. When the disc is broken, the small crystals of sodium ethanoate are released into the solution and act as nucleation sites to catalyse the crystallisation reaction of sodium ethanoate.

Which line gives the signs of ΔH , ΔS and ΔG for the overall process?

	ΔH	ΔS	ΔG
A	-	-	-
B	-	-	+
C	+	+	-
D	+	+	+

- 10 Three experiments were carried out involving acids and alkalis of the same concentration. The temperature changes were recorded as shown in the table below.

Volumes of acids and alkalis added together	$\Delta T / ^\circ\text{C}$
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NaOH(aq)	ΔT_1
50.0 cm ³ of HCl(aq) + 50.0 cm ³ of NaOH(aq)	ΔT_2
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NH ₃ (aq)	ΔT_3

Which row shows the correct relative magnitude of ΔT values?

- A $\Delta T_2 > \Delta T_3 > \Delta T_1$ **B $\Delta T_1 = \Delta T_2 > \Delta T_3$** C $\Delta T_2 = \Delta T_3 > \Delta T_1$ D $\Delta T_1 = \Delta T_2 = \Delta T_3$

Assuming the concentration of both acid and alkali are 1 mol dm⁻³.

- (i) 25.0 cm³ of HCl(aq) + 25.0 cm³ of NaOH(aq): 0.025 mol of H₂O produced, m = 50.0.
 (ii) 50.0 cm³ of HCl(aq) + 50.0 cm³ of NaOH(aq): 0.05 mol of H₂O produced, m = 100.0.
 (iii) 25.0 cm³ of HCl(aq) + 25.0 cm³ of NH₃(aq): 0.025 mol of H₂O produced, m = 50.0.

Given $\Delta T = \frac{\Delta H \times n_{\text{H}_2\text{O}}}{mc}$ and both c and ΔH_{neu} of strong acid and strong alkali are constant,

$$\Delta T \propto \frac{n_{\text{H}_2\text{O}}}{m}$$

Hence, $\Delta T_1 = \Delta T_2$

Magnitude of ΔH_{neu} of strong acid and weak alkali < ΔH_{neu} of strong acid and strong alkali

Hence, $\Delta T_1 = \Delta T_2 > \Delta T_3$

- 11 Some ΔH values are given below.

	enthalpy change of formation / kJ mol ⁻¹
Fe ₂ O ₃	- 824.2
CO	- 110.5
CO ₂	- 393.5

In the industrial production of iron, iron(III) oxide is reduced by carbon monoxide. What is the enthalpy change of reaction for one mole of iron formed?

- A - 24.8 kJ mol⁻¹
 B + 24.8 kJ mol⁻¹
C - 12.3 kJ mol⁻¹
 D + 541.2 kJ mol⁻¹

Ans: **A**



$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum \Delta H_{\text{formation of products}} - \sum \Delta H_{\text{formation of reactants}} \\ &= 3(-393.5) - [-824.2 + 3(-110.5)] \\ &= -24.6 \text{ kJ mol}^{-1}\end{aligned}$$

Hence, enthalpy change of reaction for one mole of iron formed = $24.6 \div 2 = 12.3 \text{ kJ mol}^{-1}$

12 Which standard enthalpy change is represented by the correct equation?

A	$\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	$\Delta H_f^\ominus(\text{CO}_2)$
B	$\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	$\Delta H_{\text{neut}}^\ominus$
C	$\text{K}^+(\text{g}) \rightarrow \text{K}^+(\text{aq})$	$\Delta H_{\text{sol}}^\ominus(\text{K}^+)$
D	$\text{S}(\text{g}) \rightarrow \text{S}^{2-}(\text{g}) + 2\text{e}^-$	$\Delta H_{2^{\text{nd}} \text{EA}}^\ominus(\text{S})$

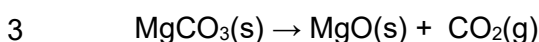
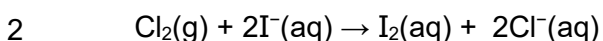
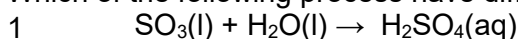
A is correct. 1 mol of $\text{CO}_2(\text{g})$ is formed from 1 mol of C(graphite) which is a solid at standard conditions and 1 mol of O_2 gas.

B is wrong. ΔH_{neut} is for 1 mol of water formed between the reaction of an acid and an alkali.

C is wrong. The equation given is for ΔH_{hyd} , enthalpy of hydration.

D is wrong. The equation given is for 1st EA + 2nd EA of sulfur.

13 Which of the following process have different signs for ΔG^\ominus and ΔS^\ominus ?



A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

		ΔG^\ominus	ΔS^\ominus
1	$\text{SO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$	-	+
2	$\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$	-	+
3	$\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$	+	+

- 14 Cyclohexane, C₆H₁₂, is prepared industrially by the hydrogenation of benzene as shown in the equation below.



Using the data in the table, what is the standard enthalpy change, ΔH_r^\ominus , of this reaction?

compound	standard enthalpy change of combustion / kJ mol ⁻¹
C ₆ H ₆ (l)	-3268
H ₂ (g)	-286
C ₆ H ₁₂ (l)	-3754

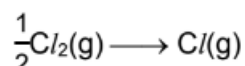
- A** -372 kJ mol⁻¹ **B** -200 kJ mol⁻¹ **C** +200 kJ mol⁻¹ **D** +372 kJ mol⁻¹

$$\begin{aligned} \Delta H_r^\ominus &= \sum n\Delta H_c^\ominus (\text{reactants}) - \sum m\Delta H_c^\ominus (\text{products}) \\ &= -3268 + 3(-286) - (-3754) = \underline{-372 \text{ kJ mol}^{-1}} \end{aligned}$$

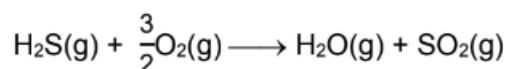
- 15 Which equation represents the standard enthalpy change stated?

	standard enthalpy change of	equation
A	atomisation of Cl ₂ (g)	Cl ₂ (g) → 2Cl(g)
B	combustion of H ₂ S(g)	H ₂ S(g) + O ₂ (g) → H ₂ (g) + SO ₂ (g)
C	formation of H ₂ SO ₄ (l)	2H(g) + 4O(g) + S(s) → H ₂ SO ₄ (l)
D	solution of K ₂ SO ₄ (s)	K ₂ SO ₄ (s) → 2K ⁺ (aq) + SO ₄ ²⁻ (aq)

Option **A** is incorrect. The standard enthalpy change of atomisation of chlorine is the energy absorbed when 1 mole of gaseous Cl atoms is formed from Cl₂(g) under standard conditions. The correct equation should be

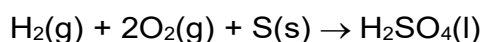


Option **B** is incorrect. The standard enthalpy change of combustion of a substance is the energy released when 1 mole of the substance is completely burnt in excess oxygen under standard conditions. The correct equation should be



Note: H₂ cannot be the end product of a combustion reaction as it can be combusted to give H₂O.

Option **C** is incorrect. The standard enthalpy change of formation of a substance is the energy change when 1 mole of the pure substance in a specified state is formed from its constituent elements in their standard states under standard conditions. The correct equation should be



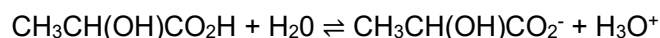
Note: The elements, hydrogen and oxygen, do not exist in the monoatomic form under standard conditions (i.e. 1 bar and 298 K).

Option **D** is correct. The standard enthalpy change of solution of a substance is the energy change when 1 mole of the substance (ionic compound) is completely dissolved in a solvent to form an infinitely dilute solution (containing aqueous ions) under standard conditions.

ANSWERS FOR CHEMICAL ENERGETICS STRUCTURED QUESTIONS PART 1

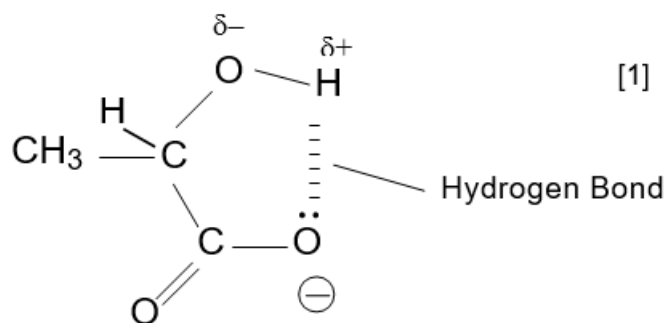
- 1 (a) Both lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, and ethanoic acid are colourless liquids at 298 K.

Lactic acid dissociates in water to form its conjugate base, lactate ion $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$.



An intramolecular hydrogen bond can be formed in the lactate ion.

- (i) Draw the structure of the lactate ion showing the intramolecular hydrogen bond formed.



[1]

Comments:

Common mistakes include:

- Missing dipoles, lone pairs, labels
- Drawing of lactic acid instead of lactate
- Hydrogen bonding to the wrong H or O (remember that only H bonded to O, N or F can be used for Hydrogen bonding!)
- Drew intermolecular hydrogen bonding (between two ions) instead of intramolecular hydrogen bonding (within one ion) as required by question
- Missing atoms and bonds

- (ii) Hence, suggest how the K_a of lactic acid would differ from that of ethanoic acid. Explain your answer.

- For lactate ion, intramolecular hydrogen bonding formed between the ionised $-\text{CO}_2^-$ group and $-\text{OH}$ group which results in the greater stability of the conjugate base/lactate ion compared to the ethanoate ion
- Lactic acid is a stronger acid with larger K_a value. [1].

Comments:

Common mistakes include:

- Explanations involving solubility
- Explanations about a second dissociation
- Acidity considerations not involving intramolecular H-Bonding despite the qualifier word "Hence"
- Answered in terms of $\text{p}K_a$
- Incorrectly related higher acidity to lower K_a

- (b) Nicotinamide adenine dinucleotide (NAD^+) is a coenzyme responsible for carrying electrons from one reaction to another in living cells.

The electrode potential for the reduction of NAD^+ in a biological system, $E(\text{pH } 7)$, in which the conditions are at 1 mol dm^{-3} , $25 \text{ }^\circ\text{C}$ and $\text{pH } 7$, is as shown. The reduced form of NAD^+ is represented as NADH .



The Nernst equation can be used to calculate the electrode potential of the above system when $[\text{NAD}^+]$ and $[\text{NADH}]$ change.

$$E = E(\text{pH } 7) - \left(\frac{0.0592}{n} \right) \log_{10} \frac{[\text{NADH}]}{[\text{NAD}^+]}$$

where n is the number of moles of electrons transferred in the system.

- (i) Using the Nernst equation given, determine the ratio $\frac{[\text{NADH}]}{[\text{NAD}^]}$ when $E = -0.350 \text{ V}$.

Since $n = 2$,

$$E = E^\circ - \left(\frac{0.0592}{2} \right) \log_{10} \frac{[\text{NADH}]}{[\text{NAD}^+]}$$

$$(-0.350) = (-0.320) - \left(\frac{0.0592}{2} \right) \log_{10} \frac{[\text{NADH}]}{[\text{NAD}^]}$$

$$\log_{10} \frac{[\text{NADH}]}{[\text{NAD}^]} = 1.01$$

$$\frac{[\text{NADH}]}{[\text{NAD}^]} = \mathbf{10.3 [1]} \text{ (3 s.f.)}$$

Comments:

Common mistakes include:

- Using \ln instead of \lg
- Incomplete calculations

- (ii) Hence, calculate the percentage of NAD^+ in the NAD^+ – NADH mixture when $E = -0.350 \text{ V}$.

$$\begin{aligned} \text{\% of } \text{NAD}^+ &= \frac{1}{(10.3+1)} \times 100\% \\ &= \mathbf{8.85\%} \quad [1] \end{aligned}$$

Comments: Poorly done. Many students cannot properly compute the percentage

[1]

During intense exercise where there is insufficient supply of oxygen, pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, is converted to lactic acid.

This process involves the conjugate bases of the two acids and the conversion of coenzyme NADH to NAD^+ , as shown below. The standard cell potential of this reaction is measured at 25°C and $\text{pH } 7$.



- (iii) Write the half-equation for the reduction of pyruvate to lactate in an acidic condition and calculate its standard electrode potential at 25°C and $\text{pH } 7$.



$$\begin{aligned} E_{\text{cell}}^{\circ} \text{ at pH } 7 &= E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ} \\ +0.135 &= E_{\text{red}}^{\circ} - (-0.320) \end{aligned}$$

$$E_{\text{red}}^{\circ} = -0.185 \text{ V} \quad [1]..[2]$$

Comments:

Very poorly done. Students are supposed to use the overall equation to deduce the reduction half-equation for pyruvate. This can be done by subtracting the oxidation half-equation involving NAD^+/NADH from the overall reaction equation.



The reduction half-equation is hence as shown below after balancing the particles and charges:



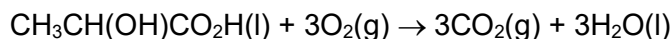
- (iv) Calculate ΔG for the anaerobic metabolism of pyruvate at $\text{pH } 7$.

$$\begin{aligned} \Delta G \text{ at pH } 7 &= -nFE_{\text{cell}}^{\circ} \\ &= -2 (96500) (+0.135) \\ &= -26\,055 \text{ J mol}^{-1} \\ &= \mathbf{-26\,100 \text{ J mol}^{-1}} \quad (3 \text{ s.f.}) \quad [1] \end{aligned}$$

Comments: Very poorly done. Many students either used the wrong E_{cell} or used the wrong number of mole of electrons transferred or simply misremembered the equation.

[1]

- (c) The standard enthalpy change of combustion of lactic acid can be represented as shown.



- (i) What do you understand by the term *standard enthalpy change of combustion of lactic acid*?

The amount of heat **evolved** when **one mole of lactic acid** in its **standard state** is **completely burned** in **excess oxygen** under standard conditions of **298 K and 1 bar**.

[1] correct definition with key words/points .

Comments: Key words such as 'standard state', 'completely' and 'excess' are frequently missing.

Students should specify the substance as 'lactic acid'.

[1]

- (ii) Using the data in Table 2.1, calculate standard enthalpy change of combustion, ΔH_c^\ominus , of lactic acid.

Table 2.1

Species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}(\text{l})$	-483.2
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8

$$\begin{aligned}\Delta H_c^\ominus &= [3(-393.5) + 3(-285.8)] - (-483.2) \\ &= -1554.7 \text{ kJ mol}^{-1} \\ &= \mathbf{-1550 \text{ kJ mol}^{-1}} \quad (3 \text{ s.f.}) \quad \mathbf{[1]} \text{ (correct value and units)}\end{aligned}$$

Comments: Students did not take into account the mole ratio of the products CO_2 and H_2O . Students are reminded to leave their answers to 3 sf

[1]

- (iii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of lactic acid.



$$\begin{aligned}\text{Heat absorbed for bond breaking} \\ &= 2 \text{ BE}(\text{C}-\text{C}) + 4 \text{ BE}(\text{C}-\text{H}) + 2 \text{ BE}(\text{C}-\text{O}) + 2\text{BE}(\text{O}-\text{H}) + \text{BE}(\text{C}=\text{O}) + 3 \text{ BE}(\text{O}=\text{O}) \\ &= 2(350) + 4(410) + 2(360) + 2(460) + (740) + 3(496) \\ &= \mathbf{6208 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{Heat released on bond formation} \\ &= 6 \text{ BE}(\text{C}=\text{O}) + 6\text{BE}(\text{O}-\text{H}) \\ &= 6(805) + 6(460) \\ &= \mathbf{7590 \text{ kJ mol}^{-1}}\end{aligned}$$

[1]
working

$$\begin{aligned}\Delta H_c^\ominus &= (+6208) + (-7590) \\ &= \mathbf{-1382 \text{ kJ mol}^{-1}} \quad \mathbf{[1]}\end{aligned}$$

Comments:

Common mistakes observed:

- ΔH is the sum of bonds **broken in reactants** – sum of bonds **formed in products**
- C-C bonds and O=O bonds in reactants not taken into account.
- Counting the number of bonds in reactants and/or products wrongly
- Using wrong bond energy values for C=O and O=O
- Including ΔH_f values in calculation

[2]

- (iv) Apart from average bond energy values found in the *Data Booklet*, suggest one other reason for the difference in your answers in (c)(ii) and (c)(iii).

In (c)(iii) calculations, bond energies used are defined for gaseous compounds. However, in (c)(ii), lactic acid and water are not gaseous in their standard state.

[1] show understanding that calculations involving bond energies are for gaseous substances.

Comments: Many students were not aware that that bond energy of a covalent bond is the average amount of heat absorbed to break one mole of that particular covalent bond in a particular compound in the **gaseous state**.

[Total: 12]

- 2 Iron oxides are chemical compounds composed of iron and oxygen. Most iron ores are oxides, making them important precursors to iron metal and its many alloys.

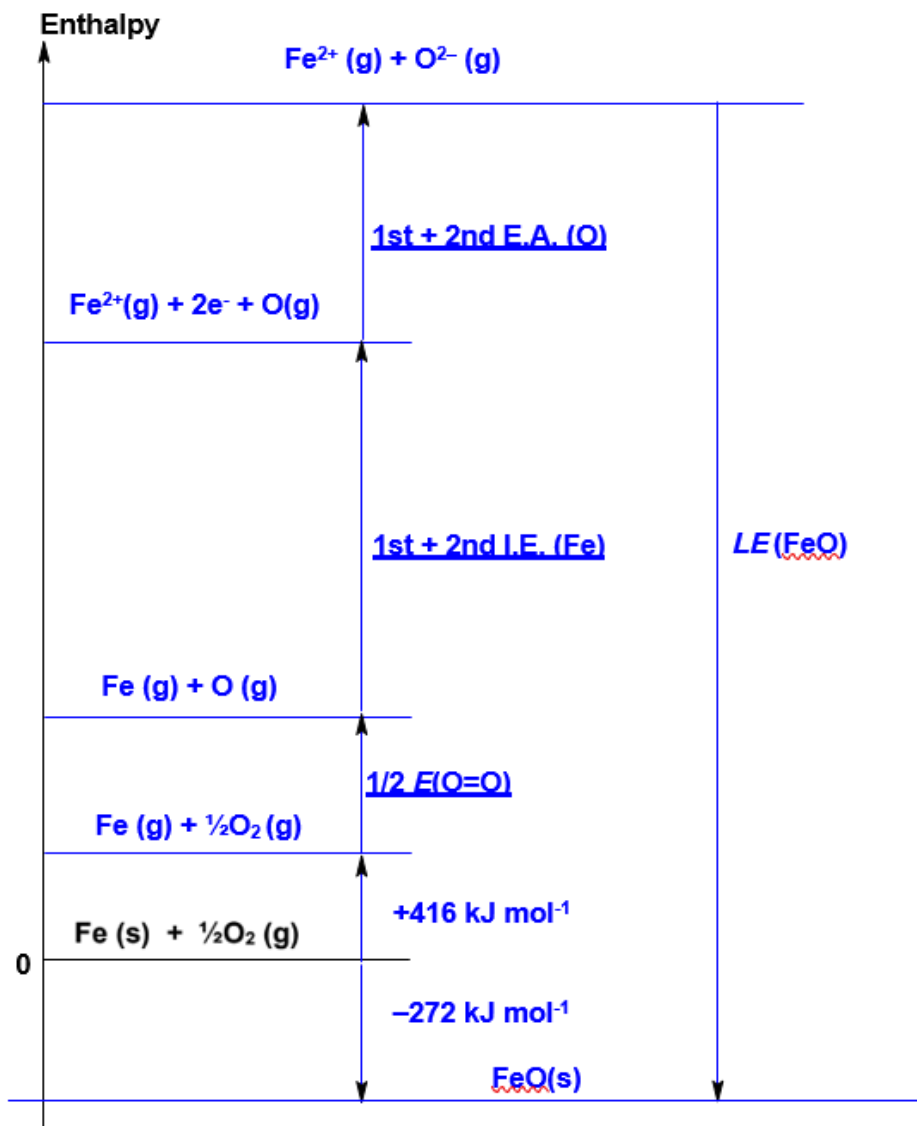
- (a) Iron (II) compounds are only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

- (i) Given the following data in Table 2.1 and data from the *Data Booklet*, draw and complete the energy diagram below to calculate the lattice energy of FeO(s) in kJ mol^{-1} .

standard enthalpy change of atomisation of Fe(s)	+416 kJ mol^{-1}
standard enthalpy change of formation of FeO(s)	-272 kJ mol^{-1}
Sum of 1 st and 2 nd electron affinity of oxygen	+157 kJ mol^{-1}

Table 2.1



By Hess Law,

$$-272 = +416 + \frac{1}{2}(496) + 762 + 1560 + 157 + LE(\text{FeO})$$

$$LE(\text{FeO}) = -3415 \text{ (or } -3420) \text{ kJ mol}^{-1}$$

- (ii) Most naturally occurring samples of iron(II) oxides are found as the mineral Wüstite.

Wüstite has the formula Fe_{20}O_x . It contains both Fe^{2+} and Fe^{3+} ions. 90% of the iron is present as Fe^{2+} and the remaining as Fe^{3+} .

By means of calculations, deduce the value of x.

Balancing of charges:

$$20 \times [0.9(+2) + 0.1(+3)] - 2x = 0$$

Solving x = 21

[1]

- (iii) State and explain how the lattice energy of FeO compares with the lattice energy of Fe_2O_3 .

Fe^{3+} ion has a higher (ionic) charge and smaller radius/size than Fe^{2+} ion.

Since $|\text{LE}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$, hence, the magnitude of LE for Fe_2O_3 is larger /

LE for Fe_2O_3 is more exothermic than that in FeO.

[2]

- (b) Another common iron oxide as hematite, Fe_2O_3 is the main source of iron for the steel industry. Fe_2O_3 will readily react with acids to form soluble salts such as the following reaction.



- (i) Define standard enthalpy change of solution.

It is the heat *change* when *1 mole of a substance is completely dissolved in water* under the standard conditions of 298 K and 1 bar so that there is no further heat change upon adding more water.

[1]

- (ii) Use the data in Table 2.2 to calculate the enthalpy change of solution of iron (II) iodide, FeI₂.

$\Delta H_{\text{latt}}(\text{FeI}_2(\text{s}))$	- 2440 kJ mol ⁻¹
$\Delta H_{\text{hyd}}(\text{Fe}^{2+}(\text{g}))$	- 1950 kJ mol ⁻¹
$\Delta H_{\text{hyd}}(\text{I}^{-}(\text{g}))$	- 308 kJ mol ⁻¹

Table 2.2

$$\Delta H_{\text{soln}} = -(-2440) + (-1950) + (2(-308))$$

$$= -126 \text{ kJ mol}^{-1}$$

[1]

- (iii) A yellow precipitate of PbI₂ forms when 25 cm³ of $x \text{ mol dm}^{-3}$ Pb²⁺ ions are added to 10 cm³ of 0.100 mol dm⁻³ FeI₂(aq).

Given that the solubility product, K_{sp} , of PbI₂ = $9.8 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$, find the minimum value for x , concentration of Pb²⁺ for precipitation to occur.

For ppt to occur,

$$\text{Ionic product} > K_{\text{sp}} \quad [\text{Pb}^{2+}] [\text{I}^{-}]^2 > 9.8 \times 10^{-9}$$

$$\left(\frac{\frac{25}{1000} \times x}{\frac{35}{1000}} \right) \left(\frac{2 \times \frac{10}{1000} \times 0.100}{\frac{35}{1000}} \right)^2 > 9.8 \times 10^{-9}$$

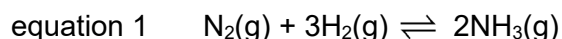
(diluted conc to be given mark)

$$x > 4.20 \times 10^{-6} \text{ mol dm}^{-3}$$

[2]

[Total: 10]

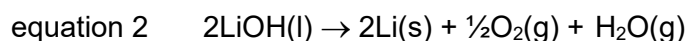
- 3(a) The Haber–Bosch process remains the primary industrial route to synthesise ammonia. It involves the breaking of the triple bond in molecular nitrogen at high pressures and temperatures and the hydrogen gas it requires to turn nitrogen to ammonia comes mainly from natural gas.



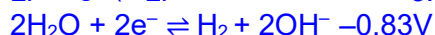
This process however is responsible for up to 3% of global CO₂ emissions.

The electrochemical lithium cycling process to make ammonia is a more sustainable approach. It is reported to have achieved an efficiency of 88.5% in lab-scale tests. The process uses electricity, which can have a renewable source, such as wind or solar energy.

In the first stage, the electrolysis of molten lithium hydroxide produces molten lithium metal at the cathode. Oxygen and steam are formed at the anode.

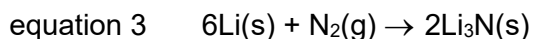


- (i) Using data from the *Data Booklet*, explain why an aqueous solution of LiOH cannot be used to produce lithium metal by electrolysis.



Based on the reduction potential values in the data booklet, since E^\ominus ($\text{H}_2\text{O}/\text{H}_2$) of water is more positive, water will be preferentially reduced (to H_2 and OH^-) as compared to Li^+ to Li. [1] [1]

The next stage in the process involves gently heating the lithium metal in a stream of nitrogen to produce lithium nitride.



- (ii) Define, with the aid of an equation, lattice energy of lithium nitride.

Lattice energy is the energy change/evolved when one mole of Li_3N ionic compound is formed from gaseous Li^+ and N^{3-} ions at standard conditions. [1]

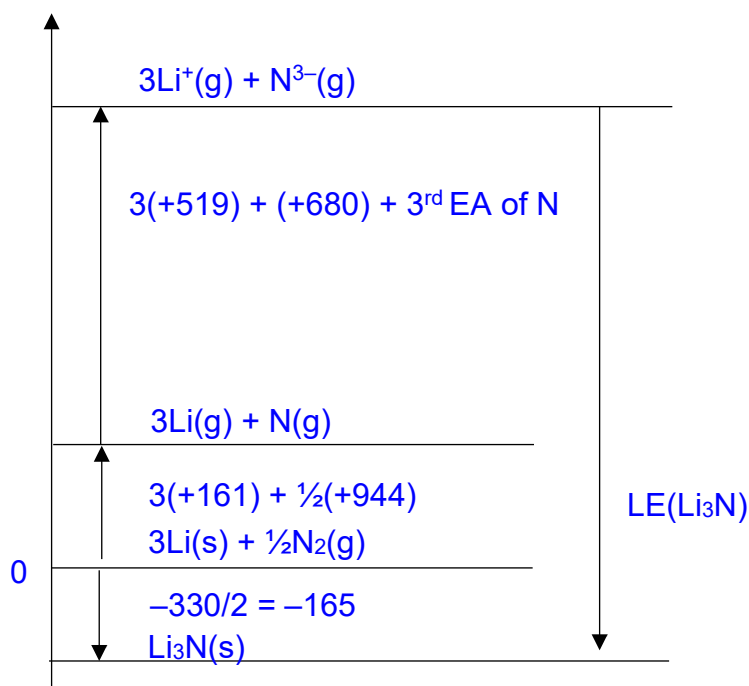


- (iii) Using the data in Table 4.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the third electron affinity of nitrogen. Show your working clearly.

Table 4.1

	value / kJ mol^{-1}
sum of 1 st and 2 nd electron affinity of N	+680
lattice energy of Li_3N	-4830
enthalpy change of sublimation of Li: $\text{Li}(\text{s}) \rightarrow \text{Li}(\text{g})$	+161
enthalpy change of reaction for the following reaction: $6\text{Li}(\text{s}) + \text{N}_2(\text{g}) \rightarrow 2\text{Li}_3\text{N}(\text{s})$	-330

energy / kJ mol^{-1}

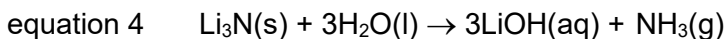


All 4 correct levels – [2]; 2,3 correct levels points – [1]

$$-165 = 3(+161) + \frac{1}{2}(+944) + 3(+519) + (+680) + 3^{\text{rd}} \text{ EA of N} + (-4830)$$

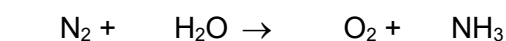
$$3^{\text{rd}} \text{ EA of N} = +1473 = +1470 \text{ kJ mol}^{-1} \quad [1] \quad [3]$$

The last stage in the process involves reacting lithium nitride with water. A solution containing ammonia and lithium hydroxide is produced.

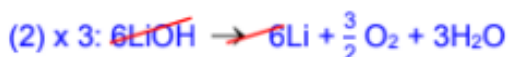


The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(iv) The following equation represents the overall equation for electrochemical lithium cycling process.



Complete the balancing of the above equation. Show your working clearly.



[1]

The standard Gibbs free energy changes of formation, ΔG_f^\ominus , of several compounds are listed in Table 4.2.

Table 4.2

compound	$\Delta G_f^\ominus / \text{kJ mol}$
LiOH(s)	-439
Li ₃ N(s)	-137
H ₂ O(l)	-237
NH ₃ (g)	-17

(v) Using your equation in a(iv), calculate the standard Gibbs free energy change, ΔG^\ominus , when 2 mol of ammonia are produced.

$$\Delta G^\ominus = \Delta G_f^\ominus(\text{products}) - \Delta G_f^\ominus(\text{reactants})$$

$$\Delta G_f^\ominus \text{ for elements} = 0$$

$$\Delta G^\ominus \text{ for the production of 2 mol NH}_3 = -17(2) - (-237)(3) = +677 \text{ kJ mol}^{-1} \quad [1]$$

[1]

- (vi) Calculate the standard Gibbs free energy change, ΔG^\ominus , for the Haber-Bosch process shown in equation 1. By considering the stability of the reactants and products, explain why this value is different from that calculated in a(v).

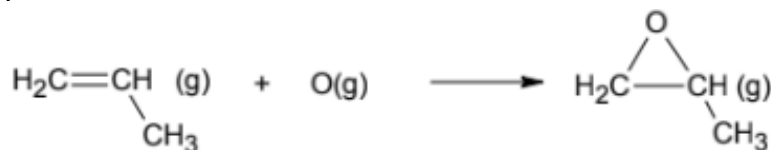
$$\Delta G^\ominus \text{ for equation 1} = -17(2) = -34 \text{ kJ mol}^{-1} \text{ [1]}$$

Based on the ΔG^\ominus data given, H_2 is thermodynamically much more stable than NH_3 as compared to their respective reactants. The overall equation derived in a(iv) involved the formation of NH_3 from H_2O and it is thus highly unfavourable ($\Delta G^\ominus > 0$). For equation 1, it simply involves the formation of NH_3 from its elements ($\Delta G^\ominus < 0$). [1]

[2]

- (b) An epoxide is a cyclic ether (C–O–C) that is highly reactive. Like all compounds containing a 3-membered ring, the bonds in 1,2-epoxypropane are weaker. This can be illustrated by the following calculation, in which you can assume that the C–H bond energy is the same in propane and 1,2-epoxypropane.

The ΔH^\ominus for the reaction between propene molecules and oxygen atoms has been calculated to be -363 kJ mol^{-1} .



- (i) Use the data from the *Data Booklet* to calculate a theoretical value for the sum of the C–C and $2 \times$ C–O bond energies in 1,2-epoxypropane.

From the *Data Booklet*,

$$\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O}) = 350 + 2 \times 360 = +1070 \text{ kJ mol}^{-1} \text{ [1]}$$

[1]

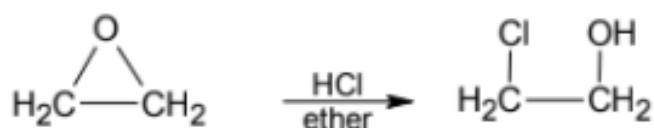
- (ii) Use the ΔH^\ominus value for the reaction between propene and oxygen atoms given above to calculate the actual value for the sum of the C–C and $2 \times$ C–O bond energies in 1,2-epoxypropane. Suggest an explanation for the difference between the theoretical and actual values.

$$\begin{aligned} \Delta H_r^\ominus &= \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed}) \\ -363 &= \text{BE}(\text{C}=\text{C}) - [\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O})] \\ -363 &= (+610) - [\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O})] \\ -363 &= 610 - [\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O})] \\ \text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O}) &= +973 \text{ kJ mol}^{-1} \text{ [1]} \end{aligned}$$

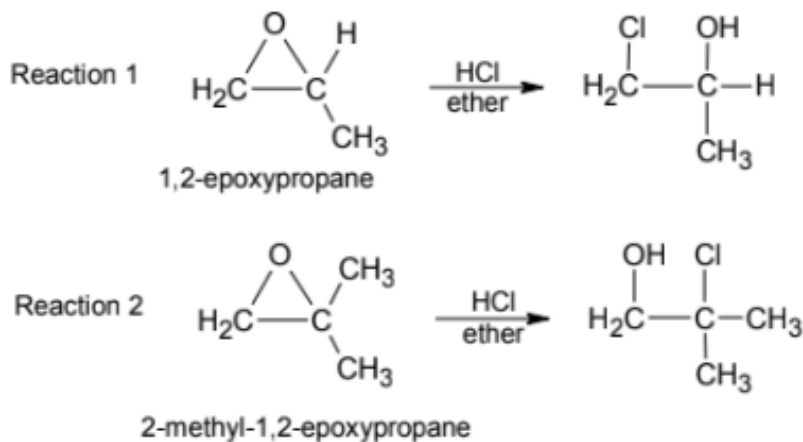
The actual value is less endothermic as the C–O and C–C bonds in the 3-membered ring are weaker due to ring strain/ angle strain (bond angles of 105° and 109° respectively are now 60° in a 3 membered ring). [1]

[2]

- (c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



The ring-opening reaction of epoxides can proceed by either S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane reacts with HCl via different mechanisms to give the following major products.



- (i) Explain why the reaction proceeds via the given predominant mechanism and not the other.

Type of mechanism for reaction 1: S_N2

- S_N2 mechanism is favoured since there is little steric hindrance as the electron deficient (δ^+) carbon ($-\text{O}-\text{CH}_2-$) in 1,2-epoxypropane is attached to only 1 bulky alkyl group. Hence the Cl^- nucleophile can attack the electron deficient (δ^+) carbon readily.
- S_N1 mechanism is not favoured as it will result in the formation of a primary carbocation that is unstable as it has no electron donating groups to disperse the positive charge.

Type of mechanism for reaction 2: S_N1

- S_N1 mechanism is favoured as there are 3 electron donating alkyl groups to the electron deficient carbon in 2-methyl-1,2-epoxypropane that help to disperse the positive charge, hence making it a stable carbocation.
- The 3 bulky alkyl groups on the C atom (C with 2 $-\text{CH}_3$ groups) also cause steric hindrance to the attacking Cl^- nucleophile making it impossible to form the pentavalent transition state in the S_N2 mechanism,

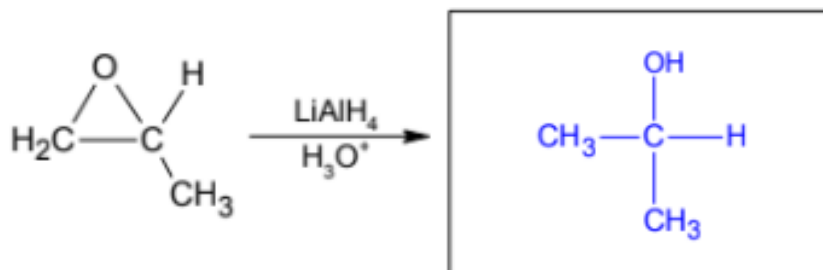
4 points – [3]

3 points – [2]

2 points – [1]

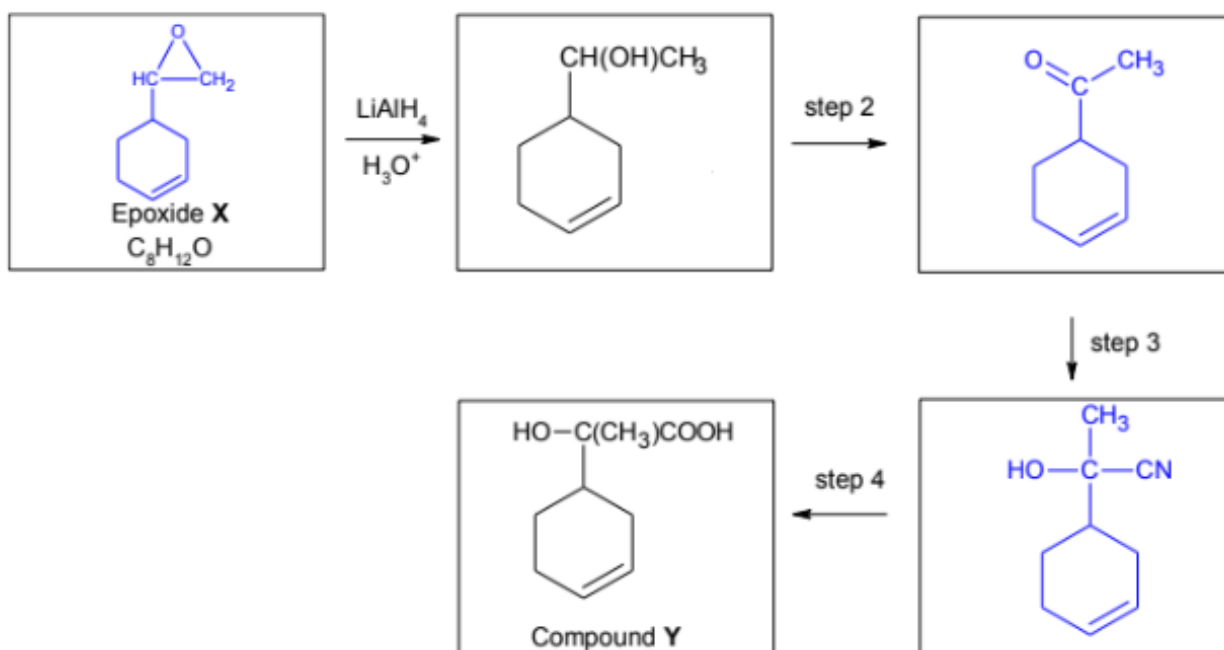
Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides. $\text{S}_{\text{N}}2$ mechanism usually predominates with these reagents.

- (ii) Draw the structural formula of the major product formed when 1,2-epoxypropane reacts with LiAlH_4 .



[1]

- (iii) Compound **Y** can be formed via a four-step synthesis with epoxide **X** as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step.



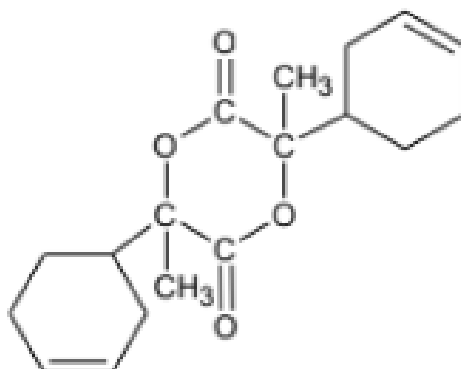
step 2: $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat under reflux [1]

step 3: HCN , traces amount of NaCN , $10 - 20^\circ\text{C}$ [1]

step 4: dilute H_2SO_4 , heat under reflux [1]

[6]

- (iv) A small amount of a sweet-smelling side product, $C_{18}H_{24}O_4$, is formed in step 4. Draw the structure of this side product.



[1]

[Total: 24]