THERMODYNAMICS

IT'S THE LAW:

1 Energy can neither b...
destroyed. It can on...

2 The entropy of an i...te
in equilibrium will...l t...
over time, approach... a
value at equilibrium...

3 As temperature appro...
zero, the entropy of a s...
approaches a constant...
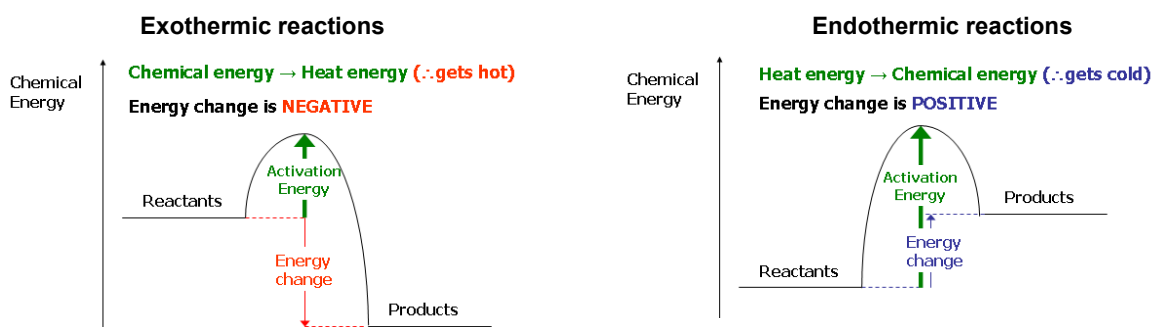
What is enthalpy?   *It is a measure of the heat content of a substance*

Enthalpy change (ΔH) =   *Change in heat content at constant pressure*

Standard conditions ($\Delta H^\ominus$) =   *100 kPa and a stated temperature*

Exothermic reactions

Chemical Energy

Chemical energy → Heat energy (∴gets hot)

Energy change is NEGATIVE

Activation Energy

Reactants

Energy change

Products

Endothermic reactions

Chemical Energy

Heat energy → Chemical energy (∴gets cold)

Energy change is POSITIVE

Activation Energy

Products

Energy change

Reactants

Standard enthalpy change of formation ($\Delta H_f^\ominus$) ("enthalpy of formation")

Enthalpy change when 1 mole of a substance is formed from its constituent elements with all reactants and products in standard states under standard conditions.

e.g. $CH_4(g)$ …….

       $H_2O(l)$ …….

       $NH_3(g)$ …….

       $C_2H_5OH(l)$ …….

       $CH_3Br(l)$ …….

       $Na_2O(s)$ …….

Note: re $\Delta H_f^\ominus$ of an element in its standard state = *0 by definition*

Standard enthalpy change of combustion ($\Delta H_c^\ominus$) ("enthalpy of combustion")

Enthalpy change when 1 mole of a substance is completely burned in oxygen with all reactants and products in standard states under standard conditions.

e.g. $CH_4(g)$ …….

       $H_2(g)$ …….

       $C_2H_6(g)$ …….

       $C_2H_5OH(l)$ …….

       $Na(s)$ …….

       $C_6H_{14}(l)$ …….

CALORIMETRY

- The enthalpy change for a reaction can be found by measuring the temperature change in a reaction.

- The heat energy given out (or taken in) is used to heat (or cool) a known mass of water. We know that it takes 4.18 J of energy to raise the temperature of 1 g of water by 1°C (i.e. 1 K).

- The amount of energy needed to make 1 g of a substance 1°C (1 K) hotter is called the *specific heat capacity* (measured in J g^{-1} K^{-1}).

- The following equation is then used to find the amount of heat energy give out (or absorbed).

$$\mathbf{q = m\,c\,\Delta T}$$

q	= heat energy given out (J)
m	= mass of substance heated (g)
ΔT	= temperature rise (K)
c	= specific heat capacity (J g^{-1} K^{-1})

- To find the enthalpy change in terms of J (or kJ) per mole, the following expression is needed: (*THINK* kJ per mole!)

$$\text{Enthalpy change (per mole)} = \frac{q}{\text{number of moles reacting}}$$

- Heat loss is a major problem with calorimetry and can lead to errors in the results. The techniques used in calorimetry are designed to reduce heat loss (one way to reduce errors from heat loss is to measure the heat capacity of the calorimeter as a whole (see flame calorimeters and bomb calorimeters)

1) Reactions taking place in solution

- The reaction is carried out in an insulated beaker and the temperature change measured.

- The reaction must be fast so that the maximum temperature is reached quickly (before it starts to cool).

- The specific heat capacity of the solution must be taken as being the 4.18 J g^{-1} K^{-1} (the same as water) and we usually use the mass of the water (not the solution) in the calculation.

2) Flame calorimeters

- Flame calorimeters are usually used to find the enthalpy of combustion of substance (usually a fuel).

- The fuel, which is in a bottle with a wick, is burned so that the heat is passed to water which it heats.

- Sometimes the specific heat capacity of water is used, but in more accurate flame calorimeters, the actual heat capacity of the flame calorimeter can be determined and used (by finding the temperature rise when a known amount of a substance with an accurately known enthalpy of combustion is tested).
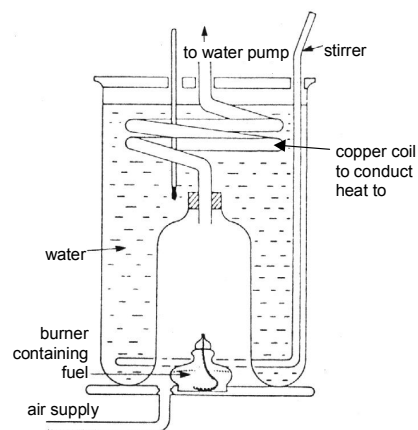
Calorimetry calculations – worked examples

1) In an experiment, 0.60 g of propane (C_3H_8) was completely burned in air. The heat evolved raised the temperature of 100 g of water by 64.9°C. Use this data to calculate the enthalpy of combustion of propane (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}).

2) 50 cm^3 of 1.0 mol dm^{-3} hydrochloric acid was added to 50 cm^3 of 1.0 mol dm^{-3} sodium hydroxide solution. The temperature rose by 6.8°C. Calculate the enthalpy of neutralisation for this reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

3) 100 cm^3 of 0.20 mol dm^{-3} copper sulphate solution was put in a calorimeter and 2.0 g of magnesium powder added. The temperature of the solution rose by 25.1°C. Work out which reagent was in excess and then calculate the enthalpy change for the reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}. Ignore the heat capacity of the metals.

# TASK 1 – CALORIMETRY CALCULATIONS 1

Basic level questions

1) In an experiment, 1.00 g of propanone (CH_3COCH_3) was completely burned in air. The heat evolved raised the temperature of 150 g of water from 18.8°C to 64.3°C. Use this data to calculate the enthalpy of combustion of propanone (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}).

2) In an experiment, 1.00 g of hexane (C_6H_{14}) was completely burned in air. The heat evolved raised the temperature of 200 g of water from 293.5 K to 345.1 K. Use this data to calculate the enthalpy of combustion of hexane (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}).

3) In an experiment, 1.56 g of propan-1-ol ($CH_3CH_2CH_2OH$) was completely burned in air. The heat evolved raised the temperature of 0.250 dm^3 of water from 292.1 K to 339.4 K. Use this data to calculate the enthalpy of combustion of propan-1-ol (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}).

4) 25 cm^3 of 2.0 mol dm^{-3} nitric acid was added to 25 cm^3 of 2.0 mol dm^{-3} potassium hydroxide solution. The temperature rose by 13.7°C. Calculate the enthalpy of neutralisation for this reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

5) 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid was added to 50 cm^3 of 2.0 mol dm^{-3} ammonia solution. The temperature rose by 12.4°C. Calculate the enthalpy of neutralisation for this reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

6) 50 cm^3 of 1.0 mol dm^{-3} nitric acid was added to 20 cm^3 of 1.0 mol dm^{-3} barium hydroxide solution. The temperature rose by 7.9°C. Calculate the enthalpy of neutralisation for this reaction (per mole of nitric acid reacting). Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

Intermediate level questions

7) 25 cm^3 of 1.00 mol dm^{-3} copper sulphate solution was put in a calorimeter and 6.0 g of zinc powder added. The temperature of the solution rose by 50.6°C. Work out which reagent was in excess and then calculate the enthalpy change for the reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}. Ignore the heat capacity of the metals.

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$
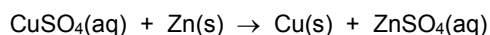
8) 50 cm^3 of 0.10 mol dm^{-3} silver nitrate solution was put in a calorimeter and 0.2 g of zinc powder added. The temperature of the solution rose by 4.3°C. Work out which reagent was in excess and then calculate the enthalpy change for the reaction (per mole of zinc that reacts). Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}. Ignore the heat capacity of the metals.

$$2\ AgNO_3(aq) + Zn(s) \rightarrow 2\ Ag(s) + Zn(NO_3)_2(aq)$$
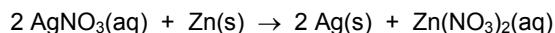
9) 3.53 g of sodium hydrogencarbonate was added to 30.0 cm^3 of 2.0 mol dm^{-3} hydrochloric acid. The temperature fell by 10.3 K. Work out which reagent was in excess and then calculate the enthalpy change for the reaction. Assume that the density of the solution is 1.00 g cm^{-3}, the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

High level questions

10) A calorimeter was calibrated by burning 2.00 g of methanol (CH_3OH) whose enthalpy of combustion is -715 kJ mol^{-1}. The temperature of the calorimeter rose from 19.6°C to 52.4°C. The same calorimeter was used to measure the enthalpy of combustion of propan-2-ol. 1.50 g of propan-2-ol $CH_3CH(OH)CH_3$ raised the temperature by from 19.8°C to 56.2°C. Calculate the heat capacity of the calorimeter and then the enthalpy of combustion of propan-2-ol.

# TASK 2 – CALORIMETRY CALCULATIONS 2

Basic level questions

1) In an experiment, 0.750 g of benzene (C_6H_6) were completely burned in air. The heat evolved raised the temperature of 200 g of water by 43.7°C. Use this data to calculate the enthalpy of combustion of benzene (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}). (Total 4)

2) 25.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid was added to 25.0 cm^3 of 2.00 mol dm^{-3} ammonia solution. The temperature rose by 12.4°C. Calculate the enthalpy of neutralisation for this reaction. Assume that the density of the solution is 1.00 g cm^{-3} and the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}. (Total 5)

3) a) Write an equation to represent the ΔH°_c of butan-1-ol ($C_4H_9OH(l)$). (1)

   b) A simple flame calorimeter was used to measure the ΔH°_c of butan-1-ol. 0.600 g of butan-1ol was burned in a simple lamp burner under a container of water. There was 250 g of water in the container and its temperature rose by 19.4°C. Using the specific heat capacity of water as 4.18 J g^{-1} K^{-1}, calculate the enthalpy of combustion of butan-1-ol. (Total 4)

4) When 80.0 g of ammonium nitrate dissolves in 1000 cm^3 of water, the temperature falls by 5.0ºC. Calculate the enthalpy change of solution of ammonium nitrate (i.e. the enthalpy change when one mole of ammonium nitrate dissolves). (Total 4)

5) Calculate the standard enthalpies of combustion of hexane given that combustion of 1.720 g of hexane released 84.06 kJ of heat. (Total 2)

6) 0.200 moles of cyclohexane, $C_6H_{12}(l)$, can release 784 kJ when it is burnt.
   a) Write an equation for the reaction that represents the enthalpy of combustion of cyclohexane. (1)
   b) Calculate the enthalpy of combustion of cyclohexane. (1)
   (Total 2)

7) When 25.0 cm^3 of 2.00 mol dm^{-3} nitric acid is added to 25 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution, the temperature rises by 6.5ºC.
   a) Write an equation for the reaction. (1)
   b) Calculate the number of moles of each reagent and state which one is in excess. (3)
   c) Calculate the enthalpy change of neutralisation for this reaction. (3)
   (Total 7)

8) 1.16 g of propanone, $CH_3COCH_3(l)$, was burnt and raised the temperature of 250 g of water in a calorimeter from 19.0ºC to 40.9ºC. Calculate the enthalpy of combustion of propanone. (Total 4)

9) When 0.92 g of ethanol, $C_2H_5OH(l)$, was burnt in this calorimeter, the temperature rose by 11.7ºC. The calorimeter contains 500 g of water.

   a) How much heat was given out by the burning ethanol? (2)
   b) How many moles of ethanol were burnt? (1)
   c) Write an equation for the reaction that represents the enthalpy of combustion of ethanol. (1)
   d) Calculate the enthalpy of combustion of ethanol. (2)
   (Total 5)
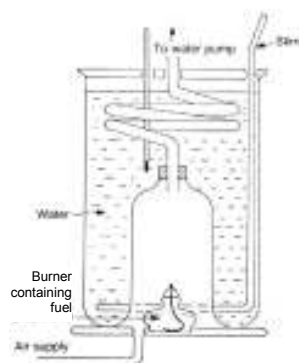
Intermediate level questions

10) When 0.500 g of powdered iron is added to 100 cm^3 of 0.200 mol dm^{-3} copper sulphate solution in an insulated vessel, the temperature rises by 3.3°C.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$
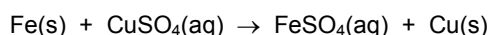
    a) Why is the iron added as a powder? (1)

    b) Calculate the heat evolved in the reaction. The specific heat capacity of the solution can be taken as 4.18 J g^{-1} K^{-1}, and the heat capacity of the iron can be ignored. (2)

    c) Calculate the number of moles of iron and copper sulphate, and so state which reagent is in excess? (3)

    d) Calculate the enthalpy change for the reaction. (2)

(Total 8)

11) Decide whether each of the following changes is exothermic or endothermic, giving a brief explanation.

    a) methane burning (1)

    b) water freezing (1)

    c) water boiling (1)

(Total 3)

12) When 0.40 g of calcium reacts with 100 cm^3 of 2.00 mol dm^{-3} hydrochloric acid, the temperature rises by 12.0ºC. The equation for the reaction is shown below. The specific heat capacity of the water is 4.18 J mol^{-1} K^{-1}.

$$Ca(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$$
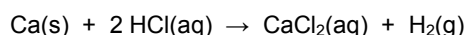
    a) Calculate the heat released in the reaction. (2)

    b) Calculate which reagent is in excess. (3)

   c) Calculate the enthalpy change for this reaction per mole of calcium reacting. (2)

(Total 7)

13) The apparatus shown was used to find the enthalpy of combustion of methanol. The experimental data is shown below.

starting temperature	= 19.4°C
final temperature	= 40.3°C
starting mass of burner + CH$_3$OH	= 28.44 g
final mass of burner + CH$_3$OH	= 27.42 g
specific heat capacity of water	= 4.18 J mol^{-1} K^{-1}
volume of water	= 250 cm^3

    a) Define enthalpy of combustion. (3)

    b) Calculate the enthalpy of combustion of methanol. (4)

(Total 7)
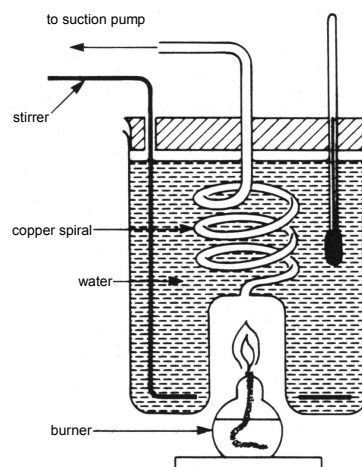
14) When 1.30 g of zinc reacts with 100 cm^3 of 2.00 mol dm^{-3} nitric acid, the temperature rises by 6.0ºC. The equation for the reaction is shown below.

$$Zn(s) + 2\,HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g)$$

    a) Calculate which reagent is in excess. (3)

    b) Calculate the heat given out in the experiment. (2)

    c) Calculate the enthalpy change for the reaction. (2)

(Total 7)

High level questions

15) a) The enthalpy of combustion of propan-1-ol, $CH_3CH_2CH_2OH(l)$, is –2020 kJ mol^{-1}. 0.600 g of propan-1-ol is burnt and used to heat 200 g of water in a calorimeter. The starting temperature of the water is 20.3ºC. How much heat is released when 0.600 g of propan-1-ol is burned? (2)

   b) Calculate the theoretical temperature of the water at the end of the experiment. (3)

   c) Is the final temperature likely to be higher or lower than this theoretical answer? Explain your answer. (2)

   (Total 7)

16) a) An experiment was performed to measure the overall heat capacity of a bomb calorimeter. A pellet of benzenecarboxylic acid (C_6H_5COOH) of mass 0.7934 g was burned, and the temperature rise found to be 2.037°C. The ΔH°_c of benzenecarboxylic acid is –3227.0 kJ mol^{-1}. Calculate the overall heat capacity of the calorimeter. (4)

   b) The same bomb calorimeter was then used to measure the ΔH°_c of butan-1-ol. 0.8233 g of butan-1-ol raised the temperature by 2.860°C. Calculate the ΔH°_c of butan-1-ol. (4)

   (Total 8)

1) Mrs Grime is on a very rare camping trip and is, not unusually, desperate for a cup of tea. However, she is very short of Calor gas. She estimates that she has 1.12 dm^{-3} of the Calor gas left (measured at 16°C and 100000 Pa). Calculate the maximum volume of water that she could boil.

   Assume that Calor gas is pure butane, $C_4H_{10}(g)$ (ΔH°_c = -3000 kJ mol^{-1}), the specific heat capacity of the water is 4.18 J g^{-1} K^{-1}, that the water is at 16°C and that 75% of the heat from the gas is taken in by the water.

   (Total 6)

2) 300 cm^3 of Coca-Cola was poured into a glass. Its temperature was 25°C. Two ice cubes, of total volume 35 cm^3 and initial temperature -10°C, were added. Given the following data, calculate by how much the temperature of the Coca-Cola will fall. (6)

   density of ice = 0.92 g cm^{-3}

   specific heat capacity of ice = 2.09 J g^{-1} K^{-1}

   enthalpy change of fusion for ice = 6.02 kJ mol^{-1} ($H_2O_{(s)} \rightarrow H_2O_{(l)}$)

   specific heat capacity of water = 4.18 J g^{-1} K^{-1}

   (Total 6)

1) Hess's Law

The enthalpy change for a reaction is independent of the route taken

A ———————→ B

C
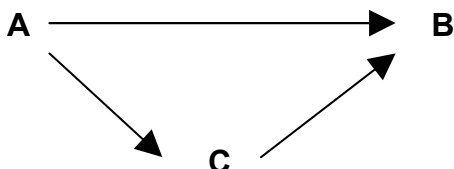
e.g. the enthalpy change to go from A → B direct is the same as going from A → C → B

2) Calculations involving enthalpies of formation ("Type 1 questions")

- If the enthalpy of formation for the reactants and products in a reaction are known, the overall enthalpy change is easy to calculate.

ΔH = [SUM of ΔH_f products] − [SUM ΔH_f reactants]

- Remember that ΔH_f of all elements is zero.

- Watch for the very frequent mistake of doing *reactants – products*, rather than *products – reactants*.

- If the overall enthalpy change for a reaction is known along with the enthalpy of formation of all but one of the reactants/products, then this equation can be used to find the missing enthalpy of formation.

Example 1

Calculate the overall enthalpy change for this reaction: $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$

ΔH°_f $CH_4(g)$ = -75, $CO_2(g)$ = -393, $H_2O(l)$ = -286 kJ/mol

Example 2

The enthalpy change for the following reaction is -2877 kJ/mol: $C_4H_{10}(g) + 6\frac{1}{2} O_2(g) \rightarrow 4 CO_2(g) + 5 H_2O(l)$

Calculate the enthalpy change of formation of butane ($C_4H_{10}(g)$) given the following data:

ΔH°_f $CO_2(g)$ = -393, $H_2O(l)$ = -286 kJ/mol

TASK 3 – HESS'S LAW 1

Basic level questions

1) Calculate the ΔH° for the following reactions given the values of ΔH°_f in the following table.

	ZnCO$_3$(s)	ZnO(s)	CO$_2$(g)	CO(g)	H$_2$O(l)	Fe$_2$O$_3$(s)	Al$_2$O$_3$(s)	C$_2$H$_4$(g)
ΔH°_f (kJ/mol)	-812	-348	-393	-111	-286	-822	-1669	+52

    a) ZnCO$_3$(s) → ZnO(s) + CO$_2$(g)

    b) 2 CO(g) + O$_2$(g) → 2 CO$_2$(g)

    c) 2 Al(s) + Fe$_2$O$_3$(s) → 2 Fe(s) + Al$_2$O$_3$(s)

    d) C$_2$H$_4$(g) + 3 O$_2$(g) → 2 CO$_2$(g) + 2 H$_2$O(l)

    e) C$_2$H$_4$(g) + 2 O$_2$(g) → 2 CO(g) + 2 H$_2$O(l)

2) The ΔH° for the following reaction is shown.

$$N_2H_4(l) + O_2(g) \rightarrow 2 H_2O(l) + N_2(g) \qquad \Delta H^\circ = -623 \text{ kJ mol}^{-1}$$
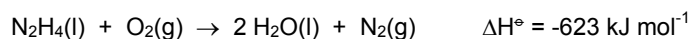
Given that the ΔH°_f of H$_2$O(g) is -286 kJ mol^{-1}, calculate the ΔH°_f of N$_2$H$_4$(l).

3) Calculate the ΔH°_f of ethane, C$_2$H$_6$(g), given the enthalpy change for the following reaction and the ΔH°_f of ethene, C$_2$H$_4$(g), which is +52 kJ mol^{-1}.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H^\circ = -137 \text{ kJ mol}^{-1}$$
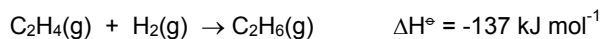
4) Use the enthalpies of formation below to calculate the enthalpy change for the following reaction.

$$3 Fe(s) + 4 H_2O(g) \rightarrow 4 H_2(g) + Fe_3O_4(s)$$
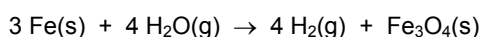
    ΔH°_f: H$_2$O(g) -242; Fe$_3$O$_4$(s) -1117 kJ mol^{-1}

5) The ΔH° for the following reaction is shown. Use it and the ΔH°_f values below to calculate the ΔH°_f of Pb(NO$_3$)$_2$(s).

$$Pb(NO_3)_2(s) \rightarrow PbO(s) + 2 NO_2(g) + \tfrac{1}{2} O_2(g) \qquad \Delta H^\circ = +301 \text{ kJ mol}^{-1}$$
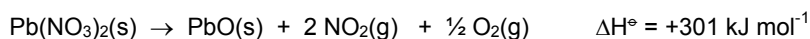
    ΔH°_f: PbO(S) -217; NO$_2$(g) +33 kJ mol^{-1}

6) Use the enthalpies of formation below to calculate the enthalpy change for the following reaction.

$$CH_3COCH_3(l) + H_2(g) \rightarrow CH_2CH(OH)CH_3(l)$$
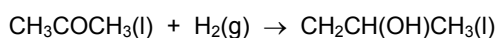
    ΔH°_f: CH$_3$COCH$_3$(l) -248; CH$_2$CH(OH)CH$_3$(l) -318 kJ mol^{-1}

3) Calculations involving enthalpies of combustion ("Type 2 questions")

Best method (for students at grade A-C)

- Questions that involve enthalpies of combustion can usually be done using the cycle shown below.

- The reaction involved across the top is often an enthalpy of formation (from elements to a compound).

- The sum of the clockwise arrows equals the sum of the anticlockwise arrows.

- Be careful when drawing your cycle to ensure that arrows are going in the right direction and the number of moles is correct.

$$\text{reactants} \xrightarrow{\quad \Delta H \quad} \text{products}$$
$$\Delta H_c \searrow \qquad \swarrow \Delta H_c$$
$$\text{oxides}$$
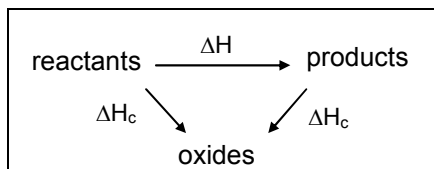
- If you use a cycle like this, there is no need to worry about getting the number of oxygen molecules in the downward arrows.

Simpler method (for students at grade D/E)

- This is a simpler method that works for most simple questions.

$$\Delta H \;=\; [\text{SUM of } \Delta H_c \text{ reactants}] - [\text{SUM } \Delta H_c \text{ products}]$$

- Note that this is *reactants – products* which is the opposite of the equation that uses enthalpies of formation.

Example 1

Calculate the enthalpy of formation of ethanol (C_2H_5OH) given the following enthalpies of combustion.

ΔH°_c $C(s)$ = -393, $H_2(g)$ = -286, $C_2H_5OH(l)$ = -1371 kJ/mol

---

Example 2

Calculate the enthalpy change for this reaction given the following data. $C(s) + 2\,H_2(g) \rightarrow CH_4(g)$

ΔH°_c $C(s)$ = -393, $H_2(g)$ = -286, $CH_4(g)$ = -890 kJ/mol

---

TASK 4 – HESS'S LAW 2

Basic level questions

1)   Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, given the following enthalpy changes.

ΔH°_c: C(s) -393; $H_2(g)$ -286 kJ mol^{-1}, ΔH°_f: $C_3H_8(l)$ -103 kJ mol^{-1}

2)   Calculate the enthalpy change for the following reaction using the enthalpies of combustion given.

$$C(graphite) \rightarrow C(diamond)$$

ΔH°_c: C(graphite) -393; C(diamond) -395 kJ mol^{-1}

3)   Calculate the enthalpy change during the fermentation of glucose using the enthalpies of combustion given.

$$C_6H_{12}O_6(s) \rightarrow 2\ C_2H_5OH(l)\ +\ 2\ CO_2(g)$$

ΔH°_c: $C_6H_{12}O_6(s)$ -2820; $C_2H_5OH(l)$ -1368 kJ mol^{-1}

4)   Calculate the enthalpy of formation of pentane, $C_5H_{12}(l)$, given the following enthalpies of combustion.

ΔH°_c : $H_2(g)$ -286; C(s) -393; $C_5H_{12}(l)$ -3509 kJ mol^{-1}

5)   Calculate the enthalpy of combustion of propanone, $CH_3COCH_3(l)$, given the information below.

ΔH°_c : $H_2(g)$ -286; C(s) -393 ΔH°_f : $CH_3COCH_3(l)$ -217 kJ mol^{-1}
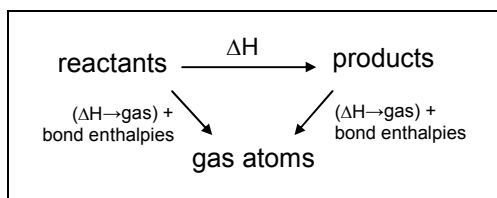
Intermediate level questions

6)   Calculate the enthalpy of combustion of $CS_2(l)$ given the following enthalpy changes.

ΔH°_c: C(s) -393; S(s) -297 kJ mol^{-1}, ΔH°_f: $CS_2(l)$ +88 kJ mol^{-1}

7)   Calculate the standard enthalpy change for the following reaction using the enthalpy changes given.

$$SO_2(g)\ +\ 2\ H_2S(g) \rightarrow 3\ S(s)\ +\ 2\ H_2O(l)$$

ΔH°_c: S(s) -297 kJmol^{-1} ΔH°_f: $H_2O(l)$ -286; $H_2S(g)$ -20 kJ mol^{-1}

4) Calculations involving bond enthalpies ("Type 3 questions")

- Bond enthalpy is the enthalpy change to break one mole of covalent bonds in the gas phase.

- For most bonds (e.g. C-H, C-C, C=O, O-H, etc.) the value for the bond enthalpy is an average taken from a range of molecules as the exact value varies from compound to compound. For some bond enthalpies (e.g. H-H, H-Cl, O=O, etc) the value is exact as only one molecule contains that bond.

- Enthalpies of reaction that have been calculated using mean bond enthalpies are not as accurate as they might be because the values used are averages and not the specific ones for that compound.

Best method (for students at grade A-C)

- This cycle works for any question that involves bond enthalpies, whether to find a bond enthalpy or ΔH for a reaction.

- Remember that substances must be in the gas state before bonds are broken, and so ΔH to go to the gas state is needed for solids and liquids. (Note - ΔH vaporisation is the enthalpy change to convert a liquid to a gas)

$$\text{reactants} \xrightarrow{\ \Delta H\ } \text{products}$$

($\Delta H \rightarrow$ gas) + bond enthalpies ↘   ↗ ($\Delta H \rightarrow$ gas) + bond enthalpies

$$\text{gas atoms}$$

- As with other cycles, the sum of the clockwise arrows equals the sum of the anticlockwise arrows. Be careful to ensure that arrow directions and number of moles are correct.

Simpler method (for students at grade D/E)

- This is the way you would have done the questions at GCSE.

- The problem is that it only works if all reactants and products are in the gas phase, though this is usually the case at AS (but not at A2).

- In this method, simply
  - add up the energy needed to break all the bonds in the reactants
  - add up the energy released forming bonds in the products
  - enthalpy change is simply:

$$\Delta H \ = \ \text{BREAK - MAKE}$$

- Sometimes you may be given the overall enthalpy change and all the bond enthalpies except one and will need to find the unknown bond enthalpy.
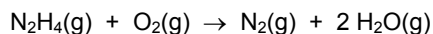

Example 1

Calculate the enthalpy change for the following reaction given the following bond enthalpies.

$$CH_3\text{-}CH_3 \ (g) \ + \ Cl_2(g) \ \rightarrow \ CH_3\text{-}CH_2Cl(g) \ + \ HCl(g)$$
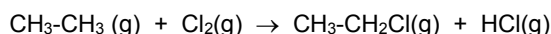
Bond enthalpies: C-C 348, C-H 412, Cl-Cl 242, C-Cl 338, H-Cl 431 kJ/mol

Example 2

Hydrazine has the formula N_2H_4 and is used as a rocket fuel (e.g. for the Apollo moon rockets). It burns in the following reaction for which the enthalpy change is -583 kJ/mol.

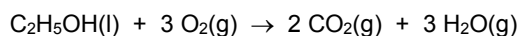$$N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

Calculate the N-N bond enthalpy in hydrazine given the following bond enthalpies.

Bond enthalpies: N-H 388, O=O 498, N≡N 944, O-H 463 kJ/mol

Example 3

Ethanol has the formula C_2H_5OH and is used as a fuel (e.g. for cars in Brazil). It burns in the following reaction for which the enthalpy change is -1015 kJ/mol.

$$C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(g)$$

Calculate the C-C bond enthalpy in ethanol given the following bond enthalpies and enthalpy of vaporisation of ethanol.

Bond enthalpies: C-H 412, O-H 463, C-O 360, C=O 743, O=O 498 kJ/mol

Enthalpy of vaporisation of ethanol, $C_2H_5OH(l)$ = 44 kJ/mol

TASK 5 – HESS'S LAW 3

Basic level questions

1) Use the following bond enthalpies to calculate $\Delta H^{\ominus}$ for the following reactions. You may assume that all species are in the gaseous state.

Bond	H–H	O=O	C–C	C=C	C–H	F–F	H–O	Br–Br	C–Br	H–Br	C=O
KJ mol^{-1}	436	496	348	612	412	158	463	193	276	366	743

a) $H\!-\!H \ + \ Br\!-\!Br \ \longrightarrow \ 2 \ H\!-\!Br$

b)

c)
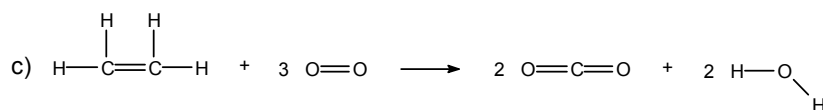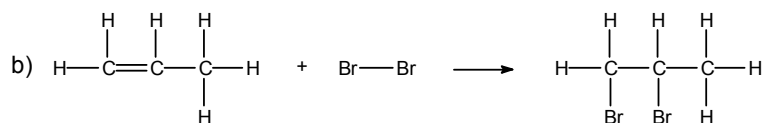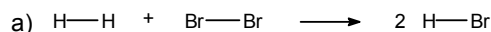
d) $\Delta H^{\ominus}_c$ of methane

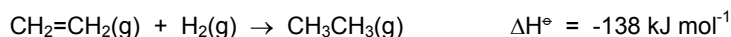## Intermediate level questions

2) Calculate the average N-H bond energy in $NH_3(g)$ using the data below.

   $\Delta H^{\ominus}_f$ of $NH_3(g)$ = -46 kJ mol^{-1}

   Bond enthalpies: N≡N = 944; H-H = 436 kJ mol^{-1}

3) Calculate the C=C bond energy in ethene using the data below.

   $CH_2=CH_2(g) \ + \ H_2(g) \ \rightarrow \ CH_3CH_3(g)$ $\Delta H^{\ominus}$ = -138 kJ mol^{-1}

   Bond enthalpies: C-C = 348; H-H = 436; C-H = 412 kJ mol^{-1}

4) Calculate the C≡C bond enthalpy in the gas propyne using the bond enthalpy values in the table above and the enthalpy changes for the reactions shown below.
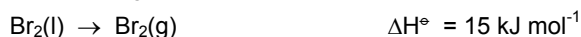
   propyne

   $C(s) \ \rightarrow \ C(g)$ $\Delta H^{\ominus}$ = +715 kJ mol^{-1} $CH_3C≡CH(g)$ $\Delta H^{\ominus}_f$ = +185 kJ mol^{-1}
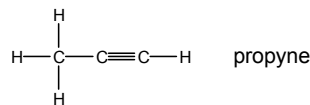
High level questions

5) Calculate the average S-F bond energy in $SF_6(g)$ using the bond data in the table, the $\Delta H^{\ominus}_f$ of $SF_6(g)$ which is -1100 kJ mol^{-1}, and

   $S(s) \ \rightarrow \ S(g)$ $\Delta H^{\ominus}$ = 223 kJ mol^{-1}

6) Calculate $\Delta H^{\ominus}_f$ for bromomethane, $CH_3Br(g)$, given the bond data in the table and

   $C(s) \ \rightarrow \ C(g)$ $\Delta H^{\ominus}$ = 715 kJ mol^{-1}

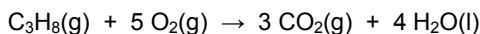 $Br_2(l) \ \rightarrow \ Br_2(g)$ $\Delta H^{\ominus}$ = 15 kJ mol^{-1}

TASK 6 – A MIXTURE OF SIMPLE THERMODYNAMICS QUESTIONS

1) Find ΔH_f of butane given that the following data.

   ΔH_c: $C_4H_{10}(g) = –2877$, $C(s) = –394$, $H_2(g) = –286$ kJ mol^{-1}

2) Find ΔH for the following reaction using the data below.

   $$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(l)$$

   ΔH_f: $C_3H_8(g) = –104$, $CO_2(g) = –394$, $H_2O(l) = –286$ kJ mol^{-1}

3) Find ΔH for the following reaction using the bond enthalpy data below.

   $$C_2H_6(g) + 3½ O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(g)$$
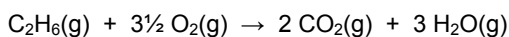
   C-C = 348, C-H = 412, O=O = 496, C=O = 743, O-H = 463 kJ mol^{-1}

4) Find ΔH_c of propan-2-ol given that the following data.

   ΔH_f: $CH_3CH(OH)CH_3(l) = –318$, ΔH_c: $C(s) = –394$, $H_2(g) = –286$ kJ mol^{-1}

5) Calculate ΔH_f of $CCl_4(l)$ given the following data.

   $CCl_4(l) \rightarrow CCl_4(g)$ = +31 kJ mol^{-1}
   $C(s) \rightarrow C(g)$ = +715 kJ mol^{-1}
   Bond enthalpy (Cl-Cl) = +242 kJ mol^{-1}
   Bond enthalpy (C-Cl) = +338 kJ mol^{-1}

6) Find ΔH for the hydrogenation of propene using the data below.

   $$CH_3CH=CH_2(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$
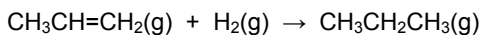
   ΔH_c: $CH_3CH=CH_2(g) = –2059$, $H_2(g) = –286$, $CH_3CH_2CH_3(g) = –2220$ kJ mol^{-1}

7) 0.55 g of propanone was burned in a calorimeter containing 80 g of water. The temperature rose by 47.3ºC. Calculate ΔH_c for propanone given the specific heat capacity of water is 4.18 J mol^{-1} K^{-1}.

8) 25 cm^3 of 2.0 mol dm^{-3} nitric acid was reacted with 25 cm^3 of 2.0 mol dm^{-3} potassium hydroxide is an insulated cup. The temperature rose from 20.2ºC to 33.9ºC. Calculate ΔH for the reaction given the specific heat capacity of water is 4.18 J mol^{-1} K^{-1}.

Answers

Full worked solutions are available to subscribers of www.chemsheets.co.uk.

Subscribe for many more exercises with answers.

___

TASK 1 – Calorimetry calculations 1

1   -1650 kJ mol^{-1} 2   -3710 kJ mol^{-1} 3   -1900 kJ mol^{-1}

4   -57.3 kJ mol^{-1} 5   -51.8 kJ mol^{-1} 6   -57.8 kJ mol^{-1}

7   -212 kJ mol^{-1} 8   -359 kJ mol^{-1} 9   +30.8 kJ mol^{-1}

10   -1984 kJ mol^{-1}

TASK 2 – Calorimetry calculations 2

1   -3800 kJ mol^{-1} 2   -51.8 kJ mol^{-1} 3   -2500 kJ mol^{-1}

4   +20.9 kJ mol^{-1} 5   -4203 kJ mol^{-1} 6   -3920 kJ mol^{-1}

7   -54.3 kJ mol^{-1} 8   -1145 kJ mol^{-1} 9   -1223 kJ mol^{-1}

10   -154 kJ mol^{-1} 11   exo, exo, endo   12   -503 kJ mol^{-1}

13   -685 kJ mol^{-1} 14   -126 kJ mol^{-1} 15   44.5°C

16   -2649 kJ mol^{-1}

CHALLENGE

1   299 cm^3 2   too good a challenge to give away the answer!!

TASK 3 – Hess's Law 1

1   +71 kJ mol^{-1}, -564 kJ mol^{-1}, -847 kJ mol^{-1}, -1410 kJ mol^{-1}, -846 kJ mol^{-1}

2   +51 kJ mol^{-1} 3   -85 kJ mol^{-1} 4   -149 kJ mol^{-1}

5   -452 kJ mol^{-1} 6   -70 kJ mol^{-1}

TASK 4 – Hess's Law 2

1   -2220 kJ mol^{-1} 2   +2 kJ mol^{-1} 3   -84 kJ mol^{-1}

4   -172 kJ mol^{-1} 5   -1820 kJ mol^{-1} 6   -1075 kJ mol^{-1}

7   -235 kJ mol^{-1}

TASK 5 – Hess's Law 3

1   -103 kJ mol^{-1}, -95 kJ mol^{-1}, -1076 kJ mol^{-1}, -698 kJ mol^{-1}

2   +391 kJ mol^{-1} 3   +598 kJ mol^{-1} 4   +836 kJ mol^{-1}

5   +300 kJ mol^{-1} 6   -39 kJ mol^{-1}

TASK 6 – Mixture

1   -129 kJ mol^{-1} 2   -2222 kJ mol^{-1} 3   -1194 kJ mol^{-1}

4   -2008 kJ mol^{-1} 5   -184 kJ mol^{-1} 6   -125 kJ mol^{-1}

7   -1669 kJ mol^{-1} 8   -57.3 kJ mol^{-1}