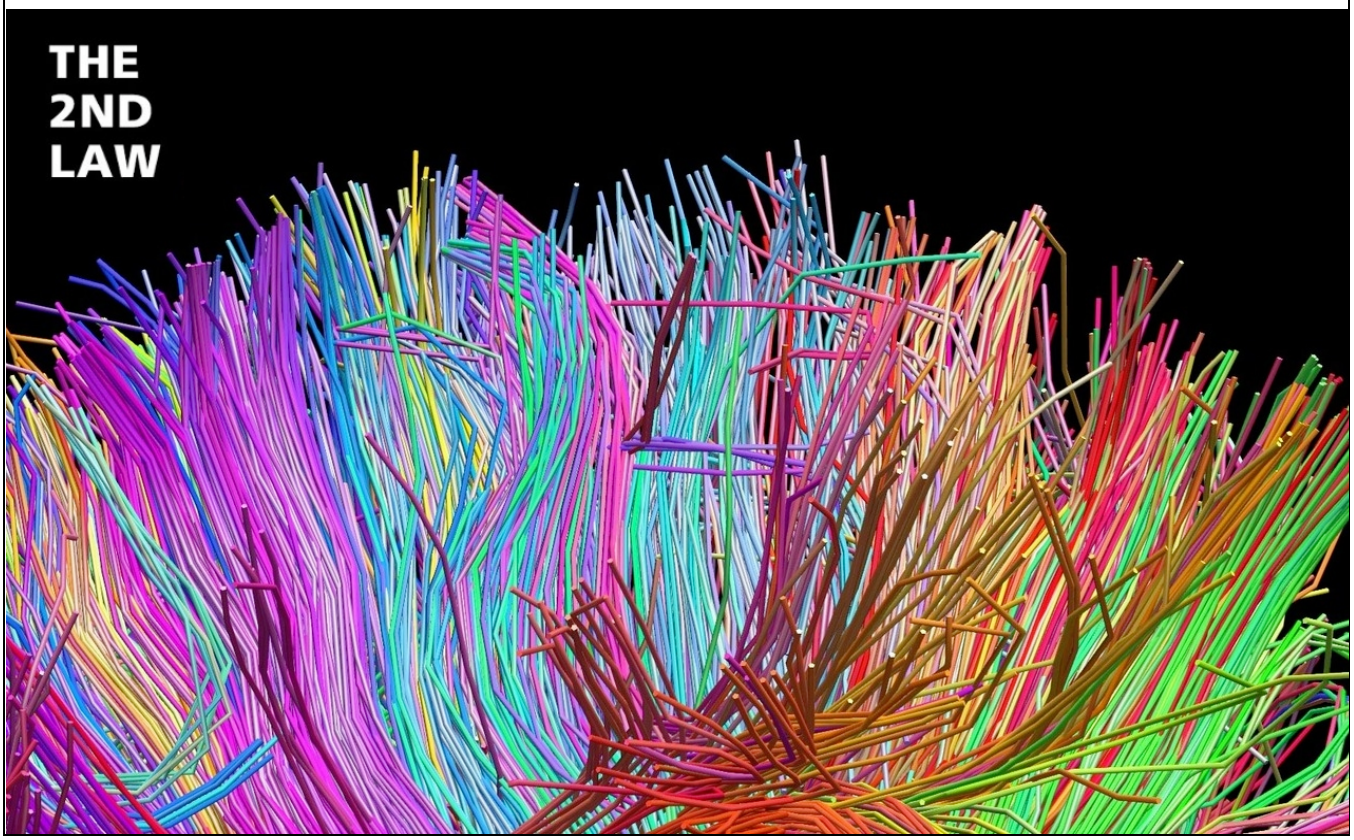
THERMODYNAMICS



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SECTION 1 – Recap of AS Energetics

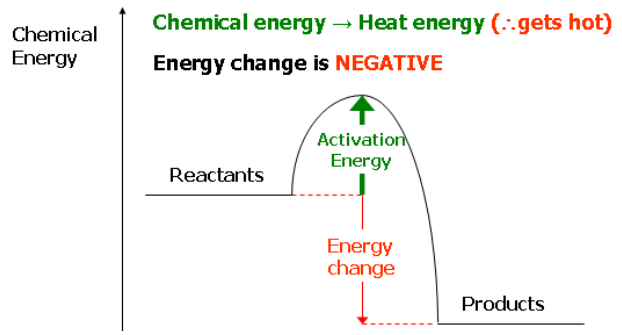
1) What is enthalpy?

- 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 (ΔH°) = *100 kPa and a stated temperature*

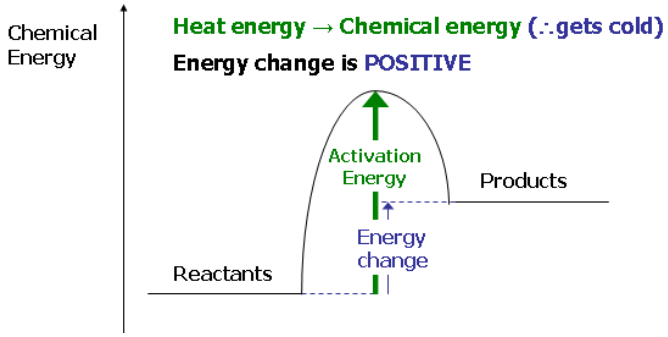
[Note that the symbol for standard conditions should be a circle with a horizontal line through it, but it is safer here to put a circle with no line as otherwise the character that may appear on the computer the document is from may substitute some random symbol!]

2) Reaction profiles

Exothermic reactions



Endothermic reactions



3) Standard enthalpy change of reaction ($\Delta_r H^{\circ}$) ("enthalpy of reaction")

This is the enthalpy change for a reaction with the quantities shown in the chemical equation. This means that the value should always be quoted along with the equation.

In this example, the second equation contains half the molar quantities of the first and so the $\Delta_r H^{\circ}$ value is half as much.

e.g. $H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$ $\quad \Delta_r H^{\circ} = -114.2\ kJ\ mol^{-1}$

$\frac{1}{2}\ H_2SO_4(aq) + NaOH(aq) \rightarrow \frac{1}{2}\ Na_2SO_4(aq) + H_2O(l)$ $\quad \Delta_r H^{\circ} = -57.1\ kJ\ mol^{-1}$

the value of $-114.2\ kJ\ mol^{-1}$ in the first equation means that 114.2 kJ of heat energy is released when 1 mole of H_2SO_4 reacts with 2 moles of NaOH.

the value of $-57.1\ kJ\ mol^{-1}$ in the second equation means that 57.1 kJ of heat energy is released when ½ mole of H_2SO_4 reacts with 1 mole of NaOH.

4) Standard enthalpy change of formation ($\Delta_f H°$) ("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 $\Delta_f H^o$ of an element in its standard state = *0 by definition*

5) Standard enthalpy change of combustion ($\Delta_c H^o$) ("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. $CH_4(g)$ ……

$H_2(g)$ ……

$C_2H_6(g)$ ……

$C_2H_5OH(l)$ ……

$Na(s)$ ……

$C_6H_{14}(l)$ ……

6) Standard enthalpy change of neutralisation ($\Delta_{neut} H°$) ("enthalpy of neutralisation")

Enthalpy change when 1 mole of water is formed in a reaction between an acid and alkali under standard conditions.

e.g. $HCl(aq) + NaOH(aq)$ ……

$H_2SO_4(aq) + NaOH(aq)$ ……

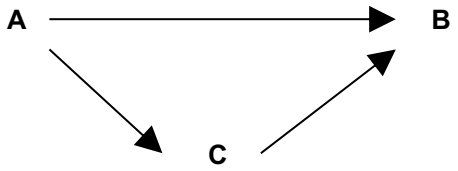
$HNO_3(aq) + KOH(aq)$ ……

$HNO_3(aq) + Ba(OH)_2(aq)$ ……

$H_2SO_4(aq) + Ba(OH)_2(aq)$……

Hess's Law Calculations

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



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

1) 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 $\Delta_f H$ products] – [SUM $\Delta_f H$ reactants]

- Remember that $\Delta_f H$ of all elements in their standard states 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 given the data that follows:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

$\Delta_f H$ $CH_4(g) = –75$, $CO_2(g) = –394$, $H_2O(l) = –286$ kJ/mol

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Example 2 The enthalpy change for the following reaction is –2877 kJ/mol:

$C_4H_{10}(g) + 6½\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l)$

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

$\Delta_f H$ $CO_2(g) = –394$, $H_2O(l) = –286$ kJ/mol

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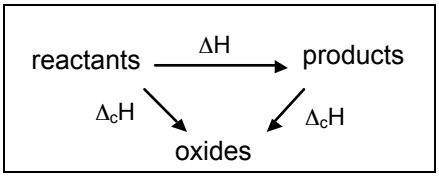
2) Calculations involving enthalpies of combustion ("Type 2 questions")

- Questions that involve enthalpies of combustion can usually be done using the cycle shown.
- 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.
- If you use a cycle like this, there is no need to worry about getting the number of oxygen molecules in the downward arrows.



Example 1 Calculate the enthalpy change for this reaction given the following data.

$C(s) + 2\ H_2(g) \rightarrow CH_4(g)$

Δ_cH C(s) = –394, $H_2(g)$ = –286, $CH_4(g)$ = –890 kJ/mol

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Example 2 Calculate the enthalpy of combustion of ethanol (C_2H_5OH) given the following enthalpy changes.

Δ_cH C(s) = –393, $H_2(g)$ = –286 kJ/mol Δ_fH $C_2H_5OH(l)$ = –75 kJ/mol

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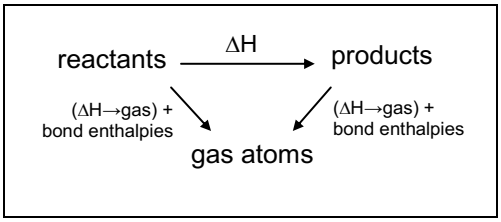
3) Calculations involving bond enthalpies ("Type 3 questions")

- 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.
- Mean bond enthalpy is the enthalpy change to break one mole of covalent bonds in the gas phase averaged over several compounds.
- 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.
- The following 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)
- 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.



Example 1 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

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Example 2 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

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4) Calorimetry calculations

- 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.

Example 1 In an experiment, 0.500 g of propan-1-ol (C_3H_7OH) was completely burned in air. The heat evolved raised the temperature of 100 g of water by 36.0°C. 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}).

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Example 2 25.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was added to 25.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution. The temperature rose by 6.7°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}.

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Example 3 50.0 cm^3 of 0.500 mol dm^{-3} copper sulphate solution was put in a calorimeter and 2.0 g of zinc powder added. The temperature of the solution rose by 24.0°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}.

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

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TASK 1 – AS Energetics Revision

1 Find $\Delta_f H$ of butane given that the following data.

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

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

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

$\Delta_f H$: $C_3H_8(g) = -104$, $CO_2(g) = -394$, $H_2O(l) = -286$ 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 $\Delta_c H$ of propan-2-ol given that the following data.

$\Delta_f H$: $CH_3CH(OH)CH_3(l) = -318$, $\Delta_c H$: $C(s) = -394$, $H_2(g) = -286$ kJ mol^{-1}

5 Calculate $\Delta_f H$ of $CCl_4(l)$ given the following data.

$CCl_4(l) \rightarrow CCl_4(g)$ = +31 kJ mol^{-1} $\quad$ $C(s) \rightarrow C(g)$ = +715 kJ mol^{-1}

Bond enthalpy (Cl-Cl) = +242 kJ mol^{-1} $\quad$ Bond enthalpy (C-Cl) = +338 kJ mol^{-1}

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

$CH_3CH{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$

$\Delta_c H$: $CH_3CH{=}CH_2(g) = -2059$, $H_2(g) = -286$, $CH_3CH_2CH_3(g) = -2220$ 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 25.0 cm^3 of 2.00 mol dm^{-3} nitric acid was reacted with 25.0 cm^3 of 2.00 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}.

9 The engines of the lunar module of Apollo 11 used methylhydrazine (CH_3NHNH_2) and dinitrogen tetraoxide. They react as follows:

$$4\ CH_3NHNH_2(l) + 5\ N_2O_4(l) \rightarrow 4\ CO_2(g) + 12\ H_2O(l) + 9\ N_2(g)$$

Calculate the enthalpy change for the reaction using the following data:

$\Delta_f H^o$: $CH_3NHNH_2(l) = +53$, $N_2O_4(l) = -20$, $CO_2(g) = -393$, $H_2O(l) = -286$ kJmol^{-1}

10 Calculate the average C-C bond enthalpy in benzene (C_6H_6) given the following data.

$\Delta_f H$ ($C_6H_6(l)$) = +49 kJmol^{-1}

$C(s) \rightarrow C(g)$ $\quad$ ΔH = +715 kJmol^{-1}

$H_2(g) \rightarrow 2\ H(g)$ $\quad$ ΔH = +436 kJmol^{-1}

$C_6H_6(l) \rightarrow C_6H_6(g)$ $\quad$ ΔH = +31 kJmol^{-1}

E (C-H) = +413 kJmol^{-1}

SECTION 2 – Definitions

Enthalpy change	Definition	Exo/endothermic	Example	
Enthalpy of formation ($\Delta_f H^o$):	Enthalpy change when **one mole** of a substance is formed from its constituent elements with all substances in their standard states	Exothermic (-ve) for most substances	e.g. $Na_2O(s)$	$2\ Na(s) + ½\ O_2(g) \rightarrow Na_2O(s)$
Enthalpy of combustion ($\Delta_c H^o$)	Enthalpy change when **one mole** of a substance undergoes complete combustion in oxygen with all substances in standard states	Exothermic (-ve)	e.g. hydrogen	$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$
Enthalpy of neutralisation ($\Delta_{neut} H^o$)	Enthalpy change when 1 mole of water is formed in a reaction between an acid and alkali under standard conditions	Exothermic (-ve)	e.g. H_2SO_4 + NaOH	$½H_2SO_4(aq) + NaOH(aq) \rightarrow ½Na_2SO_4(aq) + H_2O(l)$
Ionisation enthalpy ($\Delta_{ie} H^o$)	**First** ionisation energy = enthalpy change when each atom in one mole of **gaseous** atoms loses one electron to form one mole of **gaseous** 1+ ions.	Endothermic (+ve)	e.g. magnesium	$Mg(g) \rightarrow Mg^+(g) + e^-$
	Second ionisation energy = enthalpy change when each ion in one mole of **gaseous** 1+ ions loses one electron to form one mole of **gaseous** 2+ ions.	Endothermic (+ve)	e.g. magnesium	$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$
Electron affinity ($\Delta_{ea} H^o$)	**First** electron affinity = enthalpy change when each atom in one mole of **gaseous** atoms gains one electron to form one mole of **gaseous** 1– ions.	Exothermic (-ve) for many non-metals	e.g. oxygen	$O(g) + e^- \rightarrow O^-(g)$
	Second electron affinity = enthalpy change when each ion in one mole of **gaseous** 1– ions gains one electron to form one mole of **gaseous** 2– ions.	Endothermic (+ve) as adding –ve electron to –ve ion	e.g. oxygen	$O^-(g) + e^- \rightarrow O^{2-}(g)$
Enthalpy of atomisation ($\Delta_{at} H^o$)	Enthalpy change when **one mole of gaseous atoms** is produced from an element in its standard state.	Endothermic (+ve)	e.g. iodine	$½\ I_2(s) \rightarrow I(g)$
Hydration enthalpy ($\Delta_{hyd} H^o$)	Enthalpy change when one mole of **gaseous ions** become hydrated (dissolved in water).	Exothermic (-ve)	e.g. magnesium ions	$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$
Enthalpy of solution ($\Delta_{sol} H^o$)	Enthalpy change when one mole of an ionic **solid** dissolves in an amount of water large enough so that the dissolved ions are well separated and do not interact with each other.	Varies	e.g. magnesium chloride	$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2\ Cl^-(aq)$
Bond dissociation enthalpy ($\Delta_{dis} H^o$)	Enthalpy change when one mole of covalent bonds is broken in the **gaseous state**.	Endothermic (+ve)	e.g. I-I bond	$I_2(g) \rightarrow 2\ I(g)$
Lattice enthalpy of formation ($\Delta_{LEF} H^o$)	Enthalpy change when one mole of a **solid** ionic compound is <u>formed</u> from into its constituent ions in the **gas** phase	Exothermic (-ve)	e.g. magnesium chloride	$Mg^{2+}(g) + 2\ Cl^-(g) \rightarrow MgCl_2(s)$
Lattice enthalpy of dissociation ($\Delta_{LED} H^o$)	Enthalpy change when one mole of a **solid** ionic compound is <u>broken up</u> into its constituent ions in the **gas** phase	Endothermic (+ve)	e.g. magnesium chloride	$MgCl_2(s) \rightarrow Mg^{2+}(g) + 2\ Cl^-(g)$
Enthalpy of vaporisation ($\Delta_{vap} H^o$):	Enthalpy change when **one mole** of a liquid is turned into a gas	Endothermic (+ve)	e.g. $H_2O(l)$	$H_2O(l) \rightarrow H_2O(g)$
Enthalpy of fusion ($\Delta_{fus} H^o$):	Enthalpy change when **one mole** of a solid is turned into a liquid	Endothermic (+ve)	e.g. Mg(s)	$Mg(s) \rightarrow Mg(l)$

TASK 2 – Enthalpy Change Definitions

1 $\Delta_f H$ of $C_6H_6(l)$ ……

2 $\Delta_f H$ of $CH_3COOH(l)$ ……

3 $\Delta_c H$ of $H_2(g)$ ……

4 $\Delta_c H$ of $CH_3COOH(l)$ ……

5 1st ionisation energy of aluminium ……

6 2nd ionisation energy of aluminium ……

7 3rd ionisation energy of aluminium ……

8 1st electron affinity of chlorine ……

9 lattice enthalpy of formation of sodium oxide ……

10 lattice enthalpy of dissociation of aluminium oxide ……

11 $\Delta_{hyd} H$ of sodium ions ……

12 Enthalpy of vaporisation of bromine ……

13 $\Delta_{sol} H$ of sodium hydoxide ……

14 Enthalpy of fusion of sodium chloride ……

15 Bond dissociation enthalpy of water ……

16 Bond dissociation enthalpy of hydrogen ……

17 $\Delta_{atm} H$ of bromine ……

18 Bond dissociation enthalpy of bromine ……

19 1st electron affinity of bromine ……

20 2nd electron affinity of sulfur ……

TASK 3 – More Enthalpy Change Definitions

For each of the following reactions, name the enthalpy change. There may be more than one possible answer to some. Some answers may involve more than one enthalpy change!

e.g.1 $C(s) + 2\ H_2(g) \rightarrow CH_4(g)$ *enthalpy of formation of $CH_4(g)$*

e.g.2 $2\ CH_4(g) + 4\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l)$ *2 x enthalpy of combustion of $CH_4(g)$*

e.g.3 $H_2(g) + ½\ O_2(g) \rightarrow H_2O(g)$ *enthalpy of formation of $H_2O(l)$ + enthalpy of vaporisation of $H_2O(l)$*

1 $Ca(g) \rightarrow Ca^+(g) + e^-$ ……

2 $S(g) + 2\ e^- \rightarrow S^{2-}(g)$ ……

3 $Al_2O_3(s) \rightarrow 2\ Al^{3+}(g) + 3\ O^{2-}(g)$ ……

4 $NaBr(s) \rightarrow Na^+(aq) + Br^-(aq)$ ……

5 $I_2(s) \rightarrow 2\ I(g)$ ……

6 $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ ……

7 $4\ Al(s) + 3\ O_2(g) \rightarrow 2\ Al_2O_3(s)$ ……

8 $Ca^{2+}(g) + O^{2-}(g) \rightarrow CaO(s)$ ……

9 $Na(s) \rightarrow Na(g)$ ……

10 $P_4(s) \rightarrow 4\ P(g)$ ……

11 $HCl(g) \rightarrow H(g) + Cl(g)$ ……

12 $H_2O(l) \rightarrow 2\ H(g) + O(g)$ ……

13 $Al(g) \rightarrow Al^{3+}(g) + 3\ e^-$ ……

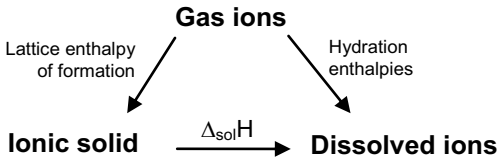
14 $Ca^{2+}(g) \rightarrow Ca^{2+}(aq)$ ……

15 $Mg(s) \rightarrow Mg^{2+}(g) + 2\ e^-$ ……

16 $Mg(s) + ½\ O_2(g) \rightarrow MgO(s)$ ……

SECTION 3 – Enthalpy of solution calculations

- This cycle works for questions involving enthalpies of solution. It is a simple cycle from a solid to gas ions to dissolved ions.
- Beware of whether the lattice enthalpy is formation or dissociation.



Example Calculate the enthalpy of solution of magnesium chloride given that the lattice enthalpy of formation of magnesium chloride is –2493 kJmol^{-1} and the enthalpies of hydration of magnesium and chloride ions are –1920 and –364 kJmol^{-1} respectively.

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TASK 4 – Enthalpy of solution calculations

1 Calculate the enthalpy of solution of NaCl given that the lattice enthalpy of formation of NaCl is –771 kJmol^{-1} and the enthalpies of hydration of sodium and chloride ions are –406 and –364 kJmol^{-1} respectively.

2 Calculate the enthalpy of hydration of bromide ions given that the hydration enthalpy of barium ions is –1360 kJmol^{-1}, the lattice enthalpy of formation for $BaBr_2$ is –1937 kJmol^{-1} and the enthalpy of solution of $BaBr_2$ = –38 kJmol^{-1}.

3 Calculate the lattice enthalpy of formation of calcium iodide given that its enthalpy of solution is –120 kJmol^{-1} and the enthalpies of hydration of calcium and iodide ions are –1650 and –293 kJmol^{-1} respectively.

4 Calculate the enthalpy of solution of the ammonium chloride using this data: ΔH_{hyd} (kJ mol^{-1}): NH_4^+ –301; Cl^- –364; Lattice enthalpy of dissociation (kJ mol^{-1}): ammonium chloride +640 kJ mol^{-1}.

SECTION 4 – Born-Haber cycles

Lattice enthalpy

- Lattice enthalpy represents the enthalpy change when the ions in one mole of a solid ionic compound are broken apart (lattice enthalpy of dissociation) or brought together (lattice enthalpy of formation).
- The lattice enthalpy of a compound is an indication of the strength of the ionic bonding – the greater the magnitude of the lattice enthalpy, the stronger the bonding.
- Generally speaking, compounds with smaller ions and/or ions with higher charges have stronger attractions and so greater lattice enthalpy.

  e.g. NaCl has a higher lattice enthalpy (and therefore stronger ionic bonding) than KCl as they Na^+ ion is smaller than the K^+ ion.

  e.g. $MgCl_2$ has a higher lattice enthalpy (and therefore stronger ionic bonding) than NaCl as the Mg^{2+} ion has a higher charge and is smaller than the Na^+ ion.

Example Place the following ionic compounds in order of decreasing magnitude of lattice enthalpy, and justify your reasoning: magnesium oxide, aluminium oxide, calcium oxide

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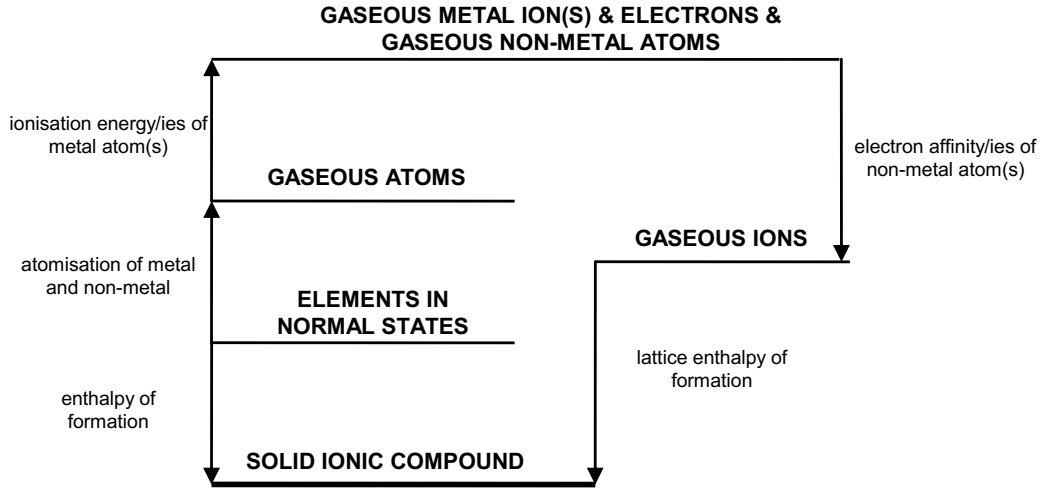
Measuring lattice enthalpy

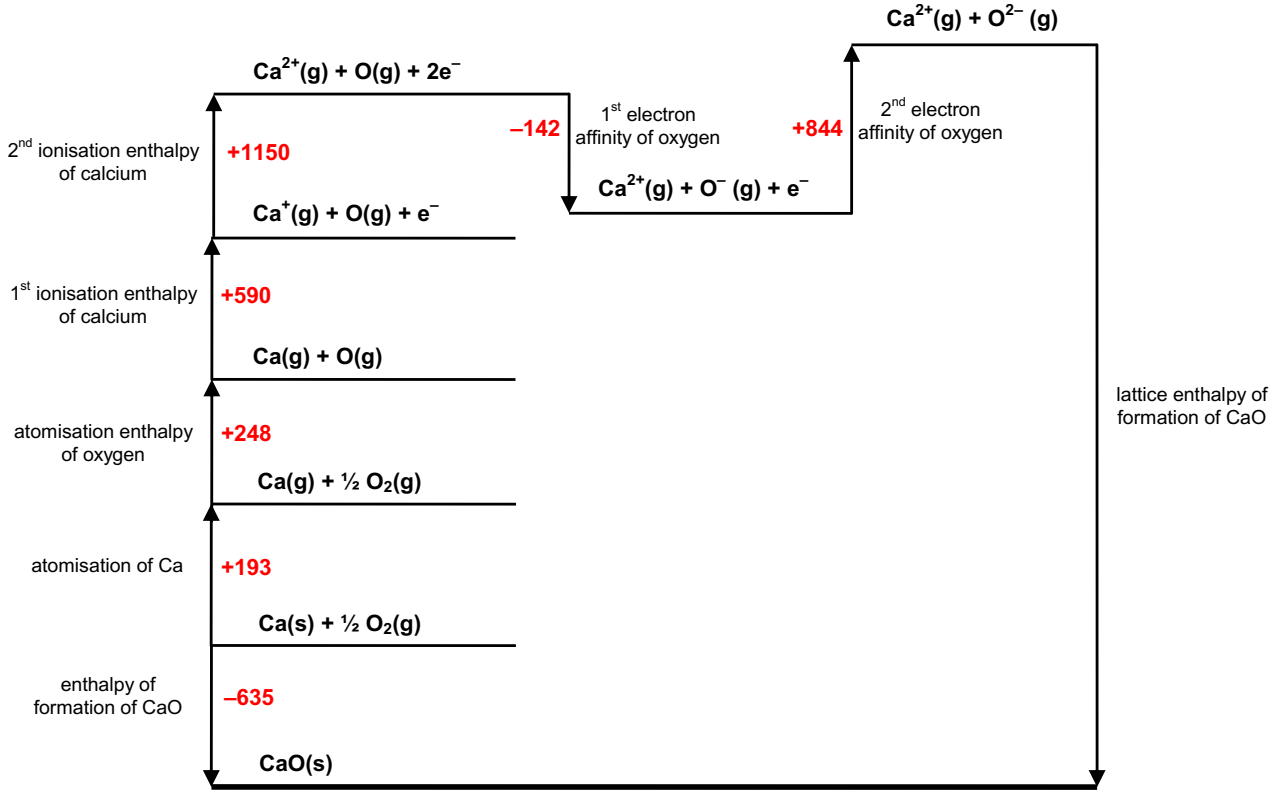
- The lattice enthalpy of a compound can be found using a Born-Haber cycle – this value is often called the 'experimental value' as the data used in the Born-Haber cycle is determined by experiments.
- A Born-Haber cycle is a cycle that includes all the enthalpy changes in the formation of an ionic compound.
- In these cycles, lattice enthalpy is usually shown as lattice enthalpy of formation (with –ve value) – this is so that an equation can be written where the enthalpy of formation of the ionic compound (not to be confused with the lattice enthalpy of formation) equals the sum of all the other enthalpy changes.
- Note that when drawing Born-Haber cycles:
  - draw a separate step for every enthalpy change (e.g. for atomisation of the metal atoms separately from the non-metal atoms, for each individual ionisation enthalpy, for each individual electron affinity)
  - second and third electron affinities are endothermic and shown be drawn going up not down
  - It is best to write the numerical values of the enthalpy changes on each step (you may also be asked to write the names of each step)



Enthalpy of formation = sum of all the other enthalpy values

Example 1 – Find the lattice enthalpy of formation of calcium oxide using a Born-Haber cycle and these enthalpy changes:

1st ionisation enthalpy of calcium = +590 kJ mol^{-1}
2nd ionisation enthalpy of calcium = +1150 kJ mol^{-1}
1st electron affinity of oxygen = –142 kJ mol^{-1}
2nd electron affinity of oxygen = +844 kJ mol^{-1}
atomisation enthalpy of calcium = +193 kJ mol^{-1}
atomisation enthalpy of oxygen = +248 kJ mol^{-1}
enthalpy of formation of calcium oxide = –635 kJ mol^{-1}



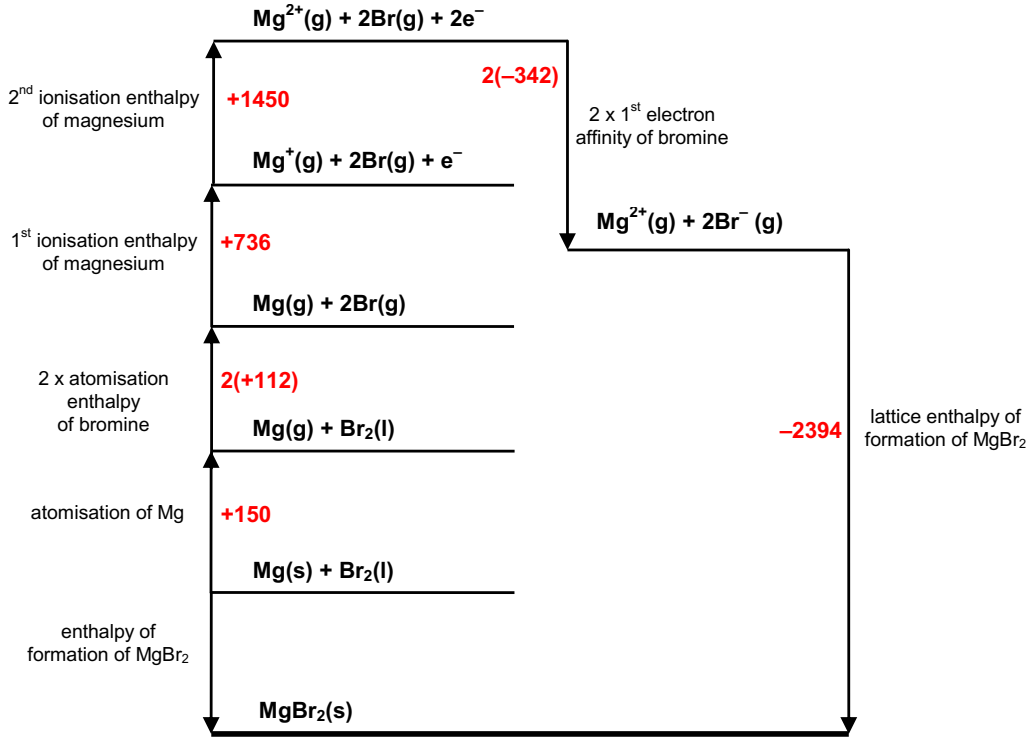
$\Delta_f H$ = sum of all the others

–635 = 193 + 248 + 590 + 1150 – 142 + 844 + LEF

LEF = – 635 – 193 – 248 – 590 – 1150 + 142 – 844 = **–3518 kJ mol^{-1}**

Example 2 – Find the enthalpy of formation of magnesium bromide using a Born-Haber cycle and these enthalpy changes:

1st ionisation enthalpy of magnesium = +736 kJ mol^{-1}
2nd ionisation enthalpy of magnesium = +1450 kJ mol^{-1}
1st electron affinity of bromine = –342 kJ mol^{-1}
atomisation enthalpy of magnesium = +150 kJ mol^{-1}
atomisation enthalpy of bromine = +112 kJ mol^{-1}
lattice enthalpy of formation of magnesium bromide = –2394 kJ mol^{-1}



$\Delta_f H$ = sum of all the others

$\Delta_f H$ = 150 + 2(112) + 736 + 1450 +2(–342) – 2394

$\Delta_f H$ = **–518 kJ mol^{-1}**

TASK 5 – Born-Haber cycle problems

Use this data in the questions that follow.

kJmol^{-1}	Na	K	Ca	Al	Co	Cu	Br	I	O	S	Cl
enthalpy of atomisation	+107	+90	+193	+314	+427		+112	+107	+248	+279	+121
1st ionisation enthalpy	+496	+418	+590	+577	+757	+745					
2nd ionisation enthalpy	+4562	+3070	+1150	+1820	+1640	+1960					
3rd ionisation enthalpy	+6910	+4600	+4940	+2740	+3230	+3550					
1st electron affinity							–342		–142	–200	–364
2nd electron affinity									+844	+649	

1 Calculate the enthalpy of formation of potassium chloride given that the lattice enthalpy of formation of potassium chloride is –710 kJmol^{-1}.

2 Calculate the lattice enthalpy of formation of sodium sulfide given that the enthalpy of formation of sodium sulfide is –370 kJmol^{-1}.

3 Calculate the enthalpy of formation of calcium bromide given that the lattice enthalpy of formation of calcium bromide is –2125 kJmol^{-1}.

4 Calculate the lattice enthalpy of formation of aluminium oxide given that the enthalpy of formation of aluminium oxide is –1669 kJmol^{-1}.

5 Calculate the first electron affinity of iodine given that the lattice enthalpy of dissociation of calcium iodide is +2054 kJmol^{-1} and its enthalpy of formation is –535 kJmol^{-1}.

6 Calculate the enthalpy of atomisation of copper given that the enthalpy of formation of CuO is –155 kJmol^{-1} and its lattice enthalpy of formation is –4149 kJmol^{-1}.

7 The lattice enthalpy of formation of the three possible chlorides of cobalt are given:

CoCl –700; $CoCl_2$ –2624; $CoCl_3$ –5350 kJmol^{-1}.

a) Using Born-Haber cycles, calculate the enthalpy of formation of each chloride.

b) Which of these chlorides is energetically stable with respect to their elements under standard conditions?

c) Which compound is likely to be formed when cobalt and chlorine react under normal conditions?

Comparing experimental to theoretical lattice enthalpy values

	Experimental lattice enthalpy	Theoretical lattice enthalpy (the perfect ionic model)
How is it calculated?	**Using a Born-Haber cycle** (all the other ΔH values are found by accurate measurement in experiments)	**By a theoretical calculation** that considers the size, charge and arrangement of ions in the lattice. It is assumed that the structure is perfectly ionic. This is a complex calculation and makes use of the Born-Landé equation (you do **not** need to know this equation) $E = -\frac{N_A M z^+ z^- q_e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$
Which is the real value?	The real value	

- There is often some distortion of the ions in an ionic compounds (i.e. they are polarised) – this means that the ions are not perfectly spherical. If there is a lot of distortion then the ions are said to have **some covalent character**. This does not mean that the compound is covalent – it is still ionic but the ions are not perfectly spherical.
- Positive ions (cations) that are small and/or highly charged are very good at distorting (i.e. they are very good at polarising) negative ions.
- Negative ions (anions) that are large and/or highly charged are easier to distort (i.e they are polarisable).
- Ionic compounds that have some covalent character often have low solubility in water (or are insoluble) and their melting points and electrical conductivity may not be as high as expected.
- Generally, the bigger the difference between the experimental and theoretical values of lattice enthalpy, the greater the covalent character of an ionic compound. If the difference is small the compound will have almost spherical ions, but if it is significant then the compound has some covalent character due to distorted ions.

Substance	NaCl	LiCl	LiI	MgO	AgCl	Al_2O_3
Experimental value (from Born-Haber cycle) / kJ mol^{-1}	–771	–846	–744	–3513	–905	–15421
Theoretical value / kJ mol^{-1}	–766	–833	–728	–3477	–770	–14910
Difference / kJ mol^{-1}	5	13	16	36	135	511
% Difference	0.6%	1.5%	2.2%	1.0%	14.9%	3.3%

  - For NaCl, the difference is only 0.6% indicating that the bonding is almost pure ionic with very little covalent character at all.
  - For LiCl, the difference is 1.5% indicating that the bonding is still very ionic but with a little more covalent character than NaCl, as the Li^+ is very smaller than Na^+ and so Li^+ is better at polarising negative ions.
  - For LiI, the difference is 2.2% indicating that the bonding is still very ionic but with a little more covalent character than LiCl, as the I^- is bigger than Cl^- and so more easily polarised.
  - For AgCl, the difference is 14.9% indicating significant covalent character.

- Note that:
  - The magnitude of the lattice enthalpy indicates the overall strength of the ionic bonding.
  - The difference between the experimental and theoretical value indicates the amount of covalent character.

Compounds being compared	Strongest ionic bonding (the biggest magnitude of lattice enthalpy)	Most covalent character (biggest difference between experimental and theoretical value
Al_2O_3 and MgO	Al_2O_3	Al_2O_3
Al_2O_3 and AgCl	Al_2O_3	AgCl

TASK 6 – Lattice enthalpy problems

1 Use the data in the table below to answer the questions that follow. The data refers to values of lattice enthalpies.

Substance	LiBr	NaBr	AgBr
Experimental value / kJ mol^{-1}	-800	-733	-890
Theoretical value / kJ mol^{-1}	-787	-732	-758

a) Are these values lattice enthalpies of dissociation or formation? Explain your answer.

b) Which of these compounds has the strongest ionic bonding? How can you tell?

c) Which of these compounds has the most covalent character? How can you tell?

d) Silver bromide is insoluble in water but sodium bromide is soluble. Suggest why this is the case using this data.

2 The lattice enthalpy of dissociation of calcium oxide calculated using a Born-Haber cycle is 3513 kJ mol^{-1}. The value calculated using the perfect ionic model is 3477 kJ mol^{-1}.

a) Calculate the percentage difference between these two values as a percentage of the actual value.

b) Calcium oxide is insoluble in water. Suggest why.

3 The theoretical value for the lattice enthalpy of formation of silver iodide is –736 kJ mol^{-1}.

a) Construct a Born-Haber cycle to calculate the lattice enthalpy of formation of silver iodide.

1st electron affinity of iodine = –314 kJ mol^{-1}
1st ionisation enthalpy of silver = +732 kJ mol^{-1}
enthalpy of formation of silver iodide = –62 kJ mol^{-1}
atomisation enthalpy of silver = +289 kJ mol^{-1}
atomisation enthalpy of iodine = +107 kJ mol^{-1}

b) How is the theoretical value for the lattice enthalpy of formation of silver iodide calculated?

c) Which is the true value of the lattice enthalpy of formation of silver iodide?

d) Silver iodide is insoluble in water. Explain why this may be the case.

SECTION 5 – Entropy

What is entropy?

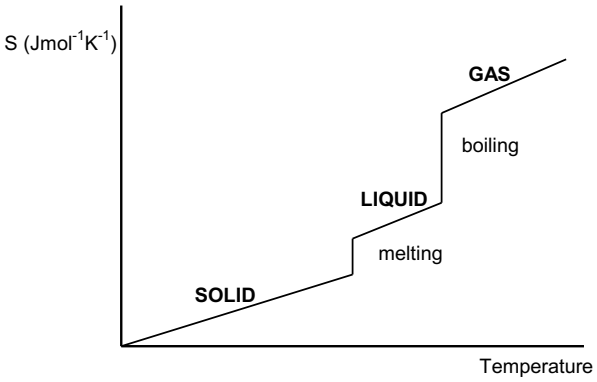
- Entropy (S) is disorder. The more disordered (or random) something is, the greater the entropy.
- Entropy is measured in J mol^{-1} K^{-1}.
- Gases have the most entropy (particles are move rapidly and randomly) whereas solids have least entropy (particles vibrating about fixed positions).
- There is a tendency for entropy to increase, i.e. for things to become more disordered. The 2nd law of thermodynamics is that over time entropy will naturally increase.

How does the entropy of a substance vary with temperature?

- The 3rd law of thermodynamics states that the entropy of a substance is zero (or close to zero) at absolute zero and increases with temperature.
- The higher the temperature, the faster the particles vibrate/move and so the greater the entropy (disorder).
- Gases have the most entropy (particles are move rapidly and randomly) whereas solids have least entropy (particles vibrating about fixed positions).

S (gas) > S (liquid) > S (solid)

- The variation with temperature and state of a substance is shown. Note how:
  - entropy increases with temperature
  - there are big increases in entropy on state changes (melting and boiling)
  - the entropy increase from liquid to gas is greater than that for solid to liquid due to the large amount of disorder in gases compared to solids and liquids.



How does the entropy of different substances compare?

- The more ordered the structure the lower the entropy.
- Structures like diamond and graphite are very highly structured and so have very low entropy.

substance	S ($Jmol^{-1}K^{-1}$)
C (diamond)	2
C (graphite)	6
SiO_2 (s)	42
H_2O (l)	70
NaCl (s)	72
$MgCl_2$ (s)	90
H_2O (g)	189
CO_2 (g)	214

Calculating entropy changes (ΔS)

- We can calculate the entropy change (ΔS) for a reaction.

$$\Delta S = [\text{SUM } S_{products}] - [\text{SUM } S_{reactants}]$$

- In reactions where there is an increase in entropy, ΔS is positive.
- In reactions where there is a decrease in entropy, ΔS is negative.
- In keeping with the 2nd law of thermodynamics, reactions in which there is an increase in entropy are favourable.

Example Calculate the entropy change for this reaction: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

S (J mol^{-1} K^{-1}): $C_2H_5OH(l) = 161$, $O_2(g) = 205$, $CO_2(g) = 214$, $H_2O(l) = 70$

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- For many reactions it is possible to tell whether entropy will increase or decrease by looking at the equation. However, sometimes you will predict that there will only be a small change in entropy (and you cannot tell if it will be positive or negative).

Example Predict whether the entropy change for these reaction will be positive or negative:

a) $NH_4NO_3(s) \rightarrow N_2O(g) + 2\,H_2O(g)$

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b) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

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TASK 7 – Entropy change calculations

1 Sketch a graph to show how the entropy of ammonia changes with temperature as it risers from absolute zero to 20ºC. The melting point of ammonia is -78ºC and the boiling point is -33ºC.

2 Predict whether there will be an increase in entropy in each of the following reactions, or whether the change will be small and so you are unable to tell. Explain your answer in each case.

a) $NaCl(s) \rightarrow NaCl(aq)$

b) $NaCl(l) \rightarrow NaCl(s)$

c) $2O_3(g) \rightarrow 3O_2(g)$

d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

e) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

f) $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$

g) $Ba(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KNO_3(aq)$

3 Calculate the entropy change in each of the following reactions. Use the entropy data below.

a) $H_2O(g) \rightarrow H_2O(l)$

b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

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

d) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$

Substance	$H_2O(g)$	$H_2O(l)$	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
Entropy (J mol^{-1} K^{-1})	189	70	93	40	214
Substance	$C_3H_8(g)$	$O_2(g)$	$Fe_2O_3(s)$	$CO(g)$	$Fe(l)$
Entropy (J mol^{-1} K^{-1})	270	205	90	198	35

SECTION 6 – Gibbs free energy change & feasibility

What is Gibbs free energy change?

- Gibbs free energy change (ΔG) combines the two thermodynamic factors of enthalpy change (ΔH) and entropy change (ΔS).

$$\Delta G = \Delta H - T\Delta S$$

- A decrease in enthalpy (i.e. ΔH being negative, i.e. an exothermic reaction) is more favourable in a reaction.
- An increase in entropy (i.e. ΔS being positive) is more favourable in a reaction.
- Overall, if ΔG is less than or equal to zero ($\Delta G \leq 0$) then a reaction is **feasible**.
- The term **feasible** means that a reaction can take place. If it is not feasible then it cannot take place.
- Note that whether a reaction is feasible or not depends on temperature, and reactions are often feasible at one temperature but not at another. The point at which a reaction switches from being feasible to not feasible is when $\Delta G = 0$.
- A reaction that is feasible may not actually take place due to having a very high activation energy.
- The term **spontaneous** is sometimes used in place of feasible. It has the same meaning in this context, meaning that a reaction is thermodynamically possible (but does not mean that it will actually happen). The term spontaneous is a little misleading and the term feasible better describes the situation.

How does temperature affect feasibility?

ΔH	ΔS	How ΔG varies with temperature	How feasibility varies with temperature
-ve	+ve	ΔG always -ve	feasible at all temperatures
-ve	-ve	lower T: ΔG -ve higher T: ΔG +ve	lower T: feasible higher T: not feasible
+ve	+ve	lower T: ΔG +ve higher T: ΔG -ve	lower T: not feasible higher T: feasible
+ve	-ve	ΔG always +ve	never feasible at any temperature

Example: Zinc carbonate decomposes on heating: $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

	$ZnCO_3(s)$	$ZnO(s)$	$CO_2(g)$
$\Delta_f H$ (kJ mol^{-1})	-812	-348	-394
S (J mol^{-1} K^{-1})	83.0	44.0	214

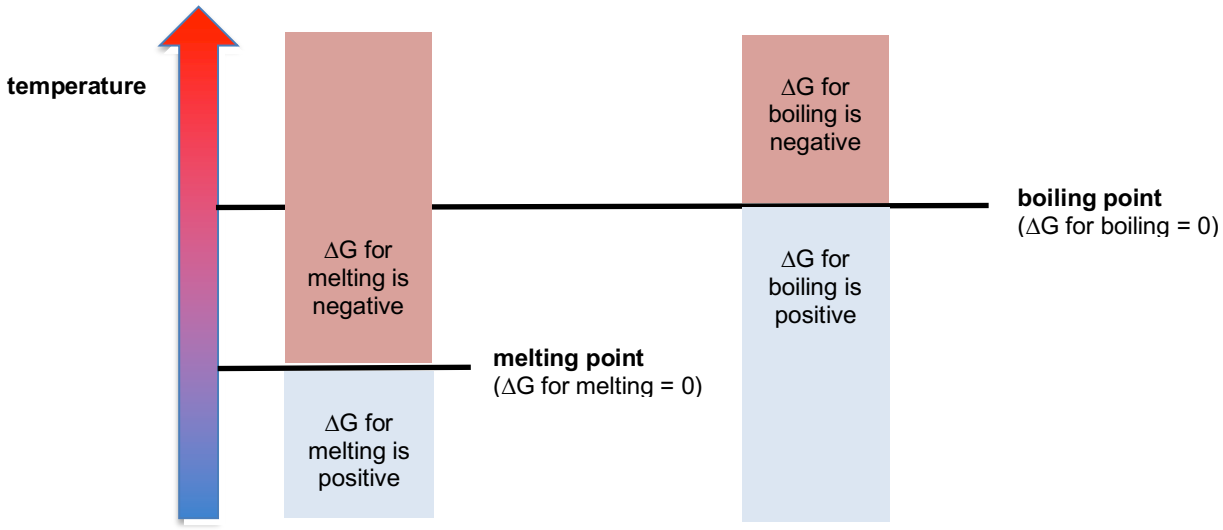
a) Calculate ΔH, ΔS and ΔG for this reaction at 298 K.

b) Is the reaction feasible at 298 K?

c) Give the temperature range in which the decomposition of $ZnCO_3$ is feasible.

Changes of state

- Changes of state are controlled in the same way.
- Below the melting point of a substance, melting is not feasible as ΔG is positive, but at the melting point it $\Delta G = 0$ and so melting becomes feasible and the substance melts.
- In a similar way, below the boiling point of a substance, boiling is not feasible as ΔG is positive, but at the boiling point it $\Delta G = 0$ and so boiling becomes feasible and the substance boils.



Example: The enthalpy change for melting potassium chloride is +25.5 kJ mol^{-1}, and the entropy change is +24.5 J mol^{-1} K^{-1}. Calculate the temperature at which potassium chloride melts.

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Example: The enthalpy of vaporisation of ethanol is +43.5 kJ mol^{-1}. The boiling point of ethanol is 78°C. Calculate the entropy change for the vaporisation of ethanol.

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TASK 8 – Gibbs free energy calculations

Use this data in the questions that follow.

substance	S (J mol^{-1} K^{-1})	ΔH_f (kJ mol^{-1})
$H_2O(g)$	189	–242
$H_2O(l)$	70.0	
$H_2(g)$	131	
$Cl_2(g)$	223	
$HCl(g)$	187	
$NaHCO_3(s)$	102	–948
$Na_2CO_3(s)$	136	–1131
$C_3H_8(g)$	270	

substance	S (J mol^{-1} K^{-1})	ΔH_f (kJ mol^{-1})
Fe(s)	27.0	
$O_2(g)$	205	
$Fe_2O_3(s)$	90.0	–822
C(graphite)	5.7	
$CO_2(g)$	214	–394
$N_2(g)$	192	
$NH_3(g)$	193	

1 a) Calculate ΔG for the following reaction at 298 K.

$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ $\Delta H = -185$ kJ mol^{-1} $\Delta S = 20.0$ J K^{-1} mol^{-1}

b) Is this reaction feasible at 298 K?

c) Why does this reaction not happen at room temperature?

2 For the decomposition: $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

a) Calculate ΔH and ΔS.

b) Calculate ΔG at 298 K.

c) Calculate the temperature range over which the reaction is feasible.

3 For the reaction: $2\ Fe(s) + {}^3/_2\ O_2(g) \rightarrow Fe_2O_3(s)$

a) Calculate ΔH and ΔS.

b) Calculate ΔG at 298 K.

c) Calculate the temperature range over which the reaction is feasible.

4 a) Calculate ΔS for this reaction at 298 K: $Mg(s) + ½\ O_2(g) \rightarrow MgO(s)$

$\Delta H = -602$ kJ mol^{-1} $\Delta G = -570$ kJ mol^{-1}

b) Explain the sign and magnitude of ΔS.

5 a) Calculate ΔH, ΔS and ΔG for the following reaction at 298 K:

$Fe_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Fe(s) + 3\ H_2O(g)$

b) Will this reaction be feasible at 298K?

c) Calculate the temperature range over which the reaction is feasible.

6 a) Calculate ΔS for the following process which takes place 91 K:

$CH_4(s) \rightarrow CH_4(l)$ $\Delta H = 0.94\ kJmol^{-1}$

b) Calculate the boiling point of methane given:

$CH_4(l) \rightarrow CH_4(g)$ $\Delta H = 8.2\ kJmol^{-1}$ $\Delta S = 73.2\ Jmol^{-1}K^{-1}$

c) Compare the magnitude of the ΔS values for melting and boiling methane and comment on the difference.

d) Explain why both melting and boiling are feasible at the temperatures shown, despite being endothermic.

7 The following enthalpy changes are at 298 K:

ΔH_{hyd} ($kJmol^{-1}$): K^+ -322; Cl^- –364 Lattice enthalpy KCl = –701 $kJmol^{-1}$

a) Calculate the standard enthalpy of solution of potassium chloride at 298 K.

b) Potassium chloride dissolves readily in water at 298 K. Deduce the **sign** of the entropy change for this reaction, and explain your reasoning.

c) Explain, in terms of the behaviour of particles, why the entropy change has the sign given in your answer to (b).

d) Use your answer to (a) to calculate the smallest possible entropy change there must be when potassium chloride dissolves in water at 298 K, given that it is a feasible change.

8 Use the data in the table to answer this question.

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$	$MgCO_3(s)$	$MgO(s)$
ΔH_f ($kJ\ mol^{-1}$)	-1207	-635	-394	-1113	-602
S ($J\ mol^{-1}\ K^{-1}$)	90	40	214	66	27

a) Calcium carbonate can decompose as shown: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

i) Calculate ΔH for this reaction.

ii) Calculate ΔS for this reaction.

iii) Calculate ΔG for this reaction at 298 K.

iv) Is the reaction spontaneous at 298 K?

v) Will increasing or decreasing the temperature help to make ΔG more negative?

vi) At what temperature will ΔG equal zero?

vii) Give the temperature range in which the decomposition of $CaCO_3$ is spontaneous.

viii) How can this reaction be spontaneous even though it is endothermic?

b) Repeat your calculations for the decomposition of $MgCO_3$ to find the temperature at which is undergoes similar decomposition.

c) i) Use your results to compare the thermal stability of $MgCO_3$ and $CaCO_3$.

ii) Suggest a reason for the difference in thermal stability of $MgCO_3$ and $CaCO_3$.

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PAGE 3 EXAMPLES

$C(s) + 2\ H_2(g) \rightarrow CH_4(g)$

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$

$½\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$

$2\ C(s) + 3\ H_2(g) + ½\ O_2(g) \rightarrow C_2H_5OH(l)$

$C(s) + 3/2\ H_2(g) + ½\ Br_2(l) \rightarrow CH_3Br(l)$

$2\ Na(s) + ½\ O_2(g) \rightarrow Na_2O(s)$

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$

$C_2H_6(g) + 3½\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$

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

$Na(s) + ¼\ O_2(g) \rightarrow ½\ Na_2O(s)$

$C_6H_{14}(g) + 9½\ O_2(g) \rightarrow 6\ CO_2(g) + 7\ H_2O(l)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$½H_2SO_4(aq) + NaOH(aq) \rightarrow ½\ Na_2SO_4(aq) + H_2O(l)$

$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

$HNO_3(aq) + ½Ba(OH)_2(aq) \rightarrow ½\ Ba(NO_3)_2(aq) + H_2O(l)$

$½H_2SO_4(aq) + ½Ba(OH)_2(aq) \rightarrow ½BaSO_4(aq) + H_2O(l)$

PAGE 4 EXAMPLES

Ex1 **–891 kJ mol^{-1}**

Ex2 **–129 kJ mol^{-1}**

PAGE 5 EXAMPLES

Ex1 **–76 kJ mol^{-1}**

Ex2 **–1571 kJ mol^{-1}**

PAGE 6/7 EXAMPLES

Ex1 **+163 kJ mol^{-1}**

Ex2 **+314 kJ mol^{-1}**

PAGE 8 EXAMPLES

Ex1 **– 1810 kJ mol^{-1} (3sf)**

Ex2 **– 56 kJ mol^{-1} (2sf)**

Ex3 **– 201 kJ mol^{-1} (3sf)**

TASK 1 – AS Energetics Revision

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 -1700 kJ mol^{-1} (2sf)
8 -57.3 kJ mol^{-1} (3sf)
9 -5116 kJ mol^{-1}
10 +507 kJ mol^{-1}

TASK 4 – Enthalpy of solution calculations

1 +1 kJ mol^{-1}
2 -307.5 kJ mol^{-1}
3 -2116 kJ mol^{-1}
4 -25 kJ mol^{-1}

TASK 5 – Born-Haber cycle problems

1 -445 kJ mol^{-1}
2 -2304 kJ mol^{-1}
3 -652 kJ mol^{-1}
4 -15421 kJ mol^{-1}
5 -314 kJ mol^{-1}
6 +339 kJ mol^{-1}
6 CoCl = +241 kJ mol^{-1}, $CoCl_2$ = -286 kJ mol^{-1}, $CoCl_3$ = -25 kJ mol^{-1}

TASK 6 – Lattice enthalpy problems

1 a) formation – as energy is released when electrostatic attractions between ions form
b) silver bromide – greatest magnitude of lattice enthalpy (using real values, i.e. the experimental values)
c) silver bromide – greatest difference between experimental and theoretical lattice enthalpy values
d) silver bromide has significant covalent character

2 a) 100 x 36/3513 = 1.02%
b) high lattice enthalpy (NB – not due to covalent character as it is only small)

3 a) see full answers
b) using the charge and size of ions assuming that the structure is perfectly ionic
c) –876 kJ mol^{-1}
d) significant covalent character

PAGE 21 EXAMPLES

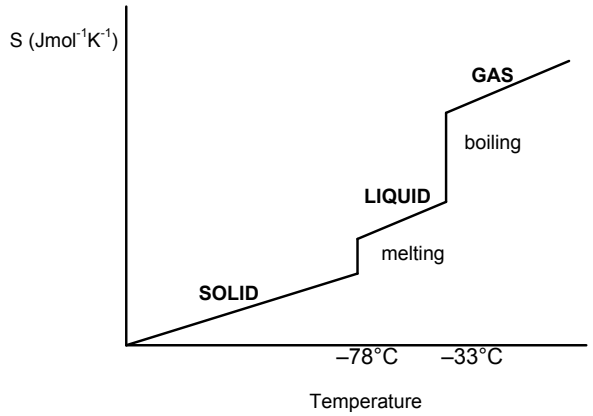
ΔS = –138 kJ mol^{-1}

$NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(g)$ increase as go from 1 mole of solid to 2 moles of gas

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ close to zero as go from 3 moles of gas to 3 moles of gas

TASK 7 – Entropy change calculations

1



2 a) increase as go from one mole of solid to two moles of aqueous ions (one mole of $Na^+(aq)$ and one mole of $Cl^-(aq)$)

b) decrease as go from one mole of liquid to one mole of solid

c) increase as go from two moles of gas to three moles of gas

d) decrease as go from four moles of gas to two moles of gas

e) close to zero as go from two moles of gas to two moles of gas

f) increase as go from one mole of solid to one mole of solid and one mole of gas

g) decrease as go from six moles of aqueous ions (Ba^{2+}, $2NO_3^-$, $2K^+$, SO_4^{2-}) to four moles of aqueous ions ($2K^+$, $2NO_3^-$) and one mole of solid

3 a) ΔS = –119 J mol^{-1} K^{-1}

b) ΔS = +161 J mol^{-1} K^{-1}

c) ΔS = –373 J mol^{-1} K^{-1}

d) ΔS = +28 J mol^{-1} K^{-1}

PAGE 24 EXAMPLE

a) ΔH = +70 kJ mol^{-1}, ΔS = +175 J mol^{-1} K^{-1} ΔG = +17.9 kJ mol^{-1}

b) Reaction is not feasible at 298 K (as ΔG is positive)

c) Reaction is feasible at temperatures greater and above 400 K (2 sf)

PAGE 25 EXAMPLES

Ex1 T = 1040 K (3 sf)

Ex2 ΔS = 124 J mol^{-1} K^{-1} (allow 2 or 3 sf)

TASK 8 – Gibbs free energy calculations

1 a) -191 kJ mol^{-1} (3sf), b) yes, feasible, c) high activation energy

2 a) ΔH = +129 kJ mol^{-1}, ΔS = +335 J mol^{-1} K^{-1}, b) +29.2 kJ mol^{-1} (3sf), c) T ≥ 385 K (3sf)

3 a) ΔH = -822 kJ mol^{-1}, ΔS = -272 J mol^{-1} K^{-1}, b) ΔG = -741 kJ mol^{-1} (3sf), c) T ≤ 3030 K (3sf)

4 a) ΔS = -107 J mol^{-1} K^{-1}

5 a) ΔH = +96 kJ mol^{-1}, ΔS = +138 J mol^{-1} K^{-1}, ΔG = +54.9 kJ mol^{-1} (3sf), b) no, c) T ≥ 696 K (3sf)

6 a) ΔS = +10 J mol^{-1} K^{-1} (2sf), b) 110 K (2sf)

7 a) ΔH = +15 kJ mol^{-1}, d) ΔS = +50.3 J mol^{-1} K^{-1}

8 a) ΔH = +178 kJ mol^{-1}, ΔS = +164 J mol^{-1} K^{-1}, ΔG = +129 kJ mol^{-1} (3sf), T ≥ 1090 K (3sf)

b) ΔH = +117 kJ mol^{-1}, ΔS = +175 J mol^{-1} K^{-1}, ΔG = +64.9 kJ mol^{-1} (3sf), T ≥ 669 K (3sf)