Hess's Law

Revision: Thermochemical Equations

Consider the thermochemical equation:

$$A + B \rightarrow C + D, \quad \Delta H = +100 kJmol^{-1}$$

1. The ΔH value is doubled, if the coefficients are doubled. The amount of energy produced by a chemical reaction is directly proportional to the amount of substance initially present, i.e. $2A + 2B \rightarrow 2C + 2D$ has $\Delta H = +200 kJmol^{-1}$

2. The reverse reaction (swapping the products for the reactants) has the same ΔH value with the opposite sign, i.e. $C + D \rightarrow A + B$ has $\Delta H = -100 kJmol^{-1}$

Hess's Law

Hess's Law states that the enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs. Hess's Law is an implications of the Law of Conservation of Energy. Regardless of the number of steps involved in a multi-step reaction, the enthalpy change for the overall reaction is the sum of the enthalpy changes of all the steps. It is also important to note that all steps must proceed at the same temperature.
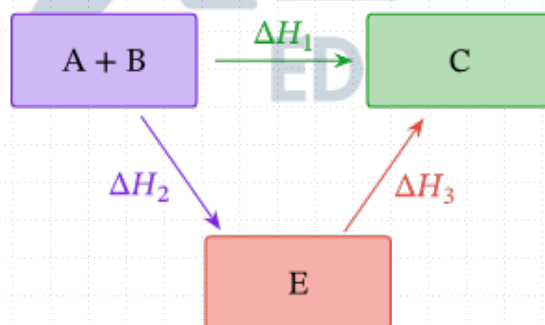
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

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The enthalpy changes of these processes can be deduced using Hess's Law and other intermediate reactions whose enthalpy is known.

For instance, without Hess's Law, it is very difficult to measure the enthalpy change associated with photosynthesis or respiration. The calculations involved will be shown later this lesson.

Reminder: Absolute enthalpy cannot be calculated, but rather enthalpy changes only. Hess's Law does not change this fact.

Manipulating Thermochemical Equations

Consider the formation of carbon dioxide from carbon and oxygen.

- This reaction occurs in two steps

- The first step forms carbon monoxide, and the second step forms carbon dioxide.

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$
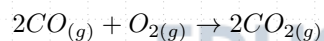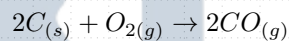
Given that the ΔH of the first reaction is $-221.0 kJmol^{-1}$ and ΔH of the second reaction is $-556.0 kJmol^{-1}$, find the ΔH for the reaction:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

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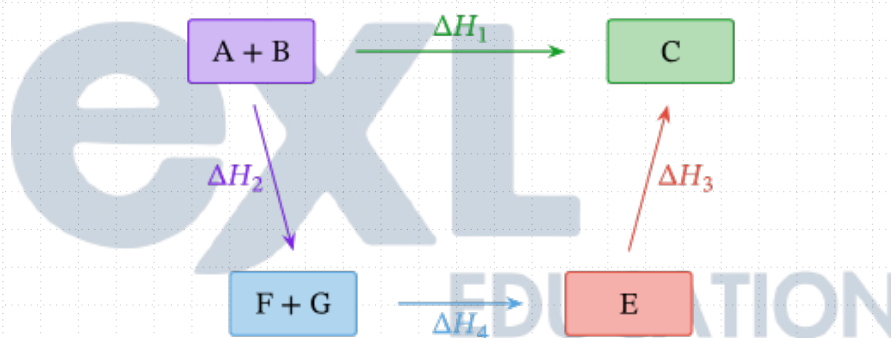
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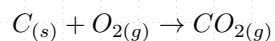
Hess Cycles

A Hess cycle or energy cycle diagram is often used to represent the enthalpy changes in a system of reactions. It must be drawn to be consistent with the Law of Conservation of Mass.

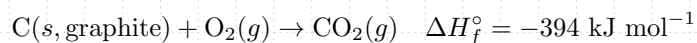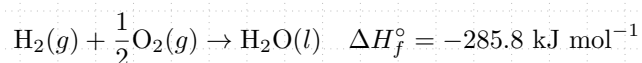A Hess cycle can be drawn with a vertical axis of increasing enthalpy:
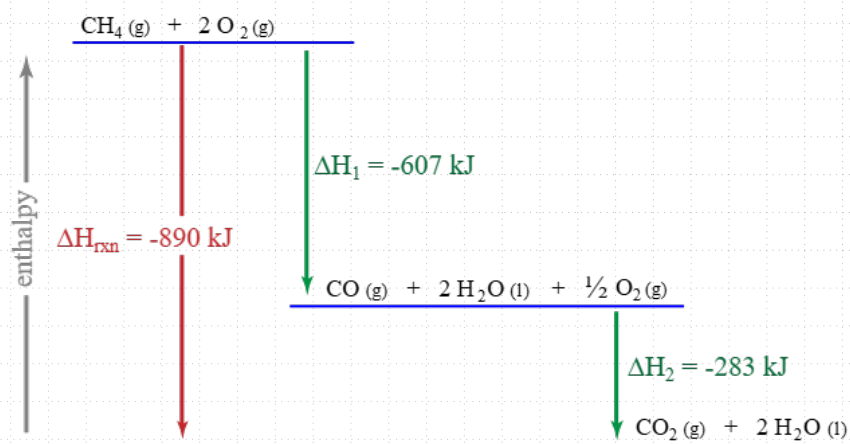
Alternatively, a Hess cycle can be drawn as a typical flowchart:

Enthalpy of Formation

Standard enthalpy of formation (ΔH_f°) is the formation of **1 mole** of a compound in its **standard state**, formed from its **elements** in their standard states.

The equations for the standard formation is written such that the stoichiometric coefficient of the formed substance is given a value of 1. For example:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^\circ = -285.8 \text{ kJ mol}^{-1}$$

$$C(s, \text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^\circ = -394 \text{ kJ mol}^{-1}$$

Note: The standard enthalpy of formation of an element in its most stable form is zero. *E.g.* Carbon exists as a solid in the form of graphite and diamond. Graphite is energetically more stable than diamond, so graphite is taken as the standard state of carbon.

The **standard enthalpy of reaction** $(\Delta H_{\text{rxn}}^\circ)$ is a reaction carried out at standard conditions (298 K and 101.3 kPa) and with everything in its standard state.

Standard enthalpy of formation can be used to calculate the **standard enthalpy of reaction**.

The ΔH° values for the reactants and products are used:

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ \text{ (products)} - \sum \Delta H_f^\circ \text{ (reactants)}$$

This equation is a direct consequence of Hess's Law and is sometimes also referred to as Hess's Law. It demonstrates that the enthalpy change of reactions at standard state conditions can be determined with knowledge of only the products and reactants and does not depend on any pathways in between.

Chloroethane Worked Example

The formation of chloroethane (C_2H_5Cl) from the reaction of ethene (C_2H_4) and hydrogen chloride (HCl) is as follows:

$$HCl(g) + C_2H_4(g) \longrightarrow C_2H_5Cl(g)$$
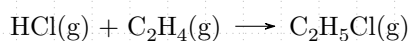
The following standard enthalpies of formation are provided:

Substance	ΔH_f° (kJ mol⁻¹)
$C_2H_4(g)$	52.2
$HCl(g)$	-92.3
$C_2H_5Cl(g)$	-109

This exercise will calculate ΔH of the reaction in **THREE** different ways.

1. Calculate the ΔH of the reaction by writing and manipulating thermochemical equations only.

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2. Calculate the ΔH of the reaction by drawing a Hess cycle to demonstrate the above reaction and the standard formations of each of the species.

3. Calculate the ΔH of the reaction using the modified Hess's Law (standard enthalpy of reaction formulae)

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Key Point Summary

The general steps to calculating enthalpy change in these questions are:

1. Write down an equation for every process listed in the question

2. Understand which equation you are required to calculate the enthalpy change for

3. Arrange the individual equations such that they cancel out to give the overall reaction OR construct an appropriate Hess cycle

4. Add/subtract the individual enthalpy changes to determine the unknown by using Hess's Law

When applying Hess's Law, note that:

1. Reversing the equation direction causes the sign of enthalpy change to be flipped

2. The states of the reactants and products are very important to note since they affect enthalpy changes (discussed later)

3. If the equation is multiplied by a factor, then the enthalpy change must also be multiplied by that same factor

Important Reminder: The modified form of Hess's Law can be used without any proof from now on. Nevertheless, you should be familiar with all three methods because they have different utilities depending on how the stimulus is presented.

Combustion Reactions

COMBUSTION is the burning of a substance in oxygen. It is an exothermic process that goes to completion. **The enthalpy change is negative** because energy has been released to the surroundings. The following data is provided:

1. The ΔH_f° of $SO_3(g)$ is -395 kJ mol^{-1}

2. $SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g)$ has $\Delta H = -98$ kJ mol^{-1}

Calculate the standard enthalpy of combustion of **one mole of sulfur**, where sulfur dioxide is the final product.

Photosynthesis

PHOTOSYNTHESIS is the reaction whereby glucose is formed in plant cells and requires the Sun's energy and chlorophyll to catalyse the reaction.

In Module 4, photosynthesis is often written as an equation in **standard states**, i.e. the state of glucose is solid.

$$6O_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$
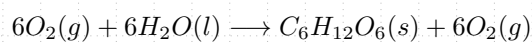
Note that the biological reaction of photosynthesis has glucose in its aqueous state.

Photosynthesis is endothermic, thus has a **positive enthalpy change** with energy being absorbed from the surroundings.

Consider the following ΔH_f° values:

Substance	ΔH_f° (kJ mol^{-1})
$C_6H_{12}O_6(s)$	-1274.5
$O_2(g)$	0
$CO_2(g)$	-393.5
$H_2O(l)$	-285.8

Calculate the enthalpy change associated with photosynthesis at standard conditions.

It is given that the molar enthalpy of dissolution of glucose is $+11 kJmol^{-1}$. Find the enthalpy change associated with photosynthesis under biological conditions.

Cellular Respiration

Cellular respiration is the reaction whereby a living organism utilises glucose aerobically (with O_2) to produce energy. It is the thermodynamic reverse reaction of photosynthesis.

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Enthalpies of Phase Change

Although phase changes are not chemical reactions, they are also associated with a change in enthalpy. Energy is required or released in the breaking or forming of intermolecular forces respectively.

Enthalpy of Fusion and Solidification

Also known as the Latent Heat of Fusion (ΔH_{fus}), the enthalpy of fusion is the enthalpy change associated with melting 1 mol of a solid to its liquid form, measured at 1 atm.

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For water, this represents the breaking of some intermolecular forces. More specifically:

- 6.01 kJ of energy is required to melt 1 mol of water at its melting point of $0°C$

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The enthalpy of solidification is the negative of the enthalpy of fusion.

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Enthalpies of Vaporisation and Condensation

Also known as the Latent Heat of Vaporisation (ΔH_{vap}), the enthalpy of vaporisation is the enthalpy change associated with heating 1 mol of a liquid to its gaseous form, measured at 1 atm.

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For water, this represents the breaking of all intermolecular forces in liquid water. More specifically:

- 40.7 kJ of energy is required to evaporate 1 mol of water at its melting point of $100°C$

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The enthalpy of condensation is the negative of the enthalpy of fusion.

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Note: The enthalpy of vaporisation tends to be larger than the enthalpy of fusion, since more energy is required to break all the intermolecular forces during evaporation.
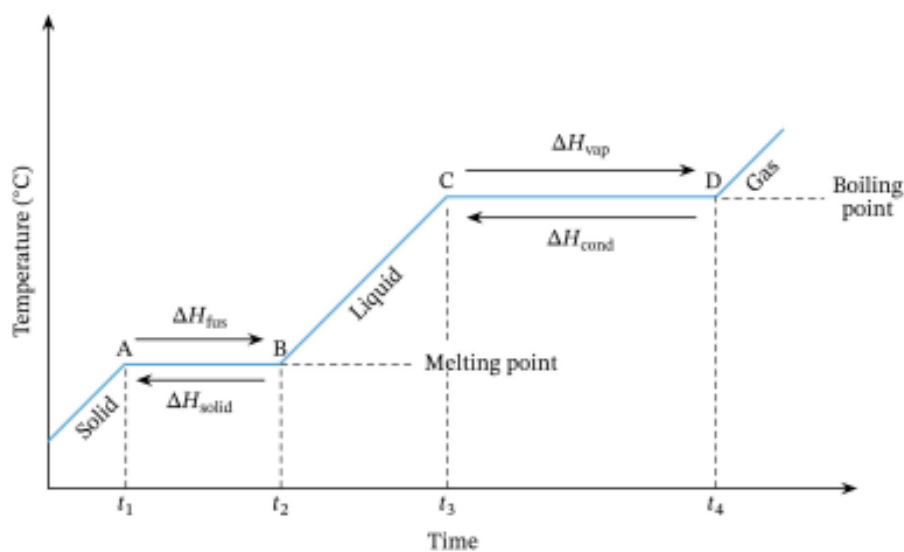
Practice Questions

1. Which of the following statements best describes Hess's Law?

   (A) All substances tend to move from a state of higher energy to lower energy

   (B) The enthalpy change in a chemical reaction is the sum of the internal energy and the product of pressure and volume

   (C) The enthalpy change in a chemical reaction is independent of the route by which the reaction occurs

   (D) If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other

2. Hess's Law is dependent on what conditions to remain constant?

   (A) The final conditions of the reaction

   (B) The initial conditions of the reaction

   (C) Neither A nor B

   (D) Both A and B

3. Using the equations given below, calculate ΔH for the formation of copper oxide.

   $CuO(s) + CO(g) \longrightarrow Cu(s) + CO_2(g) \quad \Delta H = -27 kJmol^{-1}$

   $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -283 kJmol^{-1}$

   $Cu(s) + \frac{1}{2} O_2(g) \longrightarrow CuO(s) \; \Delta H =?$

   (A) $256 kJmol^{-1}$

   (B) $-310 kJmol^{-1}$

   (C) $-256 kJmol^{-1}$

   (D) $310 kJmol^{-1}$

4. Find the standard enthalpy of formation of $NO_{(g)}$ given the followng thermochemical data:

   $N_2(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H = +66.20 kJmol^{-1}$

   $NO_2(g) \longrightarrow \frac{1}{2} O_2(g) + NO(g) \quad \Delta H = -283 kJmol^{-1}$

   (A) $-44 kJmol^{-1}$

   (B) $-22.00 kJmol^{-1}$

   (C) $+88.20 kJmol^{-1}$

   (D) $+176.4 kJmol^{-1}$

5. The energy cycle below shows two pathways to form carbon dioxide gas.
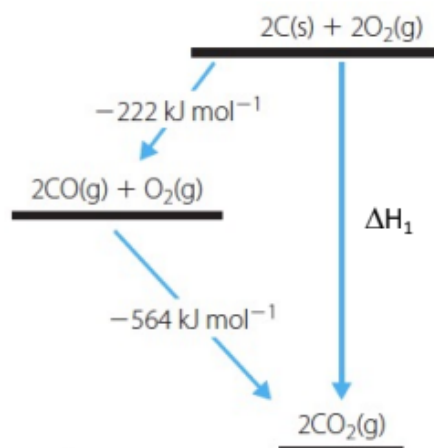
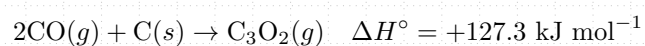
(a) Construct the two thermochemical equations from the energy cycle   2 marks

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(b) Determine ΔH_1 for the direct route.   2 marks

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6. The compound tricarbon dioxide (C_3O_2), is a gas at room temperature, which can form in the equation:

$$2CO(g) + C(s) \rightarrow C_3O_2(g) \quad \Delta H^\circ = +127.3 \text{ kJ mol}^{-1}$$

Given that ΔH_f° (CO, g) $= -110.5$ kJ mol^{-1}, **calculate** the standard enthalpy of formation of tricarbon dioxide.   2 marks

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7. The standard enthalpy change for the combustion of butane is shown below:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta H^\circ = -2878 \text{ kJ mol}^{-1}$$
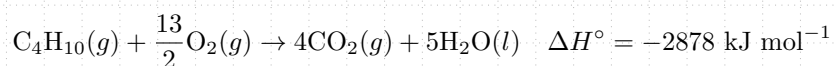
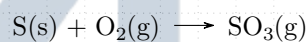**Calculate** the standard enthalpy change of formation of butane, given that: 3 marks

- ΔH_f° (CO_2, g) $= -393.5$ kJ mol^{-1}

- ΔH_f° (H_2O, l) $= -285.8$ kJ mol^{-1}

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8. Calculate ΔH^* for the reaction: 3 marks

$$S(s) + O_2(g) \longrightarrow SO_3(g)$$

Given the following data:

$$S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H^* = -395.2 \text{ kJ mol}^{-1}$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \quad \Delta H^* = -198.2 \text{ kJ mol}^{-1}$$

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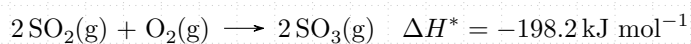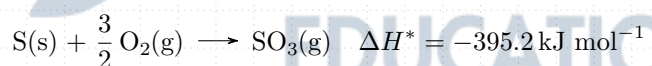
9. Kieran wishes to calculate the standard enthalpy of formation of phosphorus pentachloride. The following data is provided:

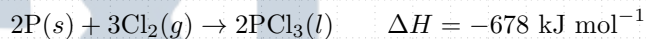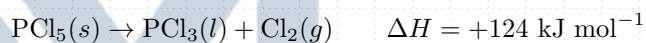| Substance	Melting point (°C)	Boiling point (°C)
P	44.1	280.0
Cl_2	-101.5	-34.0
PCl_3	-93.6	76.1
PCl_5	160.5	166.8

(a) Write the balanced equation for the standard formation of phosphorus pentachloride from its constituent elements, including states.   2 marks

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(b) Kieran has access to the following enthalpies of reaction, where all species are at their standard states:

$$PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g) \qquad \Delta H = +124 \text{ kJ mol}^{-1}$$

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l) \qquad \Delta H = -678 \text{ kJ mol}^{-1}$$

Using this data, calculate the standard enthalpy of formation of phosphorus pentachloride, showing all working.   4 marks
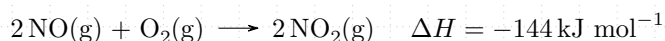
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Homework Questions

1. Which of the following statements are FALSE?

    I. Multiplying an equation by a factor does not alter the enthalpy change.

    II. States of reactants and products can affect enthalpy changes.

    III. Reversing the direction of an equation will not change the magnitude of the change in enthalpy.

    IV. Changes in enthalpy are dependent on the path taken.

    (A) I, III

    (B) II, III

    (C) I, III, IV

    (D) I, IV

2. Using the reactions given below, calculate $\Delta H^\circ(\mathrm{NO_2})$.

    $2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{NO_2(g)} \quad \Delta H = -144\,\mathrm{kJ\ mol^{-1}}$

    $\frac{1}{2}\,\mathrm{N_2(g)} + \frac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{NO(g)} \quad \Delta H = 90\,\mathrm{kJ\ mol^{-1}}$

    (A) $-234\mathrm{kJ\ mol^{-1}}$

    (B) $+36\mathrm{kJ\ mol^{-1}}$

    (C) $-54\mathrm{kJ\ mol^{-1}}$

    (D) $+18\mathrm{kJ\ mol^{-1}}$

3. For which reaction does $\Delta H_{\mathrm{reaction}} = -\Delta H_f^\circ(\mathrm{SO_3})$?

    (A) $\mathrm{SO_2(g)} + \frac{3}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{SO_3(g)}$

    (B) $\mathrm{S(s)} + 3\,\mathrm{O(g)} \longrightarrow \mathrm{SO_3(g)}$

    (C) $\mathrm{S(s)} + \frac{3}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{SO_3(g)}$

    (D) $\mathrm{SO_3(g)} \longrightarrow \mathrm{S(s)} + \frac{3}{2}\,\mathrm{O_2(g)}$

4. Which of the following is a positive value?

    (A) The enthalpy of formation of Na(s)

    (B) The enthalpy of dissolution of NaOH

    (C) The enthalpy of combustion of $\mathrm{C_3H_6(g)}$

    (D) The enthalpy of fusion of $\mathrm{H_2O}$

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5. Consider the following:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_1^\circ = -393.5 \, \text{kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad \Delta H_1^\circ = -285.8 \, \text{kJ mol}^{-1}$$

$$6\,C(s) + 6\,H_2(g) + 3\,O_2(g) \longrightarrow C_6H_{12}O_2(s) \quad \Delta H_1^\circ = -1273.3 \, \text{kJ mol}^{-1}$$
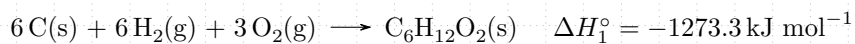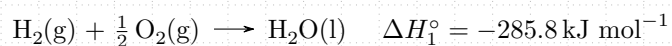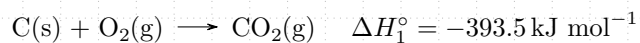
Calculate the enthalpy change of:

(a) Aerobic respiration   4 marks

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(b) Photosynthesis   1 mark

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6. Using the equations below,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \rightarrow \quad \Delta H^+ = -390 \, \text{kJ mol}^{-1}$$

$$Mn(s) + O_2(g) \longrightarrow MnO_2(s) \rightarrow \quad \Delta H^+ = -520 \, \text{kJ mol}^{-1}$$
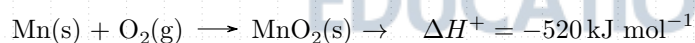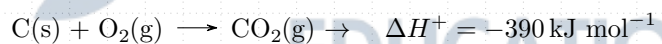
Calculate ΔH° (in kJ mol^{-1}) for the following reaction: 3 marks

$$MnO_2(s) + C(s) \longrightarrow Mn(s) + CO_2(g)$$

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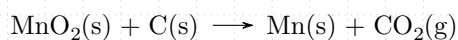
7. The table shows the standard enthalpy of formation for a range of substances.

Substance	ΔH_f° (kJ mol^{-1})
Pb(s)	0.0
Pb(NO$_3$)$_2$(s)	-451.9
Na(s)	0.0
NaNO$_3$(s)	-467.9
H$_2$O(l)	-285.8
H$_2$O(g)	-241.8
C$_2$H$_4$(g)	$+52.5$
CO$_2$(g)	-393.5
O$_2$(g)	0.0

(a) Using the table, calculate the standard enthalpy change for the following chemical reaction.

3 marks

$$2\,\text{Na(s)} + \text{Pb(NO}_3)_2\text{(s)} \longrightarrow 2\,\text{NaNO}_3\text{(s)} + \text{Pb(s)}$$

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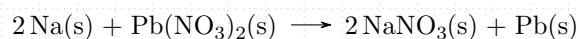
(b) State whether the reaction is exothermic or endothermic. 1 mark

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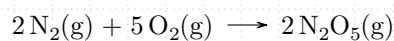
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(c) Nicholas wants to perform an experiment to find the standard enthalpy of dissolution of sodium nitrate. Find the mass of sodium nitrate that Nicholas should dissolve in 1000.0 mL of water to conduct this experiment. 2 marks
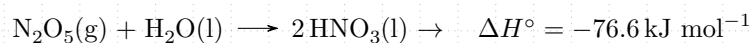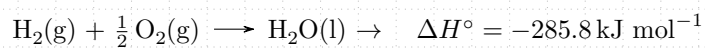
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8. Calculate ΔH° for the reaction: 3 marks

$$2\,N_2(g) + 5\,O_2(g) \longrightarrow 2\,N_2O_5(g)$$

Given the following data:

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \to \quad \Delta H^\circ = -285.8\,\text{kJ mol}^{-1}$$
$$N_2O_5(g) + H_2O(l) \longrightarrow 2\,HNO_3(l) \to \quad \Delta H^\circ = -76.6\,\text{kJ mol}^{-1}$$
$$\tfrac{1}{2}\,N_2(g) + \tfrac{3}{2}\,O_2(g) + \tfrac{1}{2}\,H_2(g) \longrightarrow HNO_3(l) \to \quad \Delta H^\circ = -174.1\,\text{kJ mol}^{-1}$$

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9. Calculate ΔH° for the reaction: 3 marks

$$2\,C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

Given the following data:

$$C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \to \quad \Delta H^\circ = -1300\,\text{kJ mol}^{-1}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \to \quad \Delta H^\circ = -394\,\text{kJ mol}^{-1}$$
$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \to \quad \Delta H^\circ = -286\,\text{kJ mol}^{-1}$$

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