For Examiner's Use

3 Alkanes such as methane, CH_4, undergo few chemical reactions. Methane will, however, react with chlorine but not with iodine.

Relevant standard enthalpy changes of formation for the reaction of methane with chlorine to form chloromethane, CH_3Cl, are given below.

	$\Delta H_f^{\ominus}$/kJ mol^{-1}
CH_4	–75
CH_3Cl	–82
HCl	–92

(a) **(i)** Use the data to calculate $\Delta H^{\ominus}_{reaction}$ for the formation of CH_3Cl.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

(ii) The corresponding reaction with iodine does **not** take place.

Use bond energy data from the *Data Booklet* to calculate a 'theoretical value' for $\Delta H_{reaction}$ for the following equation.

$$CH_4 + I_2 \rightarrow CH_3I + HI$$

(iii) Suggest why this reaction does **not** in fact occur.

....

....

[5]

3 **(a)** **(i)**

	CH_4	+	Cl_2	→	CH_3Cl	+	HCl	
$\Delta H^{\ominus}_f$	–75		0		–82		–92	(1)

$\Delta H^{\ominus}_{reaction}$ = –82 + (–92) – (–75)
= –99 kJ mol^{-1} (1)

(ii)

	CH_4	+	I_2	→	CH_3I	+	HI	
broken	C–H		I–I	made	C–I		H–I	
	410		151		240		299	(1)

$\Delta H^{\ominus}_{reaction}$ = –240 + (–299) + 410 + 151
= +22 kJ mol^{-1} (1)

(iii) activation energy is too great (1) [5]

(b) **(i)** initiation (1)

Cl_2 + uvl → 2Cl (1)

propagation (1)

CH_4 + Cl → CH_3 + HCl

CH_3 + Cl_2 → CH_3Cl + Cl both needed (1)

termination (1)

CH_3 + CH_3 → C_2H_6 **or**

CH_3 + Cl → CH_3Cl **or**

Cl + Cl → Cl_2 (1)

(ii) CH_3/methyl radical (1) [7]

Answer **all** the questions in the spaces provided.

For Examiner's Use

1 Hydrazine, N_2H_4, can be used as a rocket fuel and is stored as a liquid. It reacts exothermically with oxygen to give only gaseous products.

The enthalpy change of a reaction such as that between hydrazine and oxygen may be calculated by using standard enthalpy changes of formation.

(a) Define the term *standard enthalpy change of formation*, $\Delta H_f^{\ominus}$.

....

....

.... [3]

(b) Hydrazine reacts with oxygen according to the following equation.

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

(i) Use the data in the table to calculate the standard enthalpy change of this reaction.

compound	$\Delta H_f^{\ominus}$/kJ mol^{-1}
$N_2H_4(l)$	50.6
$H_2O(g)$	–241.8

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

(ii) Although the above reaction is highly exothermic, hydrazine does not burn spontaneously in oxygen.
Suggest a reason for this.

....

....

1 **(a)** enthalpy change when 1 mol of a compound is formed (1)
from its elements (1)
in their standard states under standard conditions (1) [3]

(b) **(i)** $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$

ΔH_f^o/kJ mol ^{1} +50.6 –241.8

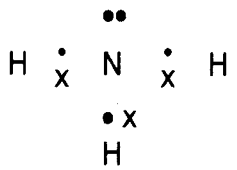
$\Delta H^o_{reaction}$ = 2(–241.8) – (+50.6) (1)

= –534.2 kJ mol ^{1} (1)

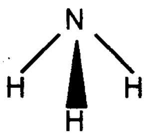
(ii) E_a is too high (1)

(iii) products are H_2O and N_2 which are harmless/non toxic
or are already present in the atmosphere (1) [4]

(c) **(i)** 'dot-and-cross' diagram (1)

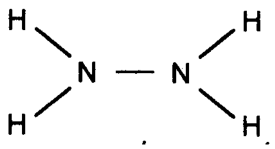


(ii)



(1)

(iii) minimum is



allow bond angle around N atom between 109° and 104° (1) [4]

(d) –2 (1) [1]

[Total: 12]

For Examiner's Use

(d) The standard enthalpy change of combustion of C_2H_2, $\Delta H^{\ominus}_{c}$, is –1300 kJ mol^{-1} at 298 K.

Values of relevant standard enthalpy changes of formation, $\Delta H^{\ominus}_{f}$, measured at 298 K, are given in the table.

substance	$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}
CO_2(g)	–394
H_2O(l)	–286

(i) Write balanced equations, with state symbols, that represent

the standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$, of C_2H_2, and

....

the standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$, of C_2H_2.

....

(ii) Use the data above and your answer to **(i)** to calculate the standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$, of C_2H_2.
Show clearly whether the standard enthalpy change of formation of C_2H_2 has a positive or negative value.

[6]

[Total: 16]

5 (a) $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ (1) [1]

(b) (i) step 1 electrophilic (1)
addition (1)
step 2 elimination **or** dehydrohalogenation (1)

(ii) reagent NaOH/KOH/OH (1)
conditions in alcohol/ethanol (1)
only allow conditions mark if reagent is correct [5]

(c) (i) **Q** is CH_3CHO (as minimum) (1)
R is CH_3CO_2H (as minimum) (1)

(ii) step 3 is addition (1)
step 4 is oxidation/redox (1) [4]

(d) (i) **combustion**
$C_2H_2(g) + {}^{5}/_{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ **or**
equation must be for the combustion of one mole of C_2H_2
H_2O must be shown as liquid (1)
correct state symbols in this equation (1)

formation
$2C(s) + H_2(g) \rightarrow C_2H_2(g)$
no mark for state symbols here (1)

(ii) let **Z** be $\Delta H^{\ominus}_f$ of C_2H_2

	C_2H_2 +	${}^{5}/_{2}O_2 \rightarrow$	$2CO_2$ +	H_2O
$\Delta H^{\ominus}_f$	**Z**	0	2(-394)	-286

$\Delta H^{\ominus}_c$ = -1300 = 2(-394) + (-286) – **Z** (1)

whence **Z** = 2(-394) + (-286) – (-1300)

= **+**226 kJ mol[1]
value (1)
sign (1)
allow ecf on wrong equation [6]

[Total: 16]

For Examiner's Use

3 Methanol, CH_3OH, is considered to be a possible alternative to fossil fuels, particularly for use in vehicles.

Methanol can be produced from fossil fuels and from agricultural waste. It can also be synthesised from carbon dioxide and hydrogen.

(a) Define, with the aid of an equation which includes state symbols, the standard enthalpy change of formation of carbon dioxide.

equation ....

definition ....

....

.... [3]

(b) Relevant $\Delta H_f^{\ominus}$ values for the reaction that synthesises methanol are given in the table.

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CO_2(g)$	–394
$CH_3OH(g)$	–201
$H_2O(g)$	–242

(i) Use these values to calculate $\Delta H^{\ominus}_{reaction}$ for this synthesis of methanol.

Include a sign in your answer.

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

$\Delta H^{\ominus}_{reaction}$ = ...kJ mol^{-1}

(ii) Suggest **one** possible environmental advantage of this reaction. Explain your answer.

....

....

[5]

3 **(a)** $C(s) + O_2(g) \rightarrow CO_2(g)$ (1)
the enthalpy change/energy change/heat change when
one mole of a compound/CO_2 (1)
is formed from its elements in their standard states (1) [3]

(b) **(i)**

	$CO_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$	+	$H_2O(g)$
$\Delta H^{\ominus}_f$/kJ mol $^{-1}$	–394		0		–201		–242

$\Delta H^{\ominus}_{reaction}$ = –201 + (–242) – (–394) (1)
–49 kJ mol $^{-1}$ (1)
correct sign (1)

(ii) removal of CO_2 from the atmosphere (1)
CO_2 is a greenhouse gas/causes global warming (1) [5]

(c) In this part, in each case, the 'effect' must be correctly stated in order to gain the explanation mark.

higher temperature
yield is reduced/equilibrium goes to LHS (1)
because forward reaction is exothermic/reverse reaction is endothermic (1)

higher pressure
yield is increased **or** equilibrium goes to RHS (1)
fewer moles/molecules on RHS **or** more moles/molecules on LHS (1)

use of catalyst
yield does not change (1)
forward and backward rates speeded up by same amount (1) [6]

[Total: 14]

For Examiner's Use

3 For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

....

....

.... [2]

In order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1

30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C.
When 0.0200 mol of potassium carbonate, K_2CO_3, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) **(i)** Construct a balanced equation for this reaction.

....

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.
Use relevant data from the *Data Booklet* and assume that all solutions have the same specific heat capacity as water.

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of K_2CO_3.
Give your answer in kJ mol^{-1} and include a sign in your answer.

(iv) Explain why the hydrochloric acid must be in an excess.

....

.... [4]

For Examiner's Use

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, $KHCO_3$.
All other conditions were the same.
In the second experiment, the temperature fell from 21.0 °C to 17.3 °C.

(c) **(i)** Construct a balanced equation for this reaction.

....

(ii) Calculate the quantity of heat absorbed in **experiment 2**.

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of $KHCO_3$.
Give your answer in kJ mol^{-1} and include a sign in your answer.

[3]

(d) When $KHCO_3$ is heated, it decomposes into K_2CO_3, CO_2 and H_2O.

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

Use Hess' Law and your answers to **(b)(iii)** and **(c)(iii)** to calculate the enthalpy change for this reaction.
Give your answer in kJ mol^{-1} and include a sign in your answer.

[2]

[Total: 11]

3 **(a)** the overall enthalpy change/energy change/ΔH for a reaction (1)

is independent of the route taken **or**
is independent of the number of steps involved
provided the initial and final conditions are the same (1) [2]

(b) **(i)** $K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2$ (1)

(ii) heat produced $= m \times c \times \delta T = 30.0 \times 4.18 \times 5.2$
$= 652.08$ J per 0.0200 mol of K_2CO_3 (1)

(iii) 0.020 mol $K_2CO_3 \equiv 652.08$ J

1 mol $K_2CO_3 \equiv \dfrac{652.08 \times 1}{0.0200} = 32604$ J

enthalpy change = –32.60 kJmol ^{1} (1)

(iv) to prevent the formation of $KHCO_3$ **or**
to ensure complete neutralisation (1) [4]

(c) **(i)** $KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2$ (1)

(ii) heat absorbed $= m \times c \times \delta T = 30.0 \times 4.18 \times 3.7$
$= 463.98$ J per 0.0200 mol of $KHCO_3$ (1)

(iii) 0.020 mol $KHCO_3 \equiv 463.98$ J

1 mol $KHCO_3 \equiv \dfrac{463.98 \times 1}{0.0200} = 23199$ J

enthalpy change = +23.20 kJmol ^{1} (1) [3]

(d) $\Delta H = 2 \times (+23.20) - (-32.60) = +79.00$ kJ mol ^{1} (2) [2]

[Total: 11]

For Examiner's Use

Answer **all** the questions in the spaces provided.

1 Carbon disulfide, CS_2, is a volatile, flammable liquid which is produced in small quantities in volcanoes.

(a) The sequence of atoms in the CS_2 molecule is sulfur to carbon to sulfur.

(i) Draw a 'dot-and-cross' diagram of the carbon disulfide molecule.
Show outer electrons only.

(ii) Suggest the shape of the molecule and state the bond angle.

shape ....

bond angle ....
[3]

(b) Carbon disulfide is readily combusted to give CO_2 and SO_2.

(i) Construct a balanced equation for the complete combustion of CS_2.

....

(ii) Define the term *standard enthalpy change of combustion*, $\Delta H^{\ominus}_{c}$.

....

....

....
[3]

For Examiner's Use

(c) Calculate the standard enthalpy change of formation of CS_2 from the following data. Include a sign in your answer.

standard enthalpy change of combustion of CS_2 = –1110 kJ mol^{-1}

standard enthalpy change of formation of CO_2 = –395 kJ mol^{-1}

standard enthalpy change of formation of SO_2 = –298 kJ mol^{-1}

[3]

(d) Carbon disulfide reacts with nitrogen monoxide, NO, in a 1:2 molar ratio.
A yellow solid and two colorless gases are produced.

(i) Construct a balanced equation for the reaction.

....

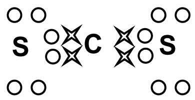
(ii) What is the change in the oxidation number of sulfur in this reaction?

from .... to ....

[3]

[Total: 12]

1 (a) (i)



S atom has 6 **and C** atom has 4 electrons (1)

S=C double bonds (4 electrons) clearly shown (1)

(ii) linear **and** 180° (1) [3]

(b) (i) $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ (1)

(ii) enthalpy change when 1 mol of a substance (1)

is burnt in an excess of oxygen/air

or is completely combusted

under standard conditions (1) [3]

(c)

	CS_2	+	$3O_2$	→	CO_2	+	$2SO_2$	
$\Delta H_f^{\ominus}$/kJ mol^{1}	x				–395		2(–298)	(1)

$\Delta H_{reaction}$ = –395 + 2(–298) – x = –1110 kJ mol^{1} (1)

gives x = –395 + (–596) + 1110 = +119 kJ mol^{1} (1) [3]

(d) (i) $CS_2 + 2NO \rightarrow CO_2 + 2S + N_2$

or

$CS_2 + 2NO \rightarrow CO + 2S + N_2O$

correct products (1)

correct equation (1)

(ii) from –2 to 0 **both** required (1) [3]

[Total: 12]