

Kekulé suggested this structure for benzene.

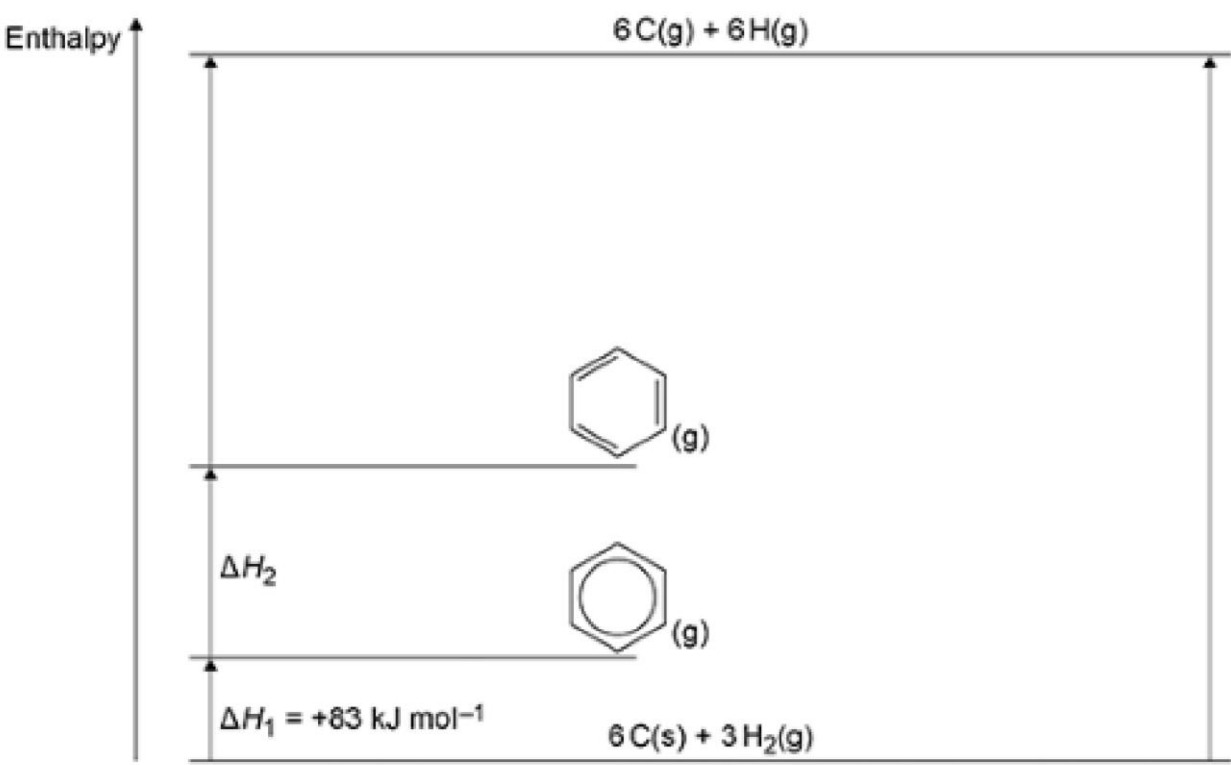


Benzene is now represented by this structure.



Figure 1 shows the relative stability of c1ccccc1 compared to C1=CC=CC=C1.

Figure 1





(a) Use Figure 1 and the data shown in the table below to calculate ΔH_2

	$\Delta H / \text{kJ mol}^{-1}$
Enthalpy of atomisation for carbon	+715
Enthalpy of atomisation for hydrogen	+218
Bond enthalpy (C–C)	+348
Bond enthalpy (C=C)	+612
Bond enthalpy (C–H)	+412

$$\Delta H_2 \text{ _____ kJ mol}^{-1}$$

(3)

(b) Explain, in terms of structure and bonding, why 

is more thermodynamically stable than 

(1)

(c) A mixture of concentrated nitric acid and concentrated sulfuric acid reacts with benzene.

Figure 2 shows the incomplete mechanism for this reaction.

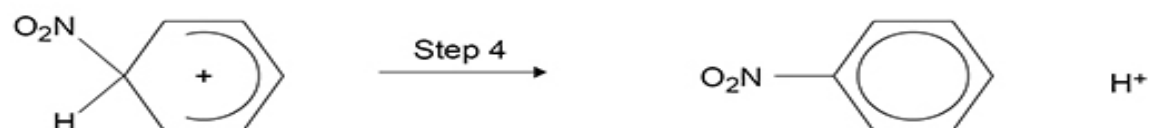
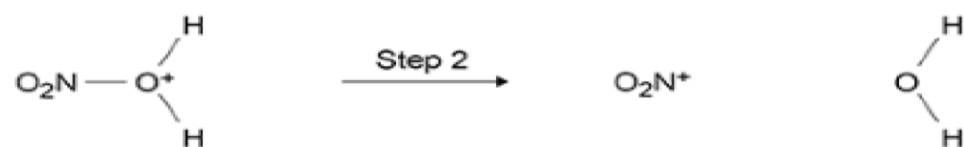
Name the mechanism.

Complete the mechanism in **Figure 2** by adding

- any lone pairs of electrons involved in each step
- **two** curly arrows in step 1
- a curly arrow in step 2
- a curly arrow in step 3
- a curly arrow in step 4.

Name of mechanism _____

Figure 2



(5)

(a) $(3 \times 612) + (3 \times 348) + (6 \times 412) = 5352$

For LHS

M1

$(6 \times 715) + (6 \times 218) = 5598$

For RHS

M2

$\Delta H_2 = M2 - M1 - 83 = +163 \text{ kJ mol}^{-1}$

M3

(b) (π) electrons delocalised

1

(c) M1 Electrophilic substitution

1

M2 for a lone pair and two curly arrows



1

M3 for a curly arrow from the bond to the O



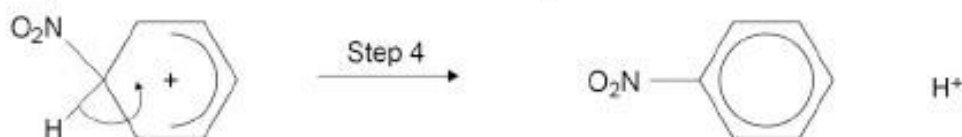
1

M4 for a curly arrow from inside the hexagon to the N or + on the N



1

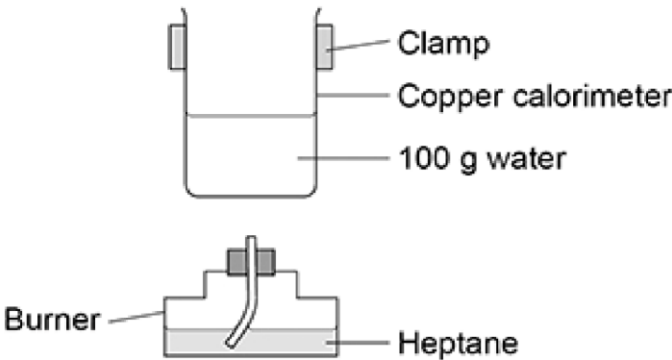
M5 curly arrow from the bond back into the hexagon



1

A student does an experiment to determine a value for the enthalpy of combustion of heptane.

The figure below shows some of the apparatus used.



- (a) Design a table to record all the readings necessary to determine an experimental value for the enthalpy of combustion for heptane in this experiment.

(2)

- (b) The student considered using a glass beaker on a tripod and gauze instead of the clamped copper calorimeter.

Suggest **two** disadvantages of using a glass beaker on a tripod and gauze.

Disadvantage 1 _____

Disadvantage 2 _____

(2)

- (c) Suggest **two** reasons why the value of enthalpy of combustion from this experiment is less exothermic than a data book value.

Reason 1 _____

Reason 2 _____

- (d) Suggest **one** addition to this apparatus that would improve the accuracy of the enthalpy value obtained.

(1)

(a)

	Temp/ °C		Mass /g
Initial		Burner before	
Final		Burner after	
(ΔT)		(Mass heptane burned)	

M1 for Temperature data including units

M2 for Burner mass data including units If either unit missing MAX 1

M1
M2

- (b) Any two from:

Glass is a poorer conductor than copper

M1

Tripod and gauze would reduce heat transfer

Tripod and gauze would have a fixed height above the flame

Heat capacity of metal is less than glass or vice versa

M2

- (c) Heat loss to surroundings or to copper/calorimeter

M1

Incomplete combustion

M2

- (d) Use a wind shield (to reduce heat loss)

Allow use a lid

Insulate the sides of the calorimeter

A value for enthalpy of solution can be determined in two ways:

- from a cycle, using lattice enthalpy and enthalpies of hydration
- from the results of a calorimetry experiment.

(a) Define the term enthalpy of lattice dissociation.

(2)

(b) The enthalpy of solution for ammonium nitrate is the enthalpy change for the reaction shown.

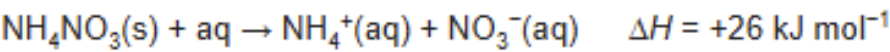


Table 1

	$\text{NH}_4^+(\text{g})$	$\text{NO}_3^-(\text{g})$
Enthalpy of hydration $\Delta_{\text{hyd}}H / \text{kJ mol}^{-1}$	-307	-314

Draw a suitably labelled cycle and use it, with data from Table 1, to calculate the enthalpy of lattice dissociation for ammonium nitrate.

Enthalpy of lattice dissociation _____ kJ mol^{-1}

(3)

- (c) A student does an experiment to determine a value for the enthalpy of solution for ammonium nitrate.

The student uses this method.

- Measure 25.0 cm³ of distilled water in a measuring cylinder.
- Pour the water into a beaker.
- Record the temperature of the water in the beaker.
- Add 4.00 g of solid NH₄NO₃ to the water in the beaker.
- Stir the solution and record the lowest temperature reached.

Table 2 shows the student's results.

Table 2

Initial temperature / °C	20.2
Lowest temperature / °C	12.2

Calculate the enthalpy of solution, in kJ mol⁻¹, for ammonium nitrate in this experiment.

Assume that the specific heat capacity of the solution, $c = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$

Assume that the density of the solution = 1.00 g cm⁻³

Enthalpy of solution _____ kJ mol⁻¹

(3)

- (d) The uncertainty in each of the temperature readings from the thermometer used in this experiment is $\pm 0.1^\circ\text{C}$

Calculate the percentage uncertainty in the temperature change in this experiment.

Percentage uncertainty _____

(1)

- (e) Suggest a change to the student's method, using the same apparatus, that would reduce the percentage uncertainty in the temperature change.

Give a reason for your answer.

Change _____

Reason _____

(2)

- (f) Another student obtained a value of $+15 \text{ kJ mol}^{-1}$ using the same method.

Suggest the main reason for the difference between this experimental value for the enthalpy of solution and the correct value of $+26 \text{ kJ mol}^{-1}$.

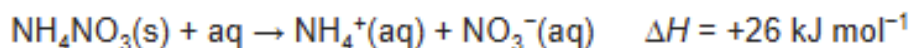
(1)

- (g) Table 3 shows some entropy data at 298 K

Table 3

	Entropy $S / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{NH}_4\text{NO}_3(\text{s})$	151
$\text{NH}_4^+(\text{aq})$	113
$\text{NO}_3^-(\text{aq})$	146

Calculate a value for the Gibbs free-energy change (ΔG), at 298 K, for the reaction when ammonium nitrate dissolves in water.



Use data from Table 3 and the value of ΔH from the equation.

Assume for the solvent, water, that the entropy change, $\Delta S = 0$

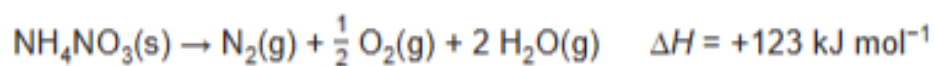
Explain what the calculated value of ΔG indicates about the feasibility of this reaction at 298 K

ΔG _____ kJ mol^{-1}

Explanation _____

(4)

- (h) Ammonium nitrate decomposes as shown.

The entropy change (ΔS) for this reaction is $+144 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculate the temperature at which this reaction becomes feasible.

Temperature _____ K

(2)

(a) The enthalpy change / ΔH when one mole of a (solid) ionic compound

Ignore standard states / conditions

Allow heat change at constant pressure when...

Ignore heat change (alone) / energy change

1

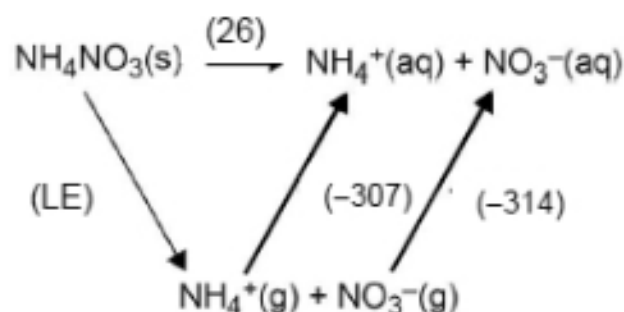
dissociates (fully) into gaseous ions

M2 Allow suitable equation with state symbols for ions

Not one mole of gaseous ions

1

(b)



Allow + water or +aq

M1 = cycle (3 'corners' with formulae and state symbols and suitable arrows)

Allow equivalent Born-Haber style energy cycle

Not ecf to M2 and M3 from incorrect cycle

1

$$\text{LE} = 26 + 307 + 314$$

$$\text{M2} = \text{working e.g. } 26 = \text{LE} - 307 - 314$$

$$= (+)647$$

1

M3 = answer (+)647 gets 3/3 if M1 given or 2/3 if not

-647 = 2/3 if M1 given or 1/3 if not

+595 / -595 = 2/3 if M1 given or 1/3 if not

-621/+621 = 1/3 if M1 given

Not ecf for M3 from incorrect expression in M2

1

- (c) ($q = mc\Delta T =$) $25.0 \times 4.18 \times (20.2 - 12.2)$ OR $25.0 \times 4.18 \times 8$
 (= 836 (J) or 0.836 (kJ))

Not if $m = 29$

Ignore sign of a

1

$$4.00 \text{ g NH}_4\text{NO}_3 = 4.00/80 \text{ OR } 0.0500 \text{ mol}$$

1

$$\Delta H_{\text{soln}}^{\ominus} = 836/0.05 = 16720 = (+)16.7(2) \text{ kJ mol}^{-1}$$

Allow ecf from M1 and/or from M2

$$-16.7(2) = 2/3$$

$$+19.4 = 2/3 \text{ (using } m = 29 \text{ in M1)}$$

$$-19.4 = 1/3$$

$$+2.68 = 2/3$$

$$-2.68 = 1/3$$

$$+587 \text{ or } +588 = 2/3$$

$$-587 \text{ or } -588 = 1/3$$

Allow 2 sig figs or more

1

- (d) $(2 \times 0.1/8) \times 100 = 2.5\%$

Allow ecf from ΔT in (c)

1

- (e) use a larger mass/amount of NH_4NO_3 / solid

Marking points are independent

Allow smaller volume of water / less water

Allow use more NH_4NO_3

Not larger volume of water

Ignore higher concentration (of NH_4NO_3)

Ignore any references to changing apparatus e.g. insulation

1

so temperature change/decrease is greater

OR final temperature is lower

Allow temperature increase is greater

Not final temperature is higherr

1

- (f) heat gain (from the surroundings) / incomplete dissolvingg

Allow incomplete reaction

Allow thermal energy gain

Not heat loss

Ignore energy gain

Ignore references to mistakes in method

1

(g) $\Delta S = (113 + 146) - 151 = +108 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$

1

$$\Delta G = \Delta H - T\Delta S \text{ OR } 26 - (298 \times 108 \times 10^{-3})$$

Allow ecf $26 - (298 \times M1 \times 10^{-3})$

Allow ecf $26 - (298 \times M1)$

Allow M2 for $26000 - (298 \times 108)$

Allow M2 for $26 - (298 \times 108)$

1

$$\Delta G = -6.184 / -6.18 / -6.2$$

$-32158 = M1 \text{ and } M2$

$-32.2 = M1 \text{ and } M2$

$-6184 = M1 \text{ and } M2$

$(+)58.2 = M2 \text{ and } M3 \text{ (ecf if } -108 \text{ for } M1)$

1

negative value for ΔG indicates reaction is feasible/spontaneous

Allow positive value for ΔG indicates reaction is NOT feasible/spontaneous

Allow < 0 or > 0 as appropriate

M4 is standalone

1

(h) Converting ΔH into J OR ΔS into kJ

1

$$(T = \Delta H / \Delta S = 123 / 144 \times 10^{-3} \text{ OR } 123000 / 144) = 854(.1666666) \text{ (K)}$$

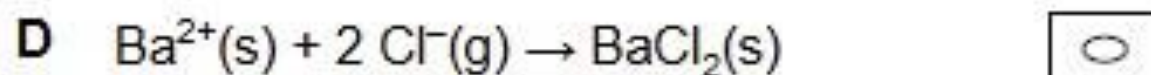
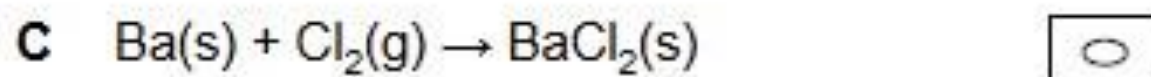
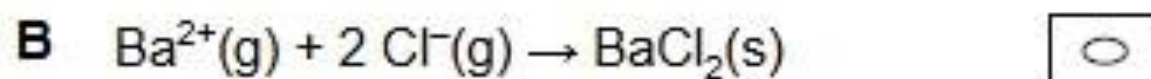
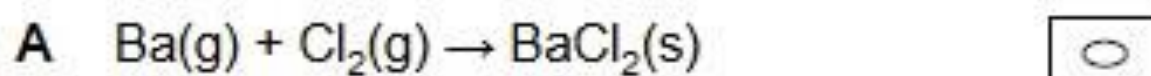
$0.854 \text{ (K)} = 1/2$

$0.00117 \text{ (K)} = 1/2 \text{ (calculation upside down)}$

2SF minimum

1

Which reaction has a standard enthalpy change equal to the standard enthalpy of formation for barium chloride?



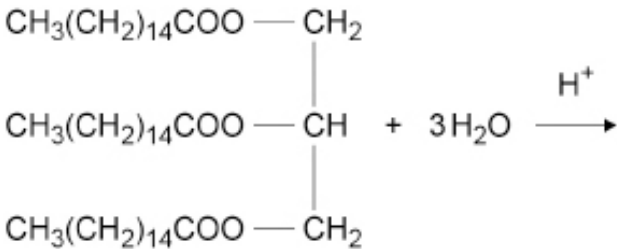
C



This question is about biofuels.

Palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$, can be made by hydrolysis of the triester in palm oil under acidic conditions.
Palmitic acid can be used as a biofuel.

(a) Complete the equation for the hydrolysis of the triester in palm oil under acidic conditions.



(2)

(b) Palmitic acid burns in air.

In a calorimetry experiment, combustion of 387 mg of palmitic acid increases the temperature of 0.150 kg of water from 23.9 °C to 37.5 °C

Calculate a value, in kJ mol^{-1} , for the enthalpy of combustion of palmitic acid in this experiment.
Give your answer to the appropriate number of significant figures.

The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$

Enthalpy of combustion _____ kJ mol^{-1}

(5)

- (c) State how the value calculated in part (b) is likely to differ from data book values.

Give one reason, other than heat loss, for this difference.

Difference _____

Reason _____

(2)

- (d) A sample of a different biofuel, made from sewage sludge, is found to contain 37.08% carbon, 5.15% hydrogen and 24.72% oxygen by mass.
The rest of the sample is sulfur.

Calculate the empirical formula of this biofuel.

Empirical formula _____

(3)

- (e) Complete combustion of the biofuel made from sewage sludge produces the greenhouse gas carbon dioxide.

Suggest **one** other possible environmental problem with the complete combustion of this biofuel.

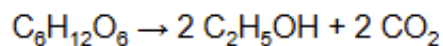
State the formula of the pollutant responsible for this problem.

Environmental problem _____

Formula _____

(2)

- (f) Ethanol is a biofuel that can be produced by the fermentation of glucose.



Glucose has the structural formula shown.

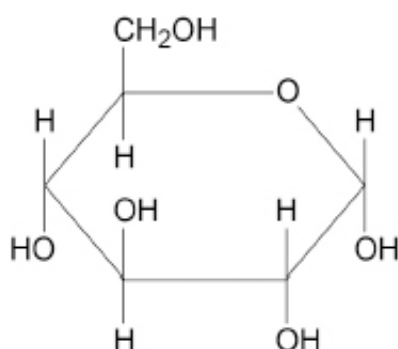


Table 1 shows some mean bond enthalpy values.

Table 1

	C-H	C-C	C-O	C=O	O-H
Mean bond enthalpy / kJ mol ⁻¹	412	348	360	805	463

Use the equation and the data in **Table 1** to calculate an approximate value of ΔH for the fermentation of glucose. For this calculation you should assume that all the substances are in the gaseous state.

$$\Delta H \text{ _____ kJ mol}^{-1}$$

(3)

- (g) The carbon dioxide produced from fermentation can be reacted with steam to make more ethanol.

The equation for this reaction is

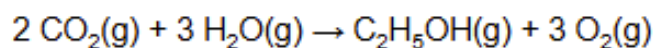


Table 2 shows some standard enthalpies of formation.

Table 2

	$\text{CO}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-394	0	-235	-242

Use the data in **Table 2** to calculate a standard enthalpy change value for this reaction.

$$\text{Standard enthalpy change _____ kJ mol}^{-1}$$

(2)

(a) M1 $3 \text{ CH}_3(\text{CH}_2)_{14}\text{COOH}$

M2 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$

Penalise additional product(s) once

2

(b) M1 $M_r = 256$

M2 $n(\text{CH}_3(\text{CH}_2)_{14}\text{COOH}) = \frac{0.387}{M1} = 1.51 \times 10^{-3}$

M3 $Q = 150 \times 4.18 \times 13.6 = 8527.2 \text{ (J)}$

M4 $\Delta H = \frac{M3}{M2} \div 1000 = (-)5641$

M5 $\Delta H = -5640 \text{ kJ mol}^{-1}$

Must be negative and 3sf (allow ecf on M4)

5

(c) M1 Less exothermic

Allow Less negative (value) / Lower

M2 Incomplete combustion

Allow products of incomplete combustion

2

(d)

		C	H	O	S
		37.08	5.15	24.72	M1 = 33.05
M2	$\div A_r$	= 3.09	= 5.15	= 1.55	= 1.030
	\div smallest	= 3	= 5	= 1.50	= 1
M3	Empirical formula = $\text{C}_6\text{H}_{10}\text{O}_3\text{S}_2$				

M1 % S = 33.05

M2 Calculation of moles

M3 Ratio of moles AND Empirical Formula

If no Sulfur used ecf for M2 and M3

M2 3.09 : 5.15 : 1.55

M3 $\text{C}_6\text{H}_{10}\text{O}_3$

3

(e) M1 Acid rain

Allow smog

M2 SO_2

Allow NO_x

2

(f) M1 Bonds broken = 9459 kJ mol^{-1}

(5C-C + 7C-O + 7C-H + 5O-H)

Allow if they cancel the common bonds

M1 4233

M2 Bonds formed = 9682 kJ mol^{-1}

(2C-C + 10C-H + 2C-O + 2O-H + 4C=O)

M2 4456

M3 $\Delta H = M1 - M2 = -223 \text{ kJ mol}^{-1}$

M3 can be awarded as ecf from their M1 and M2

3

(g) M1 $\Delta H = -235 - (2 \times -394) - (3 \times -242)$

M2 = $+1279 \text{ kJ mol}^{-1}$

If no sign assume positive

2
