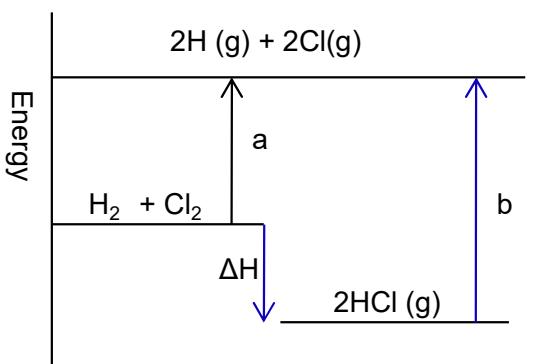


## 3.12 Hess's Law

Hess's law states that total **enthalpy change** for a reaction is **independent of the route** by which the chemical change takes place

Hess's law is a version of the first law of thermodynamics, which is that energy is always conserved.



On an energy level diagram the directions of the arrows can show the different routes a reaction can proceed by

The two routes must have the same starting point and the same end point

In this example one route is arrow 'a'

The second route is shown by arrows  $\Delta H$  plus arrow 'b'

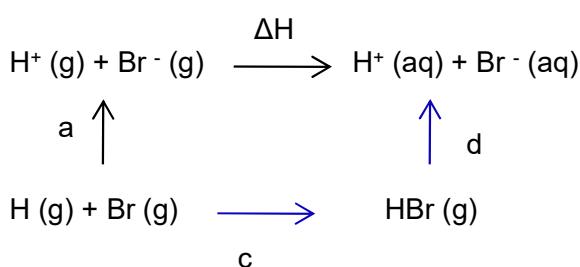
So by applying Hess's law

$$a = \Delta H + b$$

And rearranged

$$\Delta H = a - b$$

Interconnecting reactions can also be shown diagrammatically.



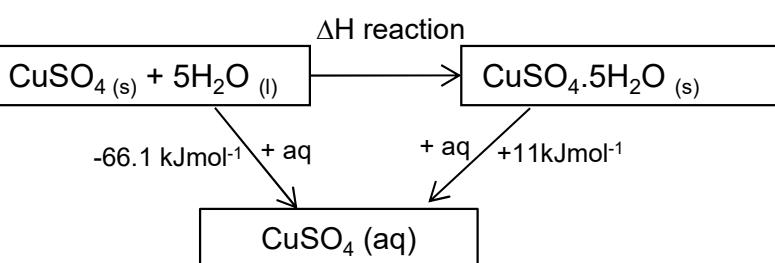
In this example one route is arrow 'a' plus  $\Delta H$   
The second route is shown by arrows 'c' plus arrow 'd'

So  $a + \Delta H = c + d$

And rearranged

$$\Delta H = c + d - a$$

Often Hess's law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.



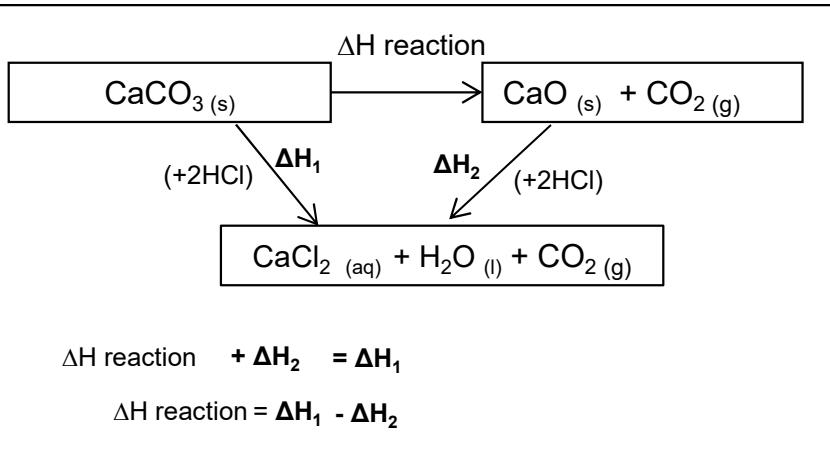
$$\Delta H \text{ reaction} + 11 \text{ kJmol}^{-1} = -66.1 \text{ kJmol}^{-1}$$

$$\begin{aligned} \Delta H \text{ reaction} &= -66.1 - 11 \\ &= -77.1 \text{ kJmol}^{-1} \end{aligned}$$

This Hess's law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

This cannot be done experimentally because it is impossible to add the exact amount of water to hydrate the copper salt and it is not easy to measure the temperature change of a solid turning into another solid.

Instead both salts are dissolved in excess water to form a solution of copper sulfate. The temperature changes can be measured for these alternative reactions and by using Hess's law the  $\Delta H$  for the original reaction can be calculated.



This Hess's law is used to work out the enthalpy change for the thermal decomposition of calcium carbonate.

This cannot be done experimentally because it is impossible to add the exact energy required to decompose the solid and to measure the temperature change of a solid at the same time.

Instead both calcium carbonate and calcium oxide are reacted with hydrochloric acid to form a solution of calcium chloride. The temperature changes can be measured for these reactions.

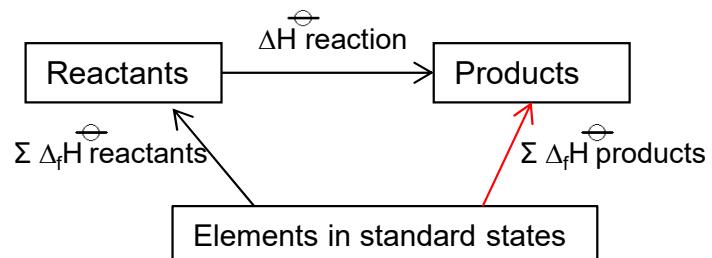
### Using Hess's law to determine enthalpy changes from enthalpy changes of formation.

This is a very common Hess's law cycle using standard enthalpies of formation to work out the enthalpy change for any chemical reaction.

Looking at the cycle on the right we can see the two routes shown with the different coloured arrows, therefore the equation is

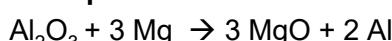
$$\sum \Delta_f H \text{ reactants} + \Delta H \text{ reaction} = \sum \Delta_f H \text{ products}$$

As this cycle is always the same we can just use the equation below in questions.



Standard enthalpies of formation can be looked up in data books for all compounds

### Example 1 Calculate the enthalpy change for this reaction.



$$\begin{aligned} \Delta_f H(\text{MgO}) &= -601.7 \text{ kJ mol}^{-1} \\ \Delta_f H(\text{Al}_2\text{O}_3) &= -1675.7 \text{ kJ mol}^{-1} \end{aligned}$$

Remember elements have  $\Delta_f H = 0$

$$\Delta H = \sum \Delta_f H \text{ products} - \sum \Delta_f H \text{ reactants}$$

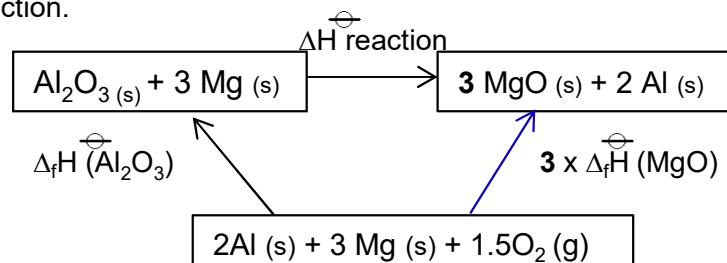
$$\Delta H = 3 \times \Delta_f H(\text{MgO}) - \Delta_f H(\text{Al}_2\text{O}_3)$$

$$\Delta H = (3 \times -601.7) - -1675.7$$

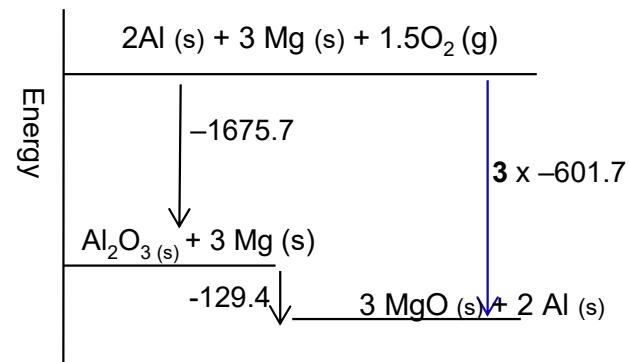
$$= -129.4 \text{ kJ mol}^{-1}$$

Note because there are 3 MgO in balanced equation then we multiply the  $\Delta_f H_f(\text{MgO})$  by 3

The calculation can also be shown diagrammatically using an energy level diagram,

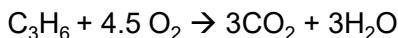


By application of Hess's Law  
 $\Delta_f H(\text{Al}_2\text{O}_3) + \Delta H \text{ reaction} = 3 \times \Delta_f H(\text{MgO})$



**Example 2.** Use the following data to calculate the enthalpy of combustion of propene.

$$\Delta_f H^\ominus C_3H_6(g) = +20 \text{ kJ mol}^{-1} \quad \Delta_f H^\ominus CO_2(g) = -394 \text{ kJ mol}^{-1} \quad \Delta_f H^\ominus H_2O(g) = -242 \text{ kJ mol}^{-1}$$



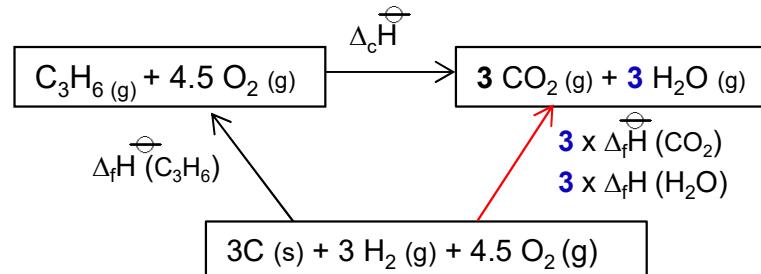
This question is identical to example 1 in how to approach it. The only difference is the enthalpy change of reaction has been defined as an enthalpy of combustion. Many students get confused because they see the words enthalpy of combustion and enthalpy of formation in the same question and do not know what cycle to use. Draw it out to check.

$$\Delta_c H = \sum \Delta_f H^\ominus \text{products} - \sum \Delta_f H^\ominus \text{reactants}$$

$$\Delta_c H = [3 \times \Delta_f H^\ominus (CO_2) + 3 \times \Delta_f H^\ominus (H_2O)] - \Delta_f H^\ominus (C_3H_6)$$

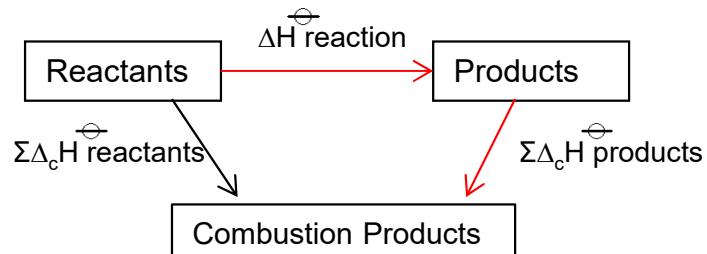
$$\Delta_c H = [(3 \times -394) + (3 \times -242)] - 20$$

$$= -1928 \text{ kJ mol}^{-1}$$



### Using Hess's law to determine enthalpy changes from enthalpy changes of combustion.

This is another common cycle where the alternative routes involve combusting all the reactants and products in oxygen and using the enthalpies of combustion to calculate the overall enthalpy change of reaction. This cycle can only be used if all the reactants and products can be combusted in oxygen.



$$\Delta H \text{ reaction} = \sum \Delta_c H^\ominus \text{reactants} - \sum \Delta_c H^\ominus \text{products}$$

**Example 3.** Use the following enthalpy combustion data to calculate the enthalpy of reaction for the following reaction.

$$\Delta_c H^\ominus CO(g) = -283 \text{ kJ mol}^{-1} \quad \Delta_c H^\ominus H_2(g) = -286 \text{ kJ mol}^{-1} \quad \Delta_c H^\ominus CH_3OH(g) = -671 \text{ kJ mol}^{-1}$$

$$\Delta H \text{ reaction} = \sum \Delta_c H^\ominus \text{reactants} - \sum \Delta_c H^\ominus \text{products}$$

$$\Delta H = \Delta_c H^\ominus (CO) + 2 \times \Delta_c H^\ominus (H_2) - \Delta_c H^\ominus (CH_3OH)$$

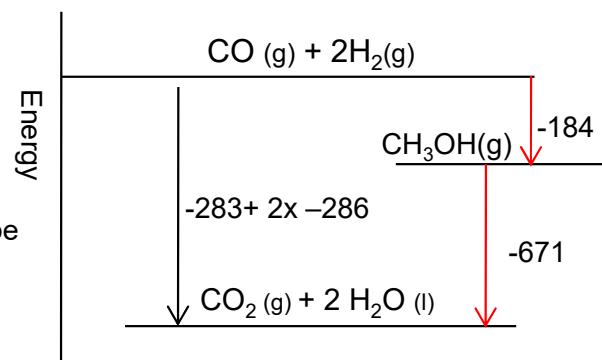
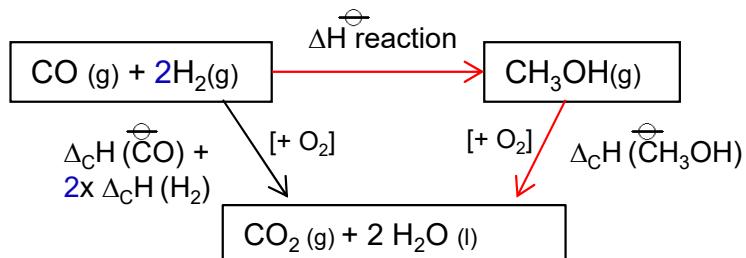
$$\Delta H = -283 + 2 \times -286 - -671$$

$$= -184 \text{ kJ mol}^{-1}$$

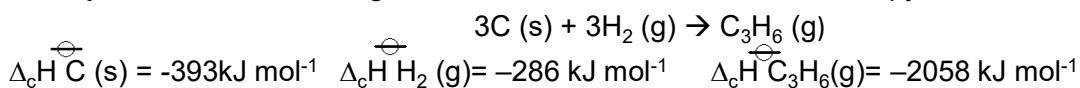
Be really careful with your minus signs

Note: unlike enthalpies of formation, elements do have an enthalpy of combustion value. Burning hydrogen in oxygen is a very exothermic reaction!

The calculation can also be shown diagrammatically using an energy level diagram,



**Example 4.** Use the following combustion data to calculate the enthalpy of formation of propene.



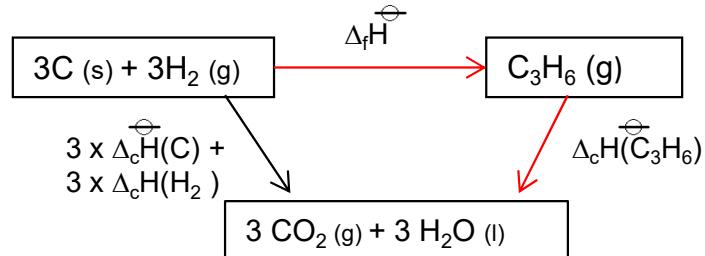
This is another example where both enthalpies of combustion and formation appear in the same question. When constructing the original equation remember to only have one mole of the compound on the right hand side of the equation because by definition the enthalpy of formation is for 1 mole of the compound formed.

$$\Delta_f^\ominus H = \sum \Delta_c^\ominus H \text{ reactants} - \sum \Delta_c^\ominus H \text{ products}$$

$$\Delta_f^\ominus H = 3 \times \Delta_c^\ominus H(\text{C}) + 3 \times \Delta_c^\ominus H(\text{H}_2) - \Delta_c^\ominus H(\text{C}_3\text{H}_6)$$

$$\Delta_f^\ominus H = 3 \times -393 + 3 \times -286 - -2058$$

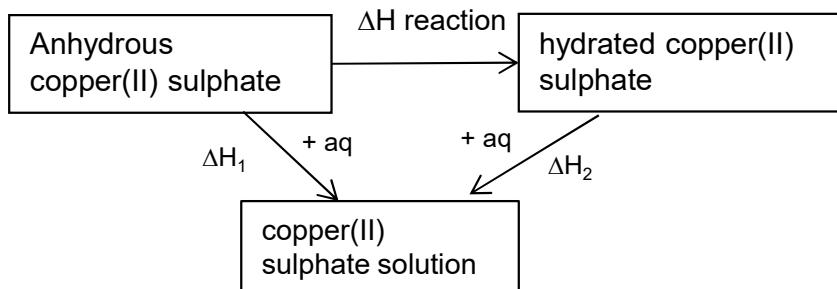
$$= +21 \text{ kJ mol}^{-1}$$



You may well notice I am using the notation  $\Delta_f^\ominus H$  and  $\Delta_c^\ominus H$  rather than  $\Delta H_f$  and  $\Delta H_c$ . I have been using the latter for many years and you will find it in almost every text book. It is actually incorrect though. The reason is in the name.  $\Delta_f^\ominus H$  is used for enthalpy **change of formation**. The definition refers to **change** in enthalpy and  $\Delta$  is the sign for change so the  $f$  or  $c$  goes next to the  $\Delta$ .  $H$  means enthalpy and there is no such thing as  $H_f$  or  $H_c$  only  $H$ . On the new syllabus AQA are using  $\Delta_f^\ominus H$  and  $\Delta_c^\ominus H$  so I am changing all my notes to agree with this.

## Questions about Hess's Law

1 A student used Hess's Law to determine a value for the enthalpy change that occurs when anhydrous copper(II) sulfate is hydrated. This enthalpy change was labelled  $\Delta H_{\text{reaction}}$



### 1 (a) State Hess's Law.

**1 (b)** Write a mathematical expression to show how  $\Delta H_{\text{reaction}}$ ,  $\Delta H_1$  and  $\Delta H_2$  are related to each other by Hess's Law.

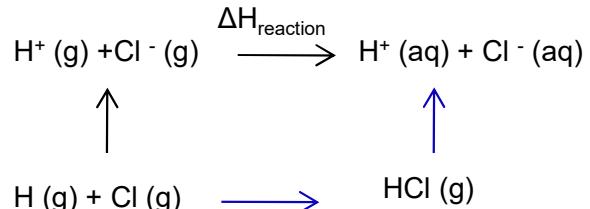
**1 (c)** Using the values below for the two enthalpy changes  $\Delta H_1$  and  $\Delta H_2$ , calculate a value for  $\Delta H_{\text{reaction}}$

$$\Delta H_1 = -156 \text{ kJ mol}^{-1}$$

$$\Delta H_2 = +12 \text{ kJmol}^{-1}$$

2) Using for following table of date and scheme of reactions, calculate a value for  $\Delta H_{\text{reaction}}$

Reaction	Enthalpy change kJ mol <sup>-1</sup>
$\text{HCl (g)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	-75
$\text{H (g)} + \text{Cl (g)} \rightarrow \text{HCl (g)}$	-432
$\text{H (g)} + \text{Cl (g)} \rightarrow \text{H}^+(\text{g}) + \text{Cl}^-(\text{g})$	+963



3) On strong heating, zinc carbonate decomposes to zinc oxide and carbon dioxide:



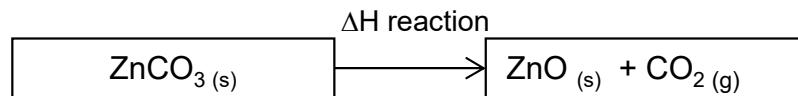
Owing to the conditions under which the reaction occurs, it is not possible to measure the enthalpy change directly. An indirect method uses the enthalpy changes when zinc carbonate and zinc oxide are neutralized with hydrochloric acid.

(i) Write the equation for the reaction of zinc carbonate with hydrochloric acid. And label this  $\Delta H_1$ .

(ii) The reaction of zinc oxide with hydrochloric acid is



Use the equations in parts (i) and (ii) to complete the Hess's Law cycle below to show how you could calculate the enthalpy change for the decomposition of  $\Delta H_{\text{reaction}}$ . Label the arrows in your cycle



(iii) Write an expression for the  $\Delta H_{\text{reaction}}$  in terms of  $\Delta H_1$  and  $\Delta H_2$ .

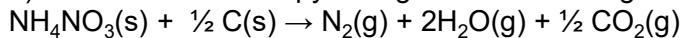
(b) Suggest **two** reasons why the value obtained by carrying out these two experiments and using the equation gives a value different to the data booklet value for the decomposition reaction of zinc carbonate.

## Questions using Enthalpy Change of Formation Data

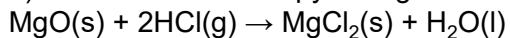
Compound	Enthalpy change of formation / Kj mol <sup>-1</sup>	Substance	Enthalpy change of formation / Kj mol <sup>-1</sup>	Compound	Enthalpy change of formation / Kj mol <sup>-1</sup>
Al <sub>2</sub> O <sub>3</sub> (s)	-1669	Fe(l)	+14	NH <sub>3</sub> (g)	-46
BaO(s)	-558	Fe <sub>2</sub> O <sub>3</sub> (s)	-822	NF <sub>3</sub> (g)	-114
CH <sub>4</sub> (g)	-75	H <sub>2</sub> O(l)	-286	NH <sub>4</sub> NO <sub>3</sub> (s)	-365
C <sub>3</sub> H <sub>7</sub> OH(l)	-304	H <sub>2</sub> O(g)	-242	NH <sub>4</sub> F(s)	-467
C <sub>4</sub> H <sub>9</sub> OH(l)	-327	H <sub>2</sub> O <sub>2</sub> (g)	-133	N <sub>2</sub> H <sub>4</sub> (g)	+74
CH <sub>3</sub> COCH <sub>3</sub> (l)	-248	HCl(g)	-92	NO <sub>2</sub> (g)	+34
CO(g)	-111	MgCl <sub>2</sub> (s)	-642	N <sub>2</sub> O(g)	+82
CO <sub>2</sub> (g)	-394	MgO(s)	-602	SO <sub>2</sub> (g)	-297

For the following questions use the enthalpy change of formation data in the table above

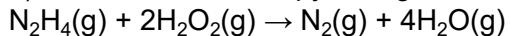
1) Calculate the enthalpy change for the following reaction



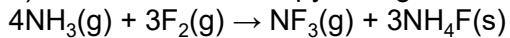
2) Calculate the enthalpy change for the following reaction



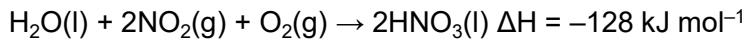
3) Calculate the enthalpy change for the following reaction



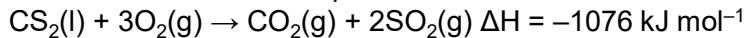
4) Calculate the enthalpy change for the following reaction



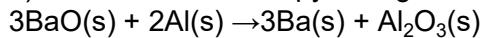
5) Use the data above and the following equation to calculate a value for the standard enthalpy of formation for nitric acid.



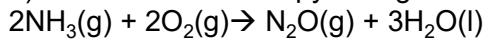
6) Use the data above and the following equation to calculate a value for the standard enthalpy of formation for carbon disulphide.



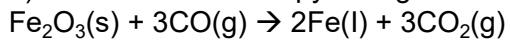
7) Calculate the enthalpy change for the following reaction



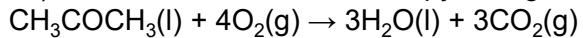
8) Calculate the enthalpy change for the following reaction



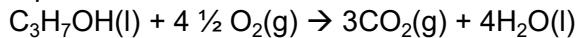
9) Calculate the enthalpy change for the following reaction



10) calculate the standard enthalpy change of combustion of propanone using equation below



11) calculate the standard enthalpy change of combustion of an alcohol C<sub>3</sub>H<sub>7</sub>OH, as shown by the equation:



12) Write an equation for the combustion of methane (CH<sub>4</sub>) and use it to calculate the enthalpy change of combustion of methane using the data in the above table

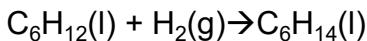
13) Write an equation for the combustion of butanol (C<sub>4</sub>H<sub>9</sub>OH(l)) and use it to calculate the enthalpy change of combustion of butanol using the data in the above table

## Questions using Enthalpy Change of Combustion Data

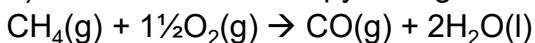
Substance	Enthalpy change of combustion / Kj mol <sup>-1</sup>	Substance	Enthalpy change of combustion / Kj mol <sup>-1</sup>	Substance	Enthalpy change of combustion / Kj mol <sup>-1</sup>
C(s)	-393.5	C <sub>4</sub> H <sub>6</sub> (g)	-2542	C <sub>2</sub> H <sub>5</sub> OH(l)	-1370
H <sub>2</sub> (g)	-285	C <sub>6</sub> H <sub>12</sub> (l)	-4003	C <sub>2</sub> H <sub>5</sub> SH(l)	-1170
S(s)	-297	C <sub>6</sub> H <sub>14</sub> (l)	-4163	CH <sub>3</sub> COOH(l)	-870
CH <sub>4</sub> (g)	-890	C <sub>7</sub> H <sub>8</sub> (l)	-3909	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> (s)	-1356
CO(g)	-283				

For the following questions use the enthalpy change of combustion data in the table above

1) Calculate the enthalpy change for the following reaction



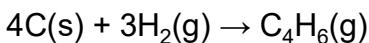
2) Calculate the enthalpy change for the following reaction



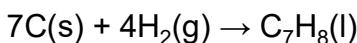
3) Use the data above and the following equation to calculate a value for the standard enthalpy of combustion for gaseous methanol.



4) Calculate the standard enthalpy change of formation of C<sub>4</sub>H<sub>6</sub> using the equation below and the data above.



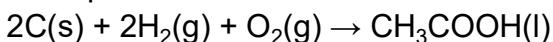
5) Calculate the standard enthalpy change of formation of C<sub>7</sub>H<sub>8</sub> using the equation below and the data above.



6) Calculate the standard enthalpy change of formation of Maleic acid C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> using the equation below and the data above.



7) Calculate the standard enthalpy change of formation of ethanoic acid CH<sub>3</sub>COOH using the equation below and the data above



8) Calculate the standard enthalpy change of formation of C<sub>2</sub>H<sub>5</sub>SH using the equation below and the data above



9) Write an equation for the formation of ethanol (C<sub>2</sub>H<sub>5</sub>OH(l)) from its elements and use it to calculate the enthalpy change of formation of ethanol using the data in the above table