Energetics

Ms. Peace

Lesson 1

5.1 Measuring Enthalpy Changes

Main
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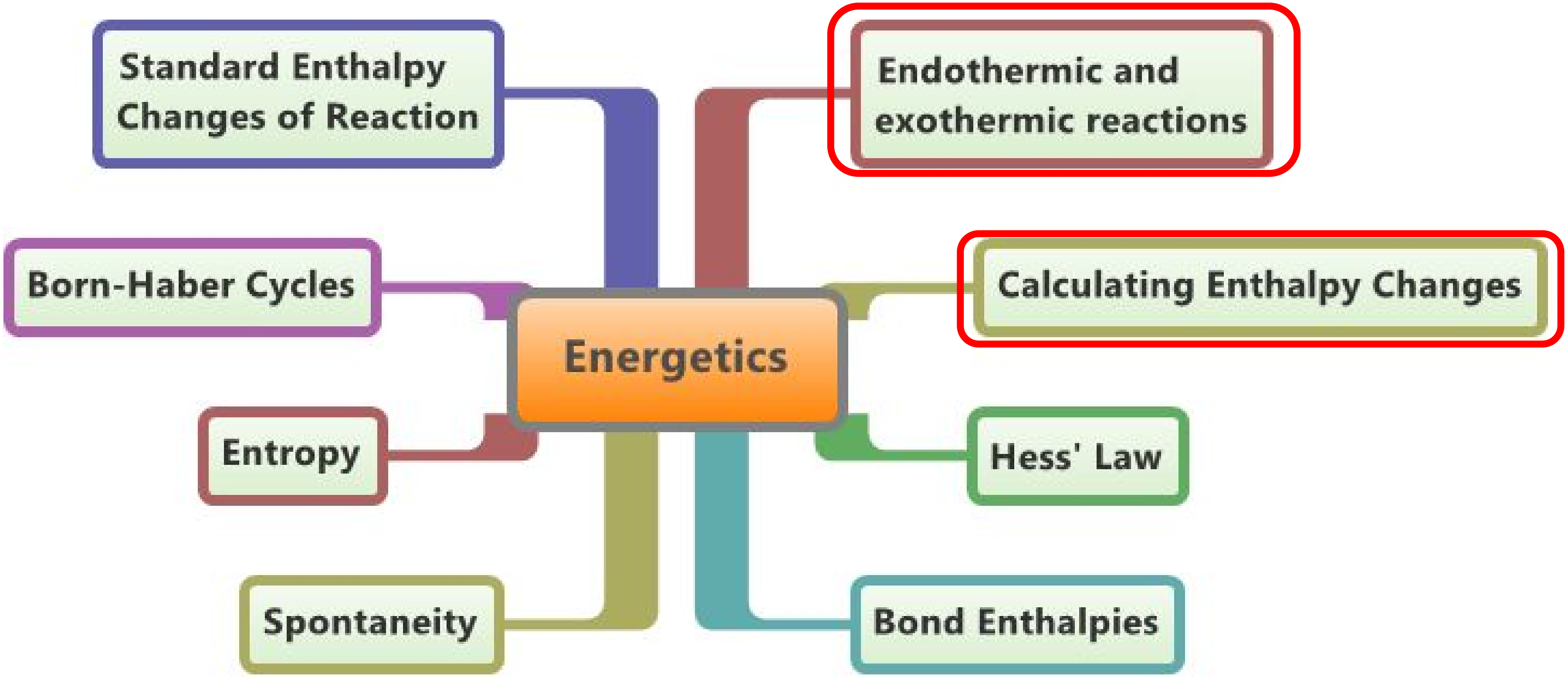


Energetics

Standard Enthalpy Changes of Reaction

Born-Haber Cycles

Entropy

Spontaneity

Endothermic and exothermic reactions

Calculating Enthalpy Changes

Hess' Law

Bond Enthalpies

Chemical Potential Energy, Heat, and Entropy

- Chemical potential energy is stored in the chemical bonds of reactants and products

- The temperature of the reacting mixture is a function of the kinetic energy of the atoms, ions, and molecules present.

- Heat, q, is a form of energy that flows from something at a higher temperature to something at a lower temperature

Main

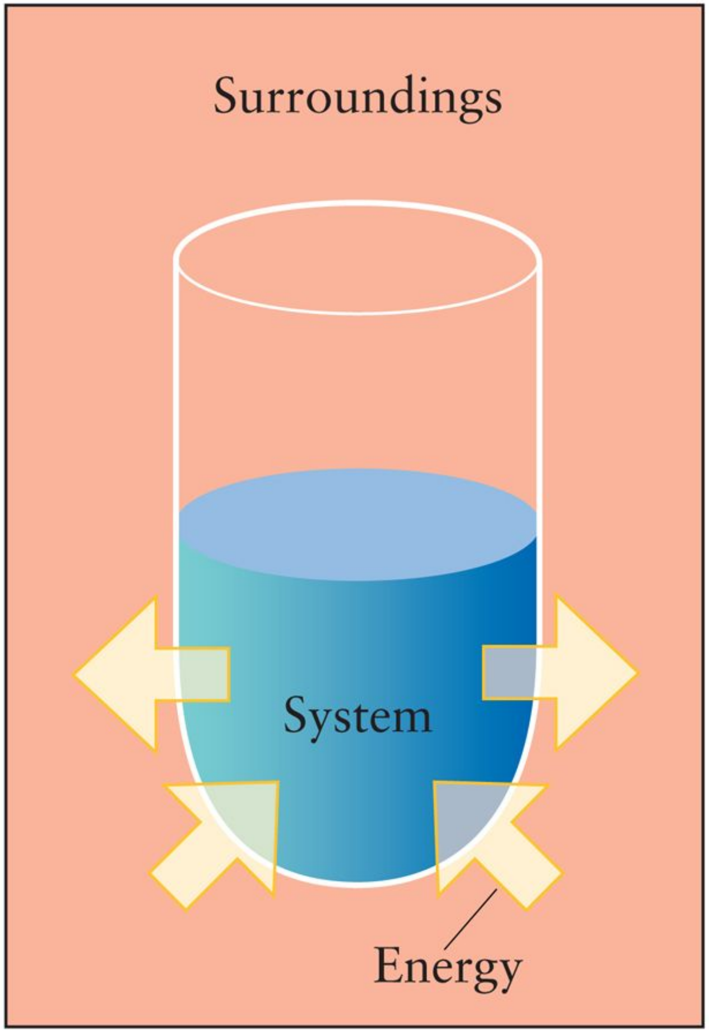
Heat and Temperature

- Heat is referred to as thermal energy, and has the ability to do work
- When heat is transferred to an object, the result is an increase in the average kinetic energy of its particles, and therefore an increase in its temperature or a change in phase
- Temperature is a measure of average kinetic energy of particles
- Internal energy is the name given to the total amount of energy in a substance. Total energy is conserved in a chemical reaction

Main

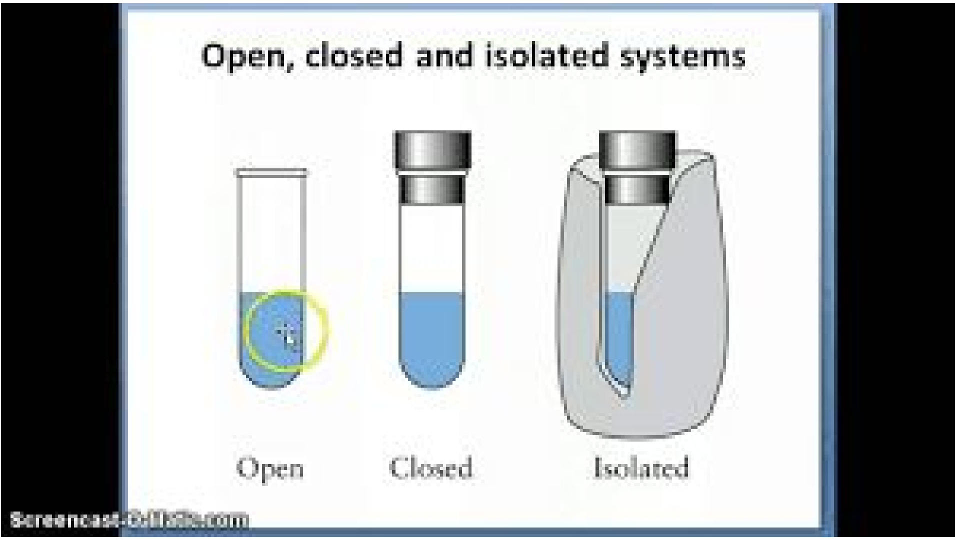
Chemical Energy

- System: reactants, products, and solvents
- Surroundings: the apparatus that contains the reaction, thermometers, any other measuring devices, the laboratory, everything external to the reacting substance



Systems

- Open system: the transfer and energy is possible across its boundary
- Closed system: allows no transfer of matter, though energy may be transferred across the boundary
- Isolated system: matter can neither enter nor exit but can only move around inside



Main

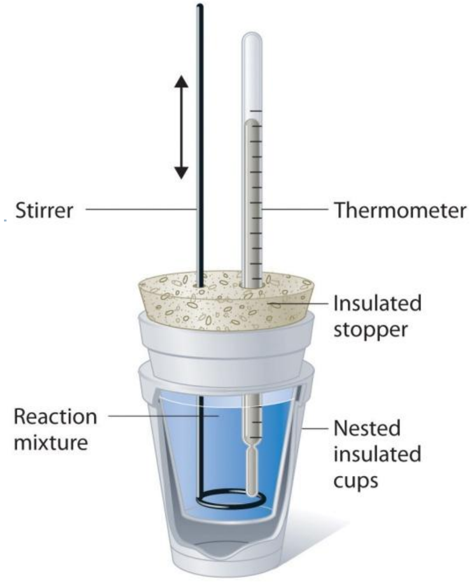
Specific heat capacity, C

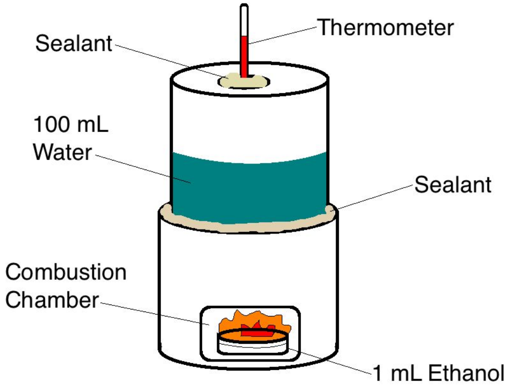
- The specific heat capacity of a substance is the amount of energy required to raise the temperature of one gram by one Kelvin.
  - $q=mc\Delta T$
- Specific heat capacity is different for different substances:

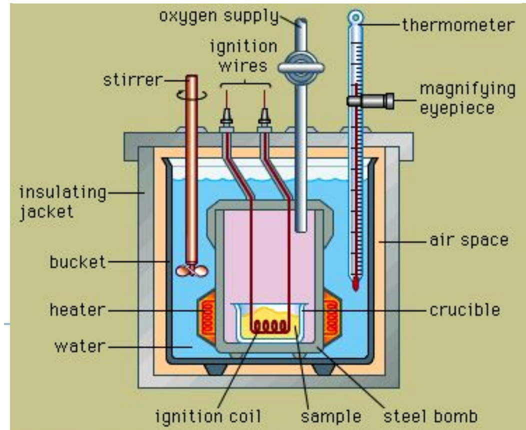
Substance	Specific Heat Capacity $J\ K^{-1}\ g^{-1}$
Water	4.18
Ethanol	2.44
Air	1.00
Iron	0.450
Copper	0.385

Calorimetry

- Calorimetry is used to measure the amount of heat released/absorbed in a reaction.
- The reaction is used to heat some water, and the temperature change measured
- If we know the mass of water used, the specific heat capacity of the water and the temperature change, we can calculate the heat change.







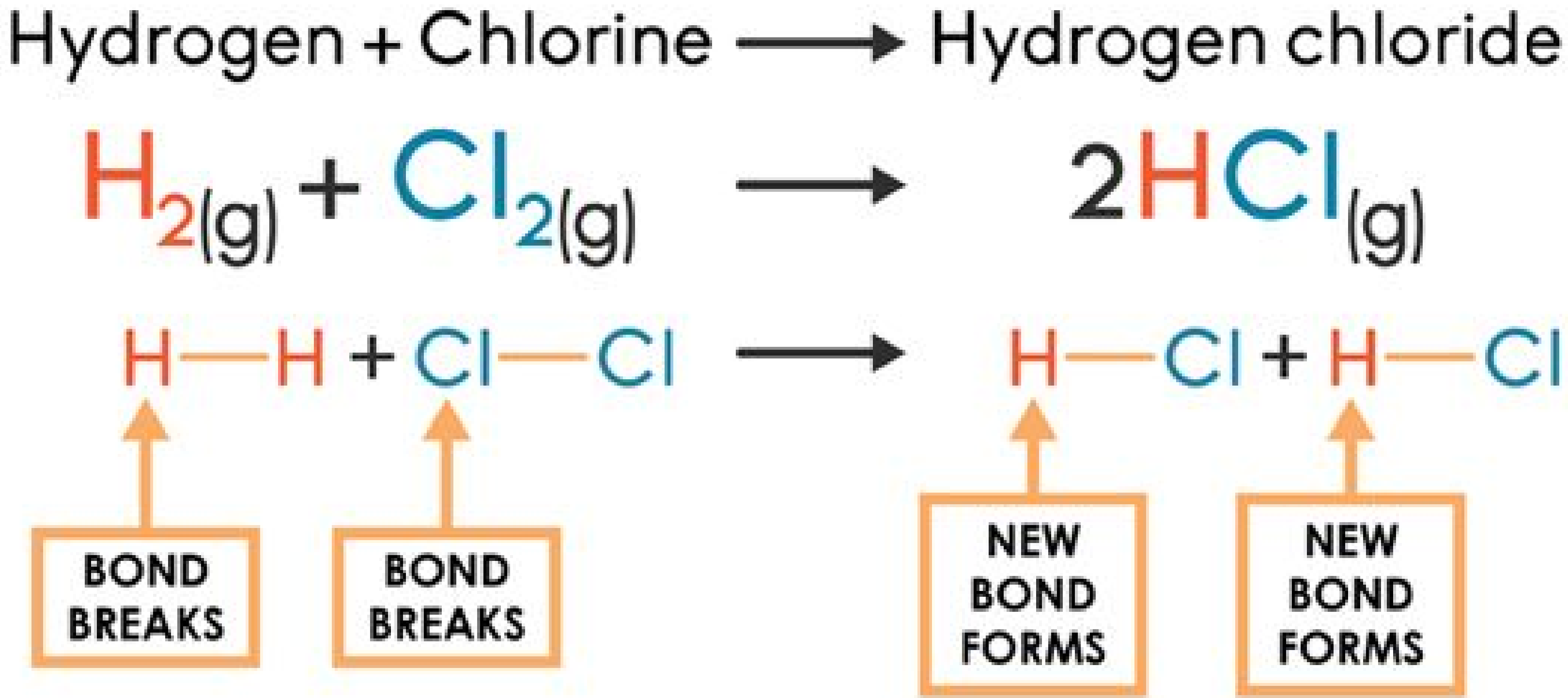
Main

Chemical Energy

- When a chemical reaction takes place, the atoms of the reactants are rearranged to create new products
- Chemical bonds in the reactants are broken and new chemical bonds are made to form the products
- Energy is required to break the chemical bonds-bond breaking is endothermic
- This energy is called the bond dissociation energy
- Energy is released when new chemical bonds are made-bond making is exothermic

Main

Chemical Energy



Hydrogen + Chlorine ⟶ Hydrogen chloride

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

$$H—H + Cl—Cl \longrightarrow H—Cl + H—Cl$$

Exothermic vs endothermic

- Exothermic reactions release energy
  - Usually they get hotter (without an external energy supply)
    - However they can give out other forms of energy such as light or electricity instead
  - Generally they are self-sustaining, stopping only when the reactants run out

- Endothermic reactions absorb energy
  - Usually they get cooler, absorbing heat from the surroundings
    - However they can absorb other forms of energy such as light or electricity instead
  - Generally they require an external energy source to keep them going and will stop either when the energy supply is halted or they run out of reactants

Main

Enthalpy and Thermochemistry

- Enthalpy is an example of a state function

- For a state function any change in value is independent of the pathway between the initial and final measurements

- Ex: taking the temperature of the water in a swimming pool early in the morning (initial value) and then again in the afternoon (final value), does not tell the whole story of any temperature fluctuations that may have occurred throughout the day

Main

Enthalpy, H (kJ/mol)

- This is a measure of the energy locked up inside chemicals
- We can only measure changes in enthalpy, ΔH, not enthalpy itself
- Substances with lower enthalpy are more stable than those with higher enthalpy
- Enthalpy level diagrams show the changes in enthalpy over the course of a reaction.

Main

Enthalpy and Thermochemistry

- Thermochemistry is the study of heat changes that occur during chemical reactions
- At constant pressure, the change in enthalpy ΔH is defined as the heat transferred by a closed system during a chemical reaction.
- ΔH values are usually expressed under standard conditions, given by ΔH°,including standard states
- Standard state refers to the normal, most pure stable state of a substance measured at 100 kPa. Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature of interest.

Main

Enthalpy, ΔH

- ΔH values are usually expressed under standard conditions, given by ΔH°,including standard states

- Standard state refers to the normal, most pure stable state of a substance measured at 100 kPa. Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature of interest.

$$\textbf{Enthalpy Change of Reaction} = \text{Sum (bond energies broken)} - \text{Sum (bond energies formed)}$$

$$\Delta H^\circ_{reaction} = \sum \Delta H_{\text{bonds broken (reactants)}} - \sum \Delta H_{\text{bonds formed (products)}}$$

Main

Enthalpy Changes in a Solution

- Standard enthalpy change of formation (ΔH°_{f}) is the enthalpy change upon the formation of one mole of a substance from its constituent elements in their standard state. (Section 12 of Data Booklet)
  - $C(s) + 2H_2 (g) \rightarrow CH_4(g)$ $\Delta H_{f,} = -74.9$ kJ mol^{-1}

- Some cases, such as the formation of phenol, result in ½ mol of diatomic atoms appearing on the reactant side.
  - $6C(s) + 3H<(g) + \frac{1}{2}\, O_2(g) \rightarrow C_6H_5OH(s)$

    $\Delta H_{f,} = -165.0$ kJ mol^{-1}

Main

Enthalpy Changes in a Solution

- Standard enthalpy change of combustion (ΔH°_c) is the heat evolved upon the complete combustion of 1 mol of substance (Section 13 of Data Booklet)
  - $C_6H_{10}(g) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O$ $\Delta H = 25.7 kJ/mol$

Utilization

- To determine their energy content, foods were traditionally placed in a calorimeter surrounded with water and completely burnt, causing the water to rise in temperature

- The temperature change was then used to calculate the energy content or “calorific value” of the food

Main

Lesson 2

5.2 Hess's Law

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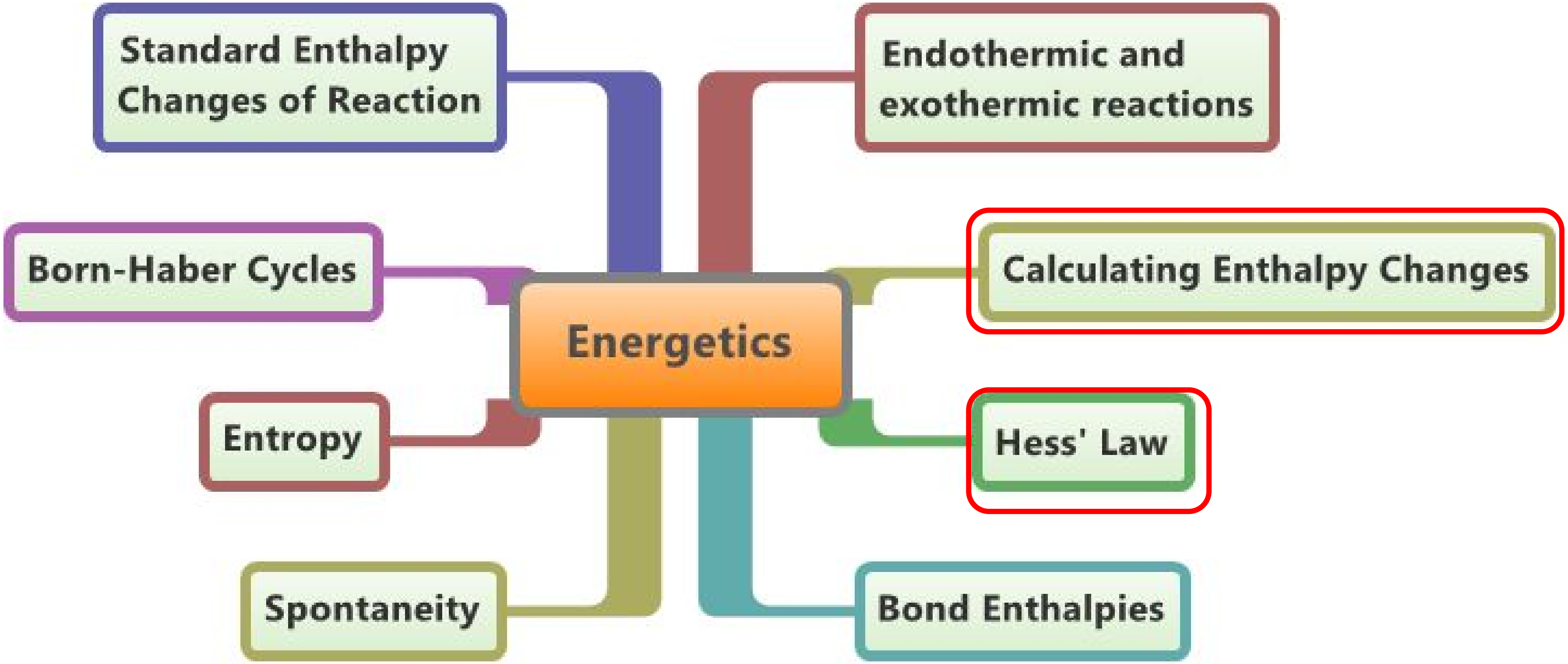

Standard Enthalpy Changes of Reaction

Born-Haber Cycles

Entropy

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Energetics

Endothermic and exothermic reactions

Calculating Enthalpy Changes

Hess' Law

Bond Enthalpies

Hess's Law

- The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.
- Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes
- Enthalpy of formation data can be found in the data booklet in section 12.
- ΔH reaction $= \Sigma(\Delta H_f$ products$) - \Sigma(\Delta H_f$ reactants$)$

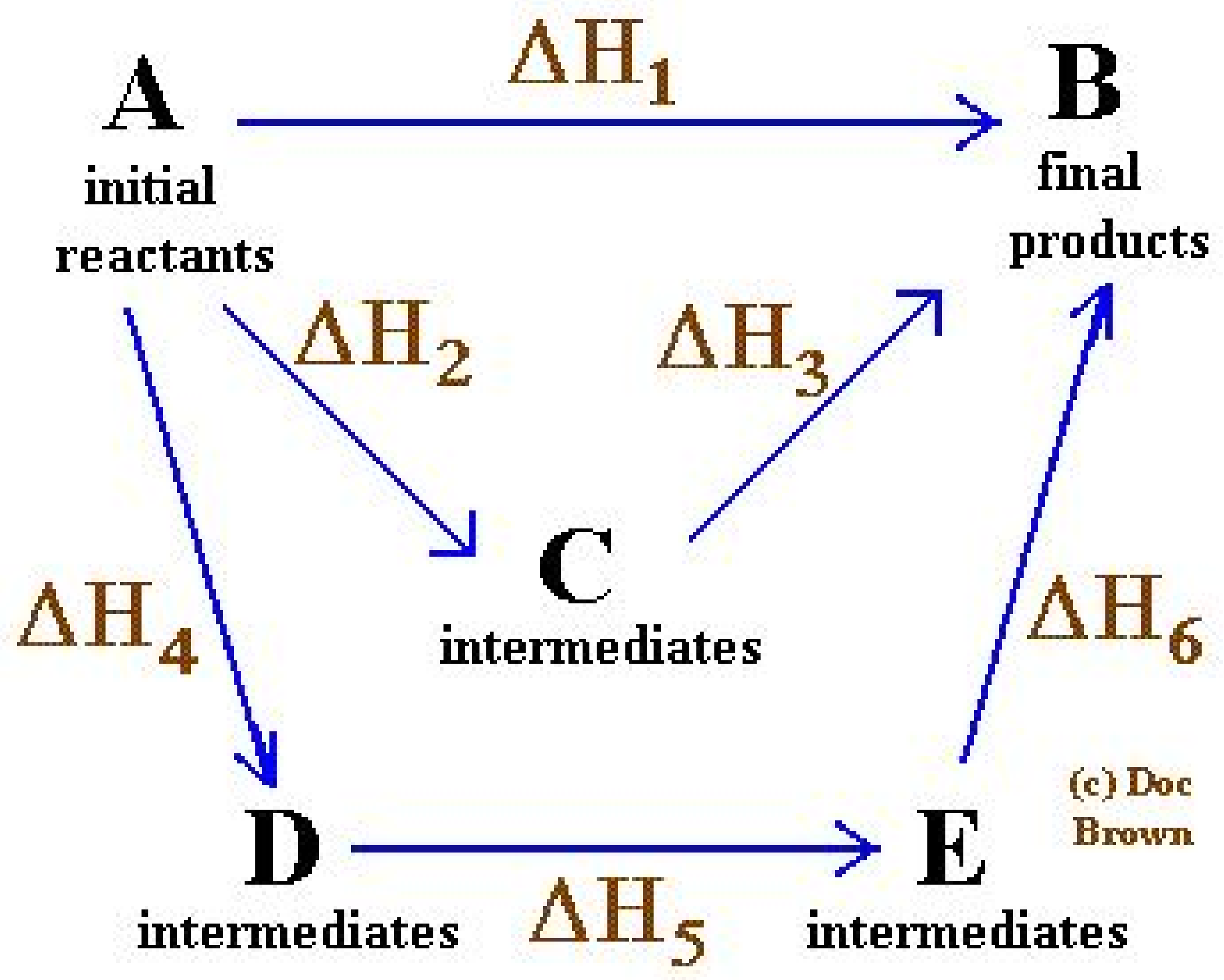
Main

Hess's Law

- A chemical equation usually shows the net reaction-it is a summary of different reactions, which when added together result in an overall reaction.

- Hess's law is an application of the conservation of energy law
  - *Regardless of the route by which a chemical reaction proceeds, the enthalpy change will always be the same providing the initial and final states of the system are the same.*

Hess's Law


ΔH_1
A
initial reactants
B
final products
ΔH_2
ΔH_3
C
intermediates
ΔH_4
ΔH_6
(c) Doc Brown
D
intermediates
ΔH_5
E
intermediates

Hess' Law

- ***The enthalpy change of a reaction is independent of the pathway of that reaction***
  - *i.e. All that matters is the start and finish points*

$$\begin{tikzcd}
A + B \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & C + D \\
& E + F \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

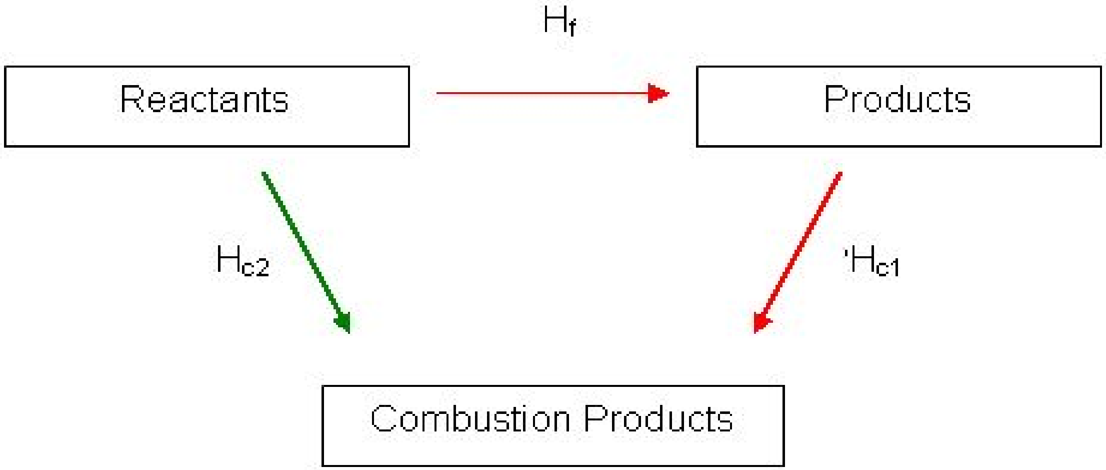
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$\begin{tikzcd}
A + B \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_2"'] & C + D \\
E + F & G + H \arrow[l, "\Delta H_3"'] \arrow[u, "\Delta H_4"']
\end{tikzcd}$$

$$\Delta H_1 = \Delta H_2 - \Delta H_3 + \Delta H_4$$

- **Note: add** when going 'with' an arrow, **subtract** when going against an arrow.

Hess's Cycle



H_f

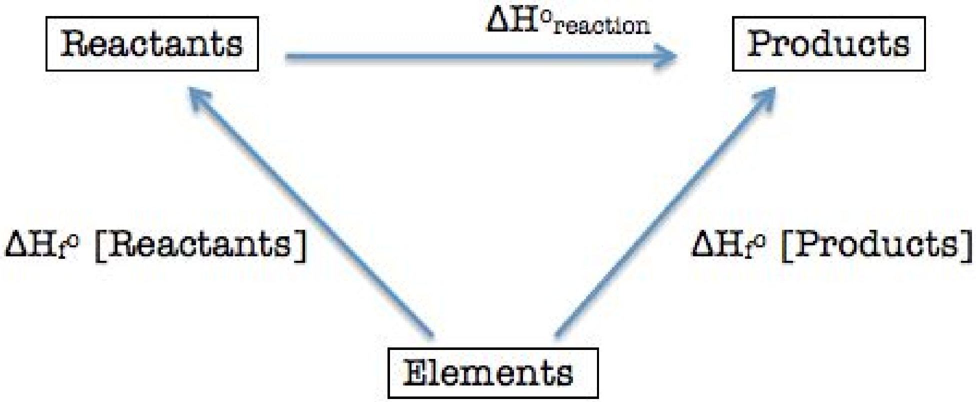
Reactants

Products

H_{c2}

$'H_{c1}$

Combustion Products



Reactants

$\Delta H^{o}_{\text{reaction}}$

Products

ΔH_f^o [Reactants]

ΔH_f^o [Products]

Elements

Why is this useful

- It is not always possible to directly measure the enthalpy change we want.
  - It may be an endothermic reaction that needs a constant heat supply
  - It may be that the reaction doesn't 'stop' where you need it to
  - It may be that the reaction is simply too slow
- Hess cycles allow us to measure enthalpy changes indirectly

Main

Example 1:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^{\ominus} = -394\ kJ\ mol^{-1},$$

$$Mn(s) + O_2(g) \rightarrow MnO_2(s) \quad \Delta H^{\ominus} = -520\ kJ\ mol^{-1}$$

Determine ΔH, *in kJ, for:* $MnO_2(s) + C(s) \rightarrow Mn(s) + CO_2(g)$

$$C(s) + \cancel{O_2}(g) \rightarrow CO_2(g) \quad \Delta H^{\ominus} = -394\ kJ\ mol^{-1}$$

$$+ \quad MnO_2(s) \rightarrow Mn(s) + \cancel{O_2}(g) \quad \Delta H^{\ominus} = 520\ kJ\ mol^{-1}$$

$$520\ kJ\ mol^{-1} + (-394 kJ\ mol^{-1}) = 126\ kJ\ mol^{-1}$$

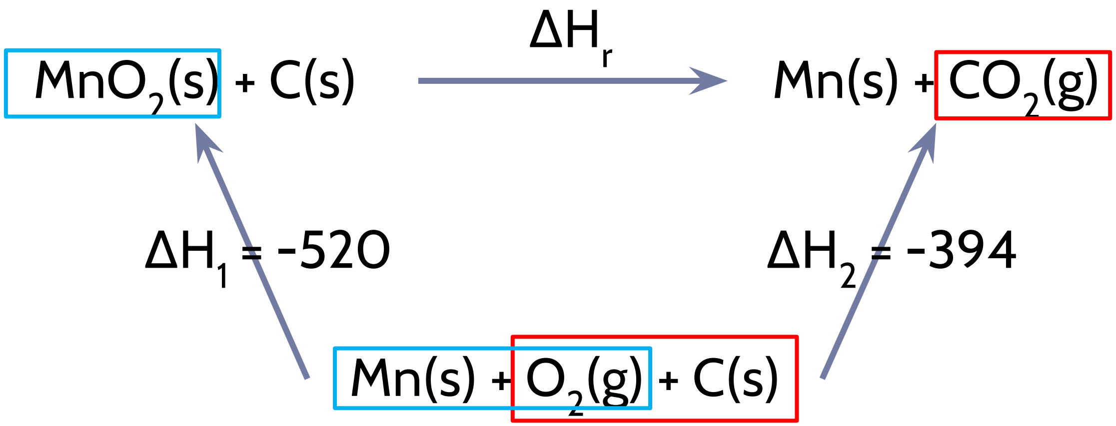
Main

Example 1

Using the equations below:

$\boxed{C(s) + O_2(g)} \rightarrow \boxed{CO_2(g)}$ $\Delta H^{\ominus} = -394\ kJ\ mol^{-1}$, $\boxed{Mn(s) + O_2(g)} \rightarrow \boxed{MnO_2(s)}$ $\Delta H^{\ominus} = -520\ kJ\ mol^{-1}$

Determine ΔH, *in kJ, for:* $MnO_2(s) + C(s) \rightarrow Mn(s) + CO_2(g)$



$$\begin{tikzcd}
\boxed{MnO_2(s)} + C(s) \arrow[rr, "\Delta H_r"] & & Mn(s) + \boxed{CO_2(g)} \\
& Mn(s) + O_2(g) + C(s) \arrow[ul, "\Delta H_1 = -520"] \arrow[ur, "\Delta H_2 = -394"'] &
\end{tikzcd}$$

$$\begin{aligned}
\Delta H_r &= -\Delta H_1 + \Delta H \\
&= -(-520)+(-394) \\
&= +126\ kJ\ mol^{-1}
\end{aligned}$$

Tip: We need to look at this a bit like a chemical jigsaw puzzle.

Drawing coloured boxes around the equations for which you have ΔH values, can help you see how the puzzle will fit together

Main

Try This:

Given: $2C(s) + O_2(g) \longrightarrow 2CO(g)$ $\Delta H^\ominus = -222\ kJ\ mol^{-1}$ ΔH_1

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\ominus = -394\ kJ\ mol^{-1}$ ΔH_2

Calculate the enthalpy change for the reaction

$$2CO(g) + O_2 \longrightarrow 2CO_2(g)$$

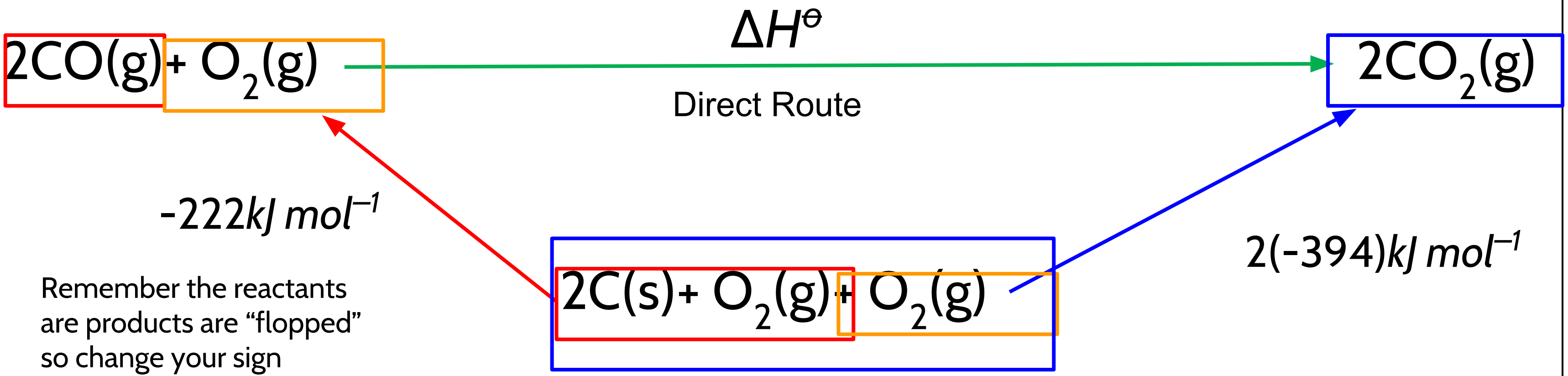
Main

The Answer!

$$
\begin{array}{lll}
 & 2CO(g) \longrightarrow 2C(g) + O_2(g) & \Delta H^{\ominus} = +222\ kJ\ mol^{-1} \\
+ & 2C(s) + 2O_2(g) \longrightarrow 2CO_2(g) & \Delta H^{\ominus} = 2(-394) kJ\ mol^{-1} \\
\hline
\end{array}
$$

$$2CO(g) + O_2 \longrightarrow 2CO_2(g)$$

$$222\ kJ\ mol^{-1} + (-784\ kJ\ mol^{-1}) = -566 kJ\ mol^{-1}$$



$\Delta H^{\ominus}$

$2CO(g) + O_2(g)$

Direct Route

$2CO_2(g)$

$-222 kJ\ mol^{-1}$

$2(-394) kJ\ mol^{-1}$

$2C(s) + O_2(g) + O_2(g)$

Remember the reactants
are products are “flopped”
so change your sign

$$\Delta H^{\ominus} = 222\ kJ\ mol^{-1} + (-784\ kJ\ mol^{-1}) = -566 kJ\ mol^{-1}$$

Main

International Mindedness

- Recycling of materials is often an effective means of reducing the environmental impact of production, but varies in its efficiency in energy terms in different countries.

Main

Theory of Knowledge

- Hess' Law is an example of the application of the Conservation of Energy. What are the challenges and limitations of applying general principles to specific instances?

Main

Utilization

- Hess's Law has significance in the study of nutrition, drugs, and Gibbs free energy where direct synthesis from constituent elements is not possible.

Lesson 3

5.3 Bond Enthalpies

Main Menu

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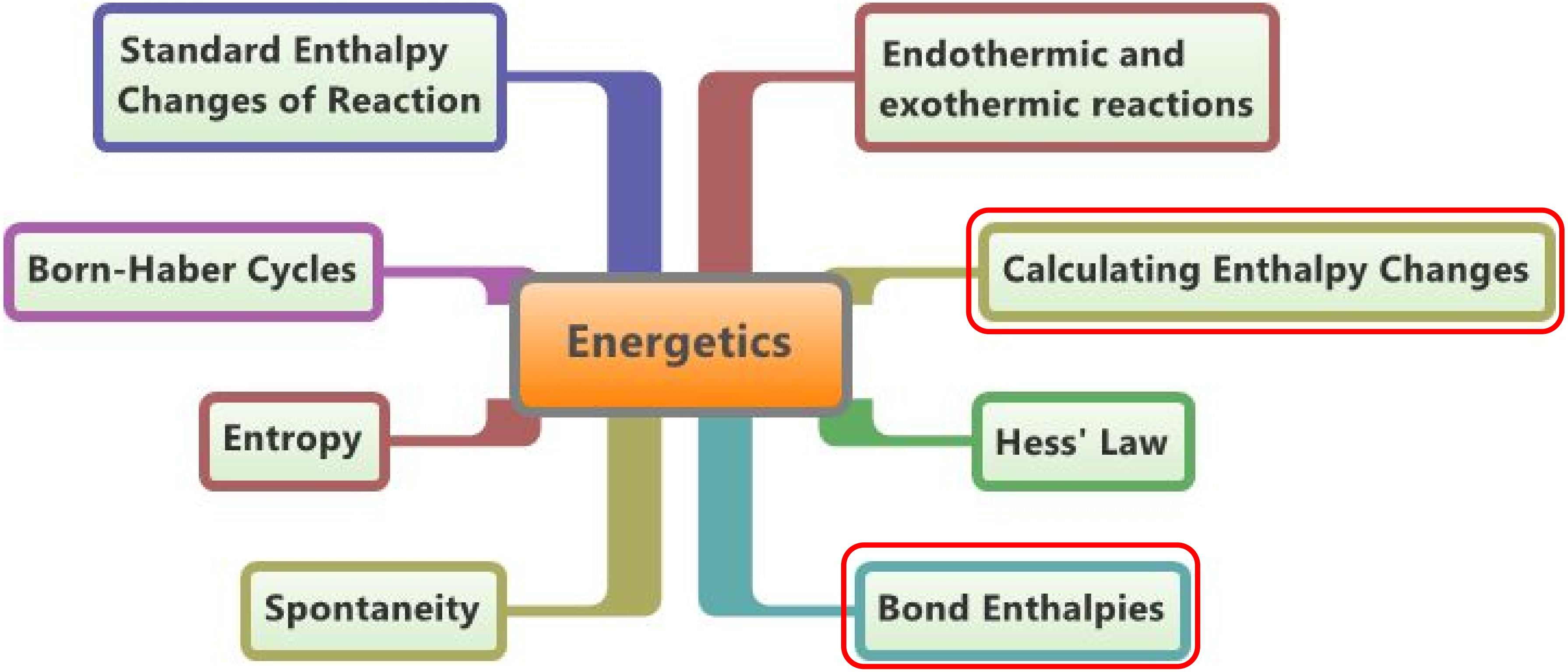
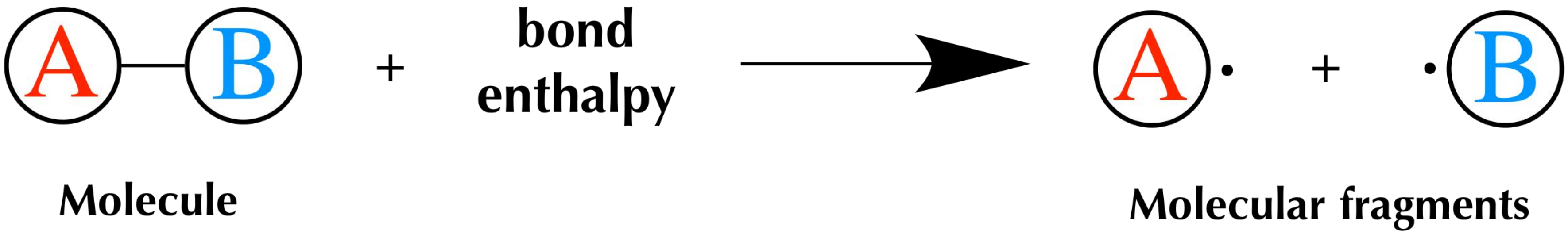


Main

Bond Enthalpy

- Bond enthalpy is defined in terms of breaking bonds.
- Bond-forming releases energy and bond-breaking requires energy
- Average bond enthalpy is the energy needed to break one mole of a bond in a gaseous covalent molecule under standard conditions



Main

Bond Enthalpy

- Bond enthalpy is often referred to as bond dissociation enthalpy and selected values are provided in section 11 of the Data Booklet.

- These are average values and are only an approximation.

- They are derived from experimental data involving the breaking of the same bond found in a wide variety of compound.

Main

Bond Enthalpy

- In CH_4, the bond enthalpy of each C-H bond will vary as the chemical environment of the individual bonds changes.
- If a CH_4 molecule underwent a series of steps in which one hydrogen atom was removed at a time, the bond dissociation enthalpy would be different each time as the chemical environment changes upon the removal of successive hydrogen atoms.
- Bond enthalpies do not take into account the intermolecular forces that exist.
- These limitations are not considered to be significant and the values are acceptable to use

Main

Average Bond Enthalpy

- The average energy required to break one mole of a chemical bond to produce two moles of gaseous atoms at 298K.

- Bond enthalpies are always positive

- These are average values, they do not take into account:
  - Variations in strengths of the same bond in different compounds
    - For example: the strength of a C-H bond will vary slightly depending on whether it is in methane, ethene, glucose and so on
  - Energy changes due to state changes (from intermolecular forces)
  - Energy changes due to dissolution in water

- This means enthalpy changes calculated from bond enthalpies will generally be less accurate than those calculated by other means

Main

Bond Enthalpies

- Determine the enthalpy change for the following reaction

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

ΔH = **BONDS BROKEN - BONDS MADE**

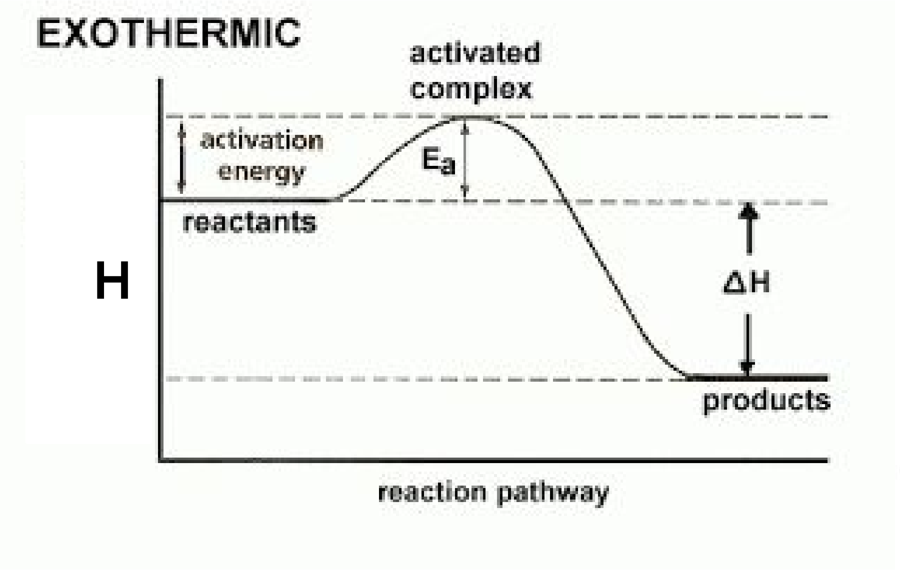
= (4 x C-H + 2 x O=O) - (2 x C=O + 4 x O-H)

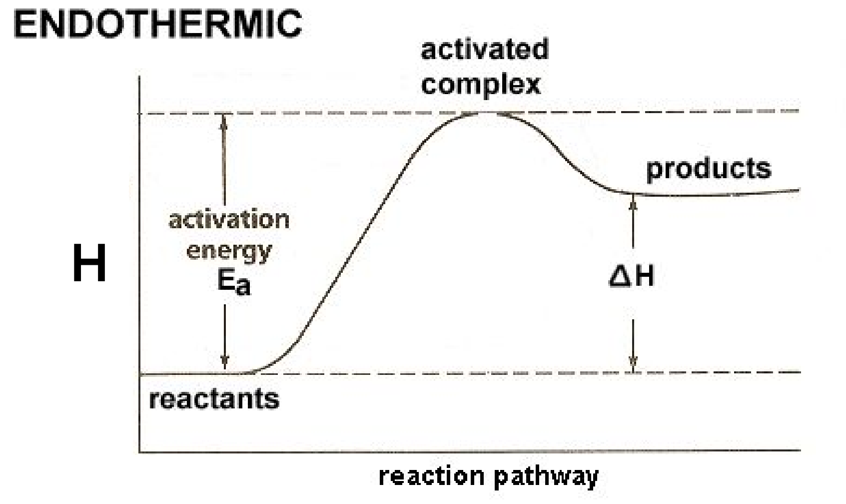
= (4 x 413 + 2 x 498) - (2 x 746 + 4 x 464)

= 2648 – 3348

= **<u>-700 kJ mol</u>**$^{-1}$

Potential Energy Diagram





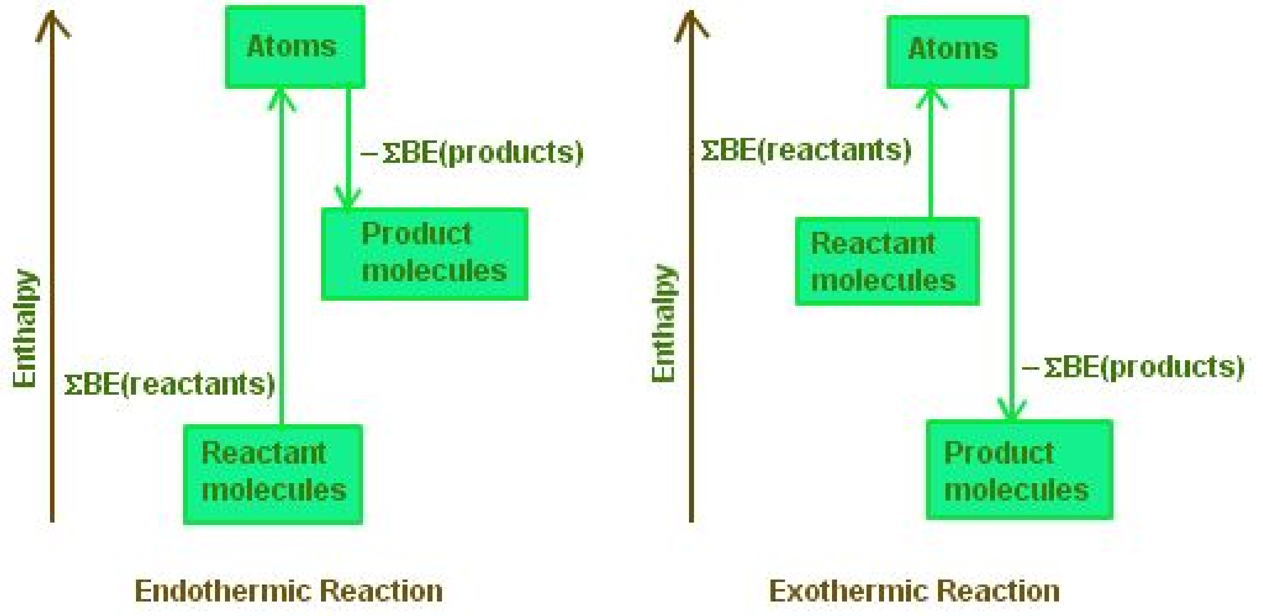
- ΔH is negative (H goes down)
- Activation energy small
- Products more stable
- Break weaker bonds, make stronger bonds
- Chemical energy turned into heat energy

- ΔH is positive (H goes up)
- Activation energy large
- Products less stable
- Break stronger bonds, make weaker bonds
- Heat energy turned into chemical energy

Main

Enthalpy Level Diagrams

- Used for IB level courses

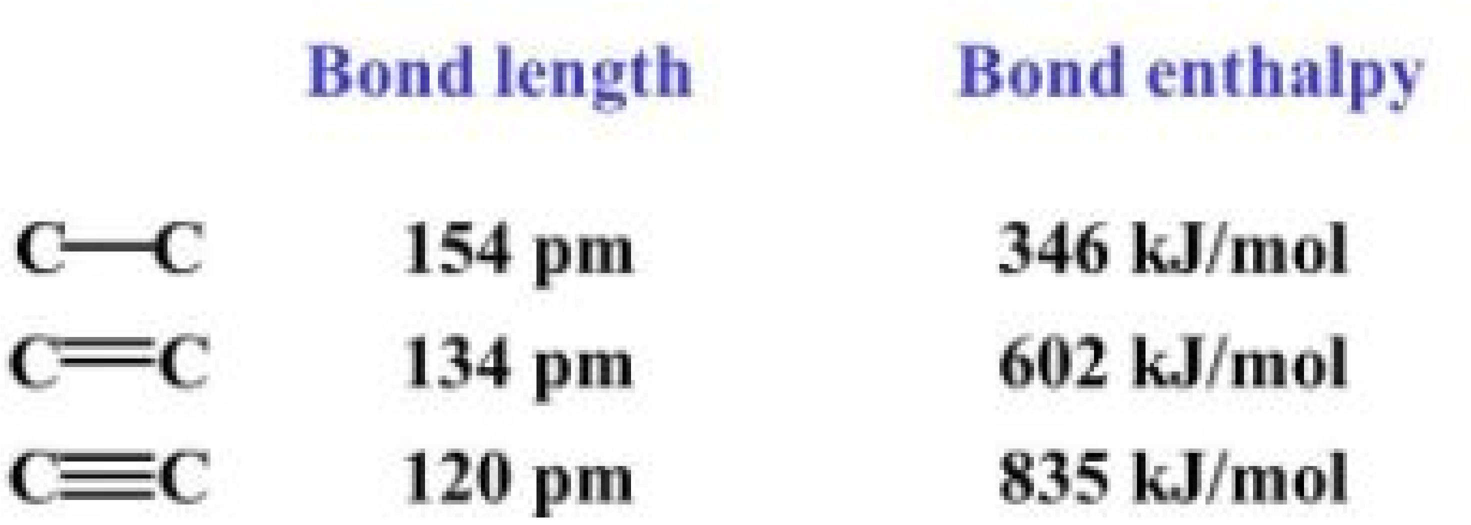


- Do not provide information about activation energy and so on.

Main

Bond Length

- The bond length reflects the strength of the covalent bond
    - A longer bond length corresponds to a lower value of bond enthalpy



	Bond length	Bond enthalpy
$C-C$	154 pm	346 kJ/mol
$C=C$	134 pm	602 kJ/mol
$C\equiv C$	120 pm	835 kJ/mol

Main

KNOW THE DIFFERENCE

- To calculate bond enthalpy:

ΔH reaction $= \Sigma$(BE bonds broken) - Σ(BE bonds formed)

- To calculate the enthalpy of formation:

  ΔH reaction $= \Sigma(\Delta H_f$ products) - $\Sigma(\Delta H_f$ reactants)

Main

Comparing Enthalpy Values

- The reason for differences is that when calculating the enthalpy change using bond enthalpy values, it is assumed that the reaction takes place in the gaseous state, with no intermolecular forces involved.

- Experimentally derived enthalpy values involved standard states which could be liquid, etc.

Main

Ozone

- The bond dissociation enthalpy of an oxygen molecule, O2, is 498 kJ mol^{-1}

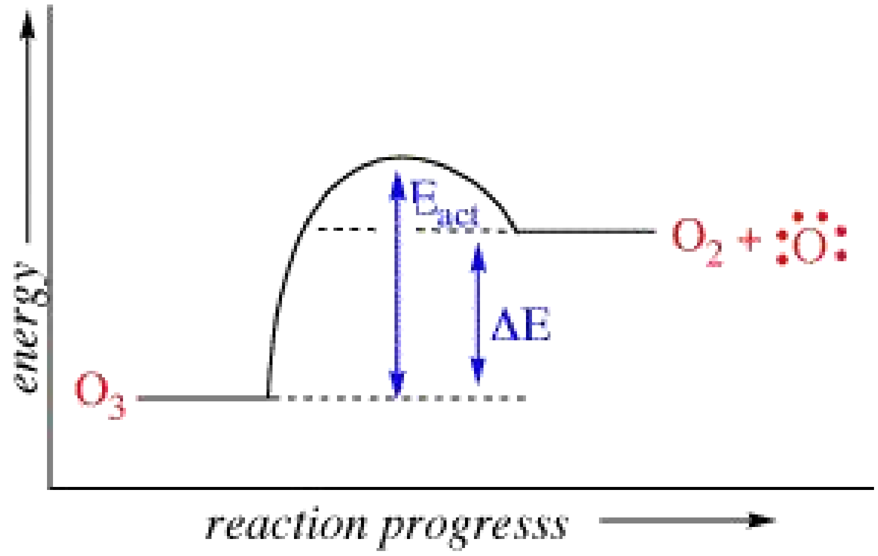
- The energy required to break an oxygen-oxygen bond within an ozone molecule is 364 kJ mol^{-1}

- The consequence of this is that an ozone molecule is decomposed by UV rays more readily than an oxygen molecule

Main

Ozone

- Energy profile shows that the oxygen molecule and oxygen atom have a greater combined energy than the reactant ozone molecule
- The products of this reaction are less stable and exist at a higher energy



Main

Lesson 4

15.1 Energy Cycles

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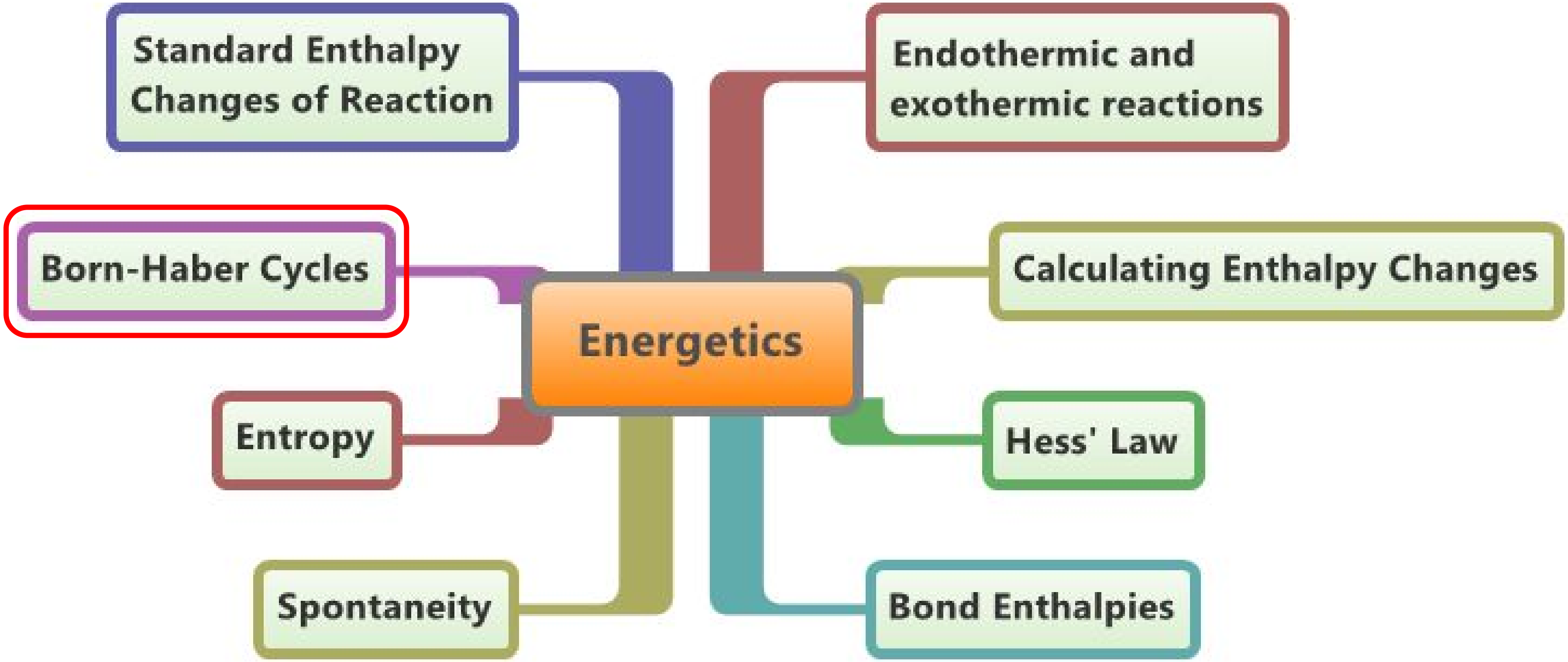

Standard Enthalpy Changes of Reaction

Born-Haber Cycles

Entropy

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Energetics

Endothermic and exothermic reactions

Calculating Enthalpy Changes

Hess' Law

Bond Enthalpies

Main

Haber Cycle

- Born-Haber Cycles are energy cycles for the formation of certain ionic compounds

- A Born-Haber cycle can be used to calculate quantities that are difficult to measure directly such as lattice energies

- The formation of an ionic compound as a sequence of steps whose energies can be determined.

Main

Lattice Enthalpy, ΔH°_{lat}

- **Lattice enthalpy** is the enthalpy change that occurs from the conversion of an ionic compound into its gaseous ions
  - This is an endothermic process, requiring energy to be put in.

$$MX(s) \rightarrow M^{+}(g) + X^{-}(g)$$

- Experimental values at 298K can be found in section 18 of the Data Booklet

Compound	Lattice Enthalpy kJ mol-1
LiF	1049
LiBr	820
KF	829
CaF_2	2651

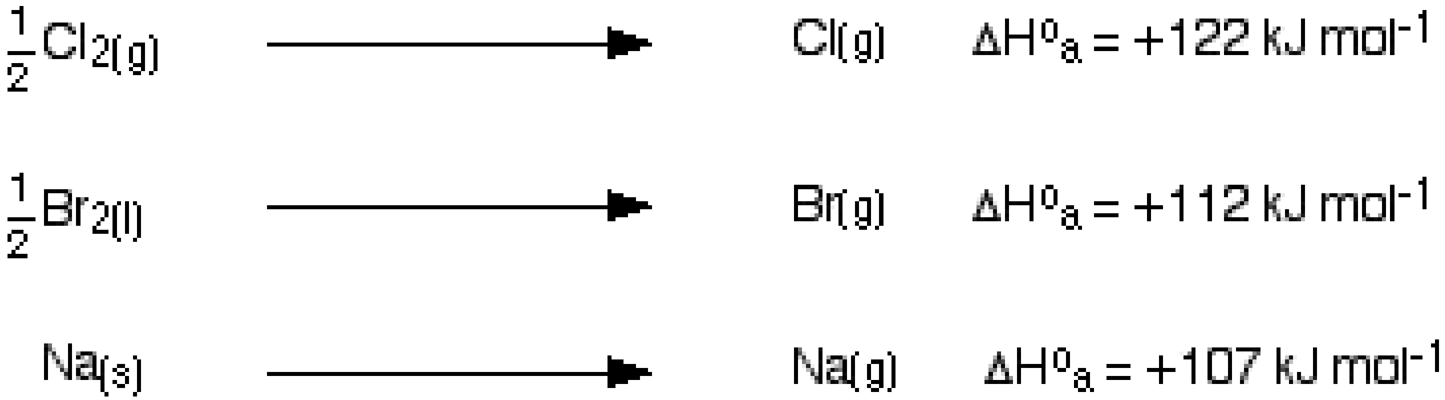
Main

Enthalpy of Atomization, ΔH°_{at}

- **Enthalpy of atomization** is the enthalpy change that occurs when one mole of gaseous atoms is formed from the element in the standard state under standard conditions
  - This is an endothermic process, requiring energy to be put in.

$$M(s) \rightarrow M(g)$$

$$\tfrac{1}{2} X_2(g) \rightarrow X(g)$$



$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H^0_a = +122\ \text{kJ mol}^{-1}$$

$$\frac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)} \qquad \Delta H^0_a = +112\ \text{kJ mol}^{-1}$$

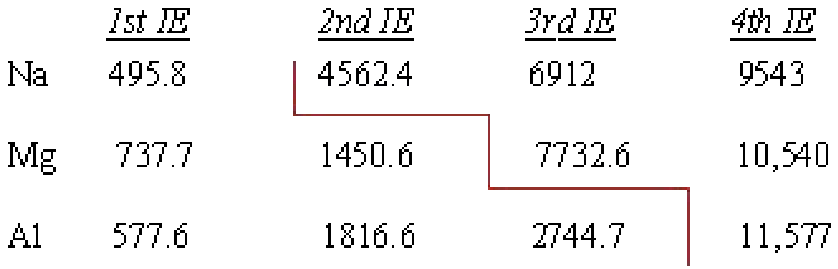
$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H^0_a = +107\ \text{kJ mol}^{-1}$$

Ionization Energy, ΔH°_{IE}

- **Ionization energy** is the standard enthalpy change that occurs on the removal of 1 mol of electrons from 1 mol of atoms or positively charged ions in the gaseous phase
- For metals ions with multiple valence electrons the first, second, and sometimes third ionization energies are defined
  - This is an endothermic process, requiring energy to be put in.

$$IE_1: M(g) \rightarrow M^+(g) + e^-$$

$$IE_2: M^+(g) \rightarrow M^{2+}(g) + e^-$$



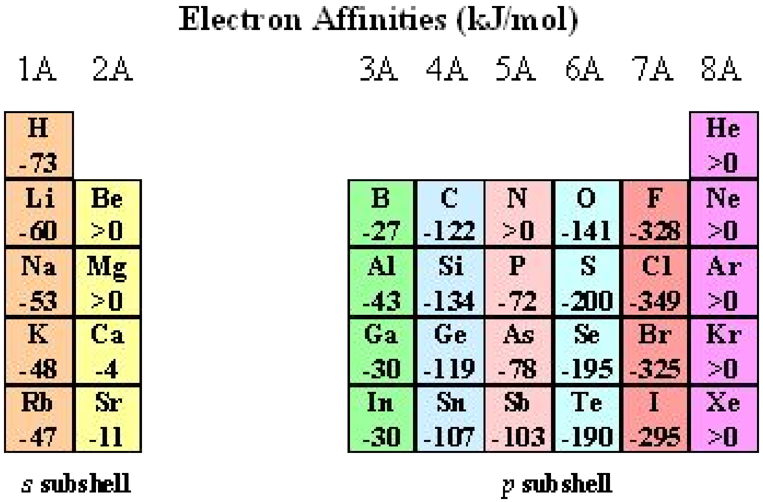
	1st IE	2nd IE	3rd IE	4th IE
Na	495.8	4562.4	6912	9543
Mg	737.7	1450.6	7732.6	10,540
Al	577.6	1816.6	2744.7	11,577

Main

Electron Affinity, ΔH°_{EA}

- **Electron affinity** is the enthalpy change that occurs when an electron is added to an isolated atom in the gaseous state
  - This is an exothermic process, releasing energy.
    - Can be positive, but this rarely occurs.

$$X(g) + e^- \rightarrow X^-(g)$$



Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H -73							He >0
Li -60	Be >0	B -27	C -122	N >0	O -141	F -328	Ne >0
Na -53	Mg >0	Al -43	Si -134	P -72	S -200	Cl -349	Ar >0
K -48	Ca -4	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr >0
Rb -47	Sr -11	In -30	Sn -107	Sb -103	Te -190	I -295	Xe >0

s subshell

p subshell

Main

Construction Born-Haber Cycles

- The lattice energy, the enthalpy of atomization, the ionization energy, and the electron affinity are combined to construct the Born-Haber cycle and find the enthalpy of formation of an ionic compound

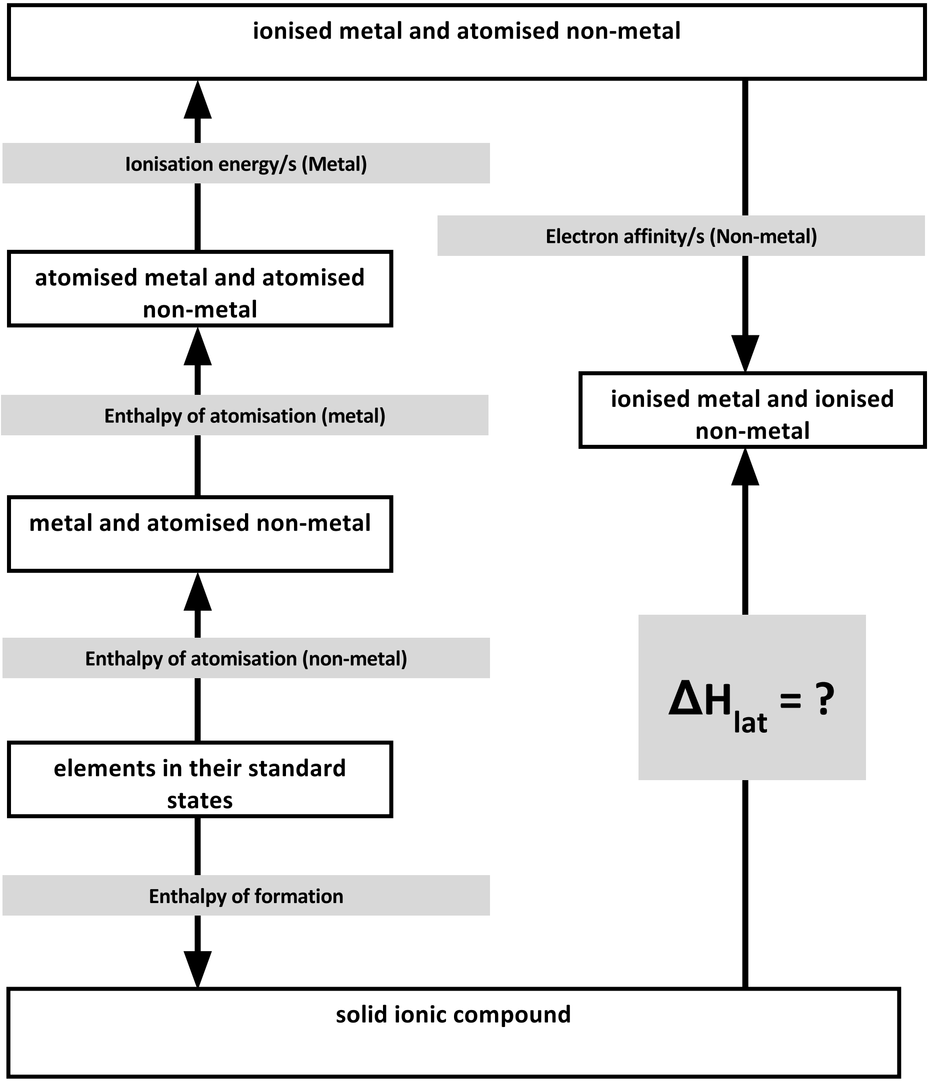
- The standard Born-Haber cycle focuses on the processes involved and the relationships between the individual steps rather than the magnitude of each energy change

Main

Born-Haber Cycles

- Lattice enthalpies are difficult to measure directly, so we use Born-Haber cycles
  - These are just a specialised type of Hess cycle

- To calculate ΔH_{lat} :
  - Start at the bottom and work round clockwise, adding and subtracting according to the arrows.



Main

Born-Haber Cycle for Sodium Chloride

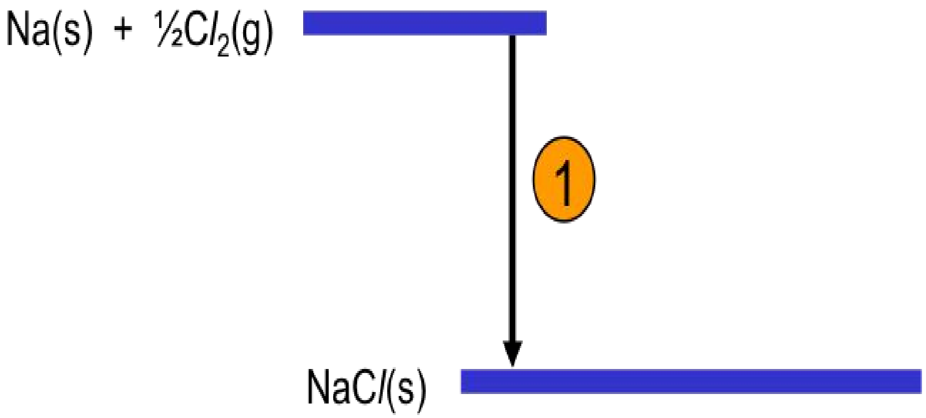
		kJ mol^{-1}
Enthalpy of formation of NaCl	$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$	**– 411**
Enthalpy of sublimation of sodium	$Na(s) \longrightarrow Na(g)$	**+ 108**
Enthalpy of atomisation of chlorine	$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	**+ 121**
1st Ionisation Energy of sodium	$Na(g) \longrightarrow Na^+(g) + e^-$	**+ 500**
Electron Affinity of chlorine	$Cl(g) + e^- \longrightarrow Cl^-(g)$	**– 364**
Lattice Enthalpy of NaCl	$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$	**?**

Main

Born-Haber Cycle-NaCl

① Enthalpy of formation of NaCl

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$



This is an exothermic process so energy is released. Sodium chloride has a lower enthalpy than the elements which made it.

VALUE = - 411 kJ mol^{-1}

Main

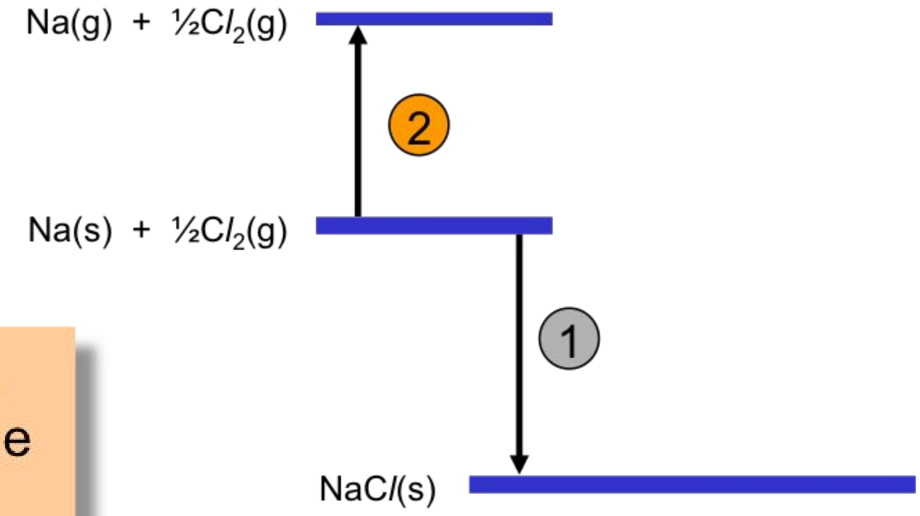
Born-Haber Cycle-NaCl

① **Enthalpy of formation of NaCl**

$Na(s) + ½Cl_2(g) \longrightarrow NaCl(s)$

② **Enthalpy of sublimation of sodium**

$Na(s) \longrightarrow Na(g)$



This is an endothermic process. Energy is needed to separate the atoms. Sublimation involves going directly from solid to gas.

VALUE = + 108 kJ mol^{-1}

Main

Born-Haber Cycle-NaCl

① **Enthalpy of formation of NaCl**

$Na(s) + ½Cl_2(g) \longrightarrow NaCl(s)$

② **Enthalpy of sublimation of sodium**

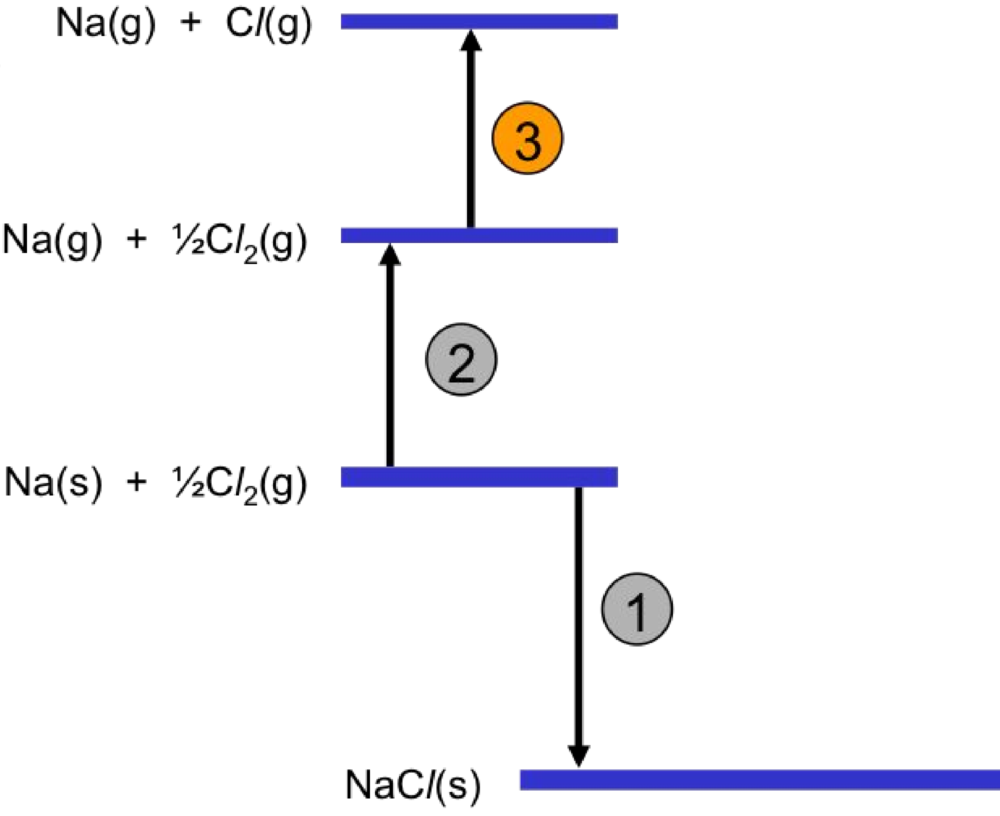
$Na(s) \longrightarrow Na(g)$

③ **Enthalpy of atomization of chlorine**

$½Cl_2(g) \longrightarrow Cl(g)$

Breaking covalent bonds is an endothermic process. Energy is needed to overcome the attraction the atomic nuclei have for the shared pair of electrons.

VALUE = + 121 kJ mol^{-1}



Born-Haber Cycle-NaCl

① **Enthalpy of formation of NaC*l***

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$

② **Enthalpy of sublimation of sodium**

$Na(s) \longrightarrow Na(g)$

③ **Enthalpy of atomization of chlorine**

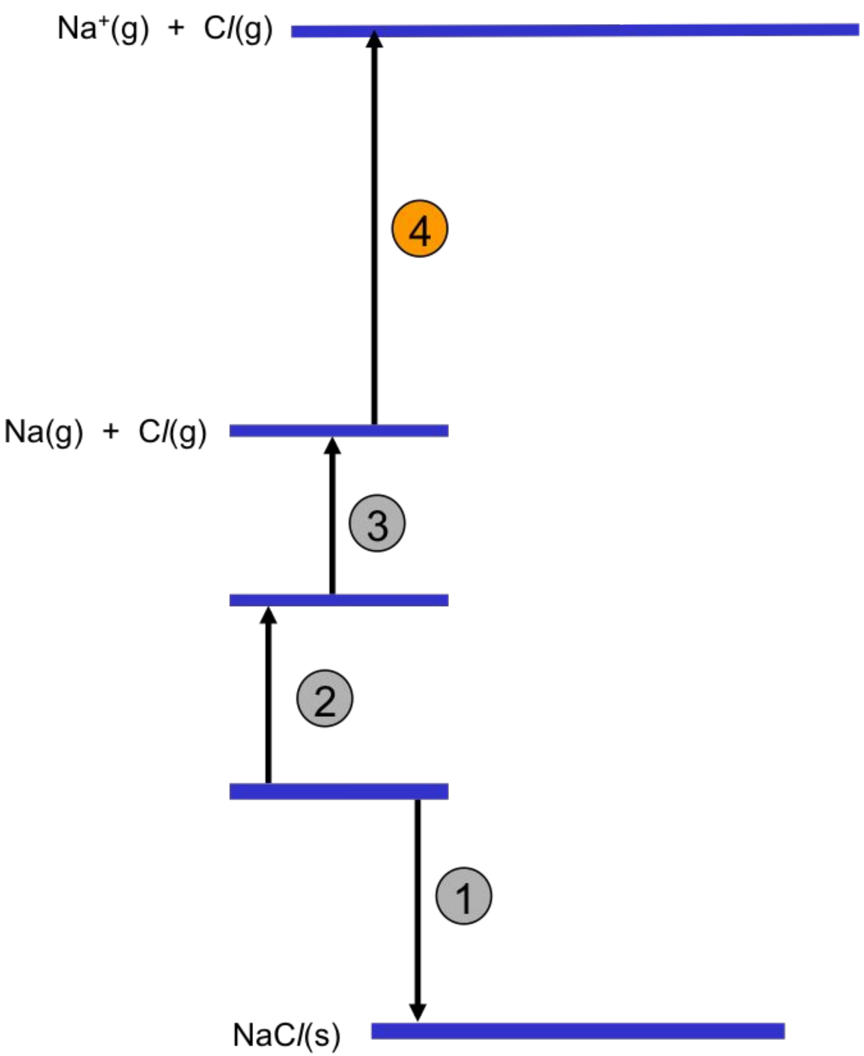
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

④ **1st Ionization Energy of sodium**

$Na(g) \longrightarrow Na^+(g) + e^-$

All Ionisation Energies are endothermic. Energy is needed to overcome the attraction the protons in the nucleus have for the electron being removed.

VALUE = + 500 kJ mol^{-1}



Born-Haber Cycle-NaCl

① **Enthalpy of formation of NaCl**

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$

② **Enthalpy of sublimation of sodium**

$Na(s) \longrightarrow Na(g)$

③ **Enthalpy of atomization of chlorine**

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

④ **1st Ionization Energy of sodium**

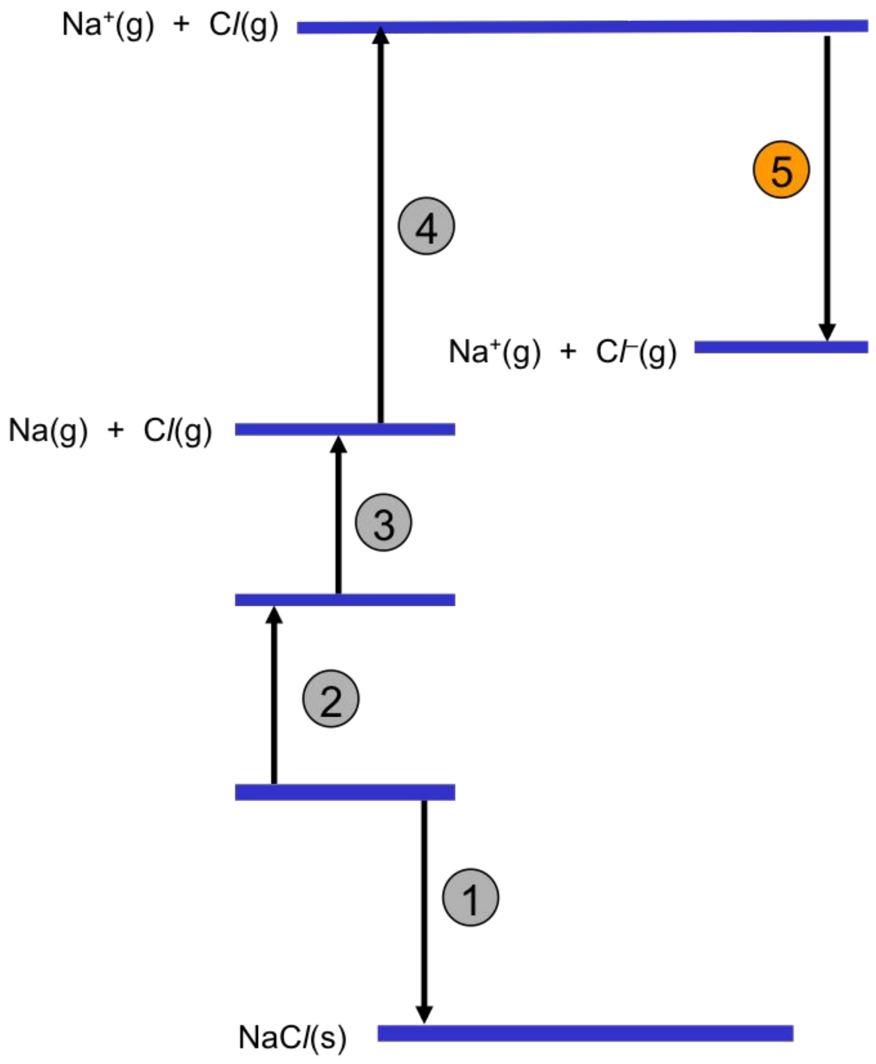
$Na(g) \longrightarrow Na^+(g) + e^-$

⑤ **Electron Affinity of chlorine**

$Cl(g) + e^- \longrightarrow Cl^-(g)$

Electron affinity is exothermic. Energy is released as the nucleus attracts an electron to the outer shell of a chlorine atom.

VALUE = - 364 kJ mol^{-1}



Born-Haber Cycle-NaCl

① **Enthalpy of formation of NaCl**

$Na(s) + ½Cl_2(g) \longrightarrow NaCl(s)$

② **Enthalpy of sublimation of sodium**

$Na(s) \longrightarrow Na(g)$

③ **Enthalpy of atomization of chlorine**

$½Cl_2(g) \longrightarrow Cl(g)$

④ **1st Ionization Energy of sodium**

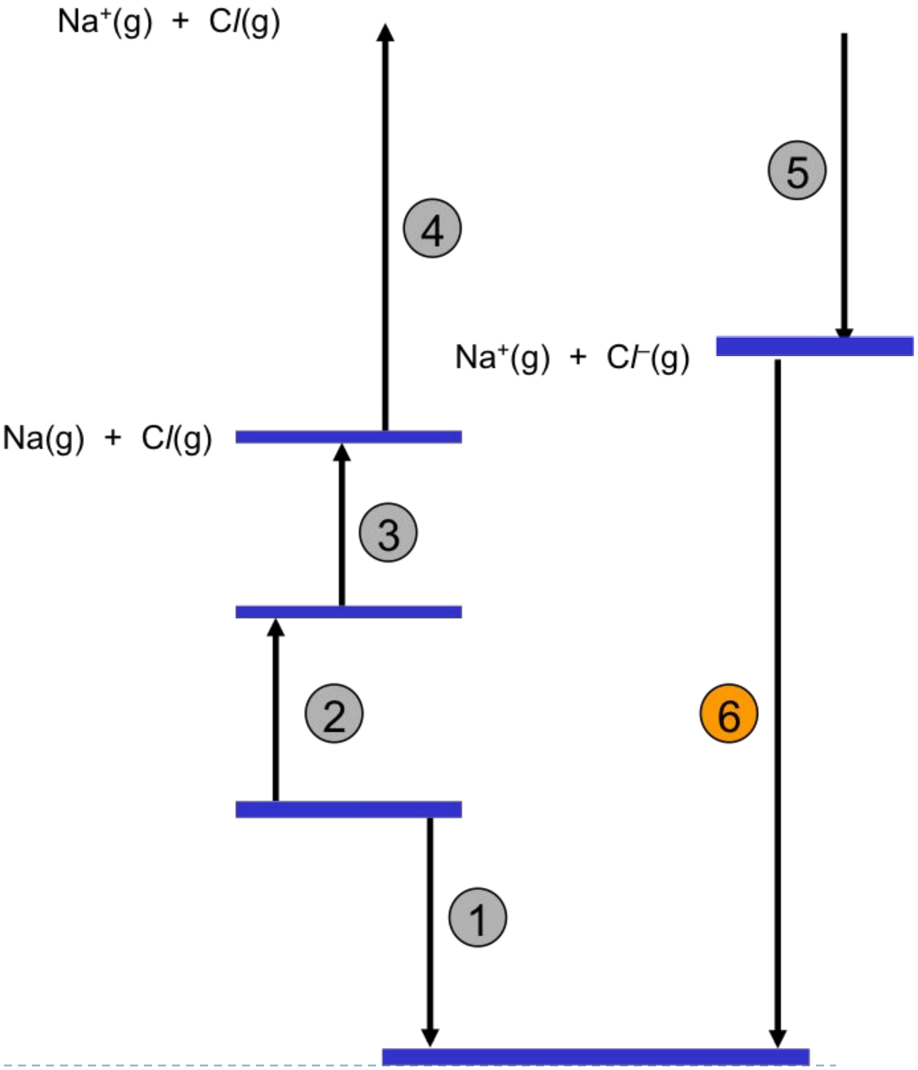
$Na(g) \longrightarrow Na^+(g) + e^-$

⑤ **Electron Affinity of chlorine**

$Cl(g) + e^- \longrightarrow Cl^-(g)$

⑥ **Lattice Enthalpy of NaCl**

$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$



Lattice Enthalpy is exothermic. Oppositely charged ions are attracted to each other.

Born-Haber Cycle-$MgCl_2$

1. **Enthalpy of formation of $MgCl_2$**

   $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

2. **Enthalpy of sublimation of Mg**

   $Mg(s) \longrightarrow Mg(g)$

3. **Enthalpy of atomization of Cl**

   $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ x2

4. **1st Ionization Energy of Mg**

   $Mg(g) \longrightarrow Mg^+(g) + e^-$

5. **2nd Ionization Energy of Mg**

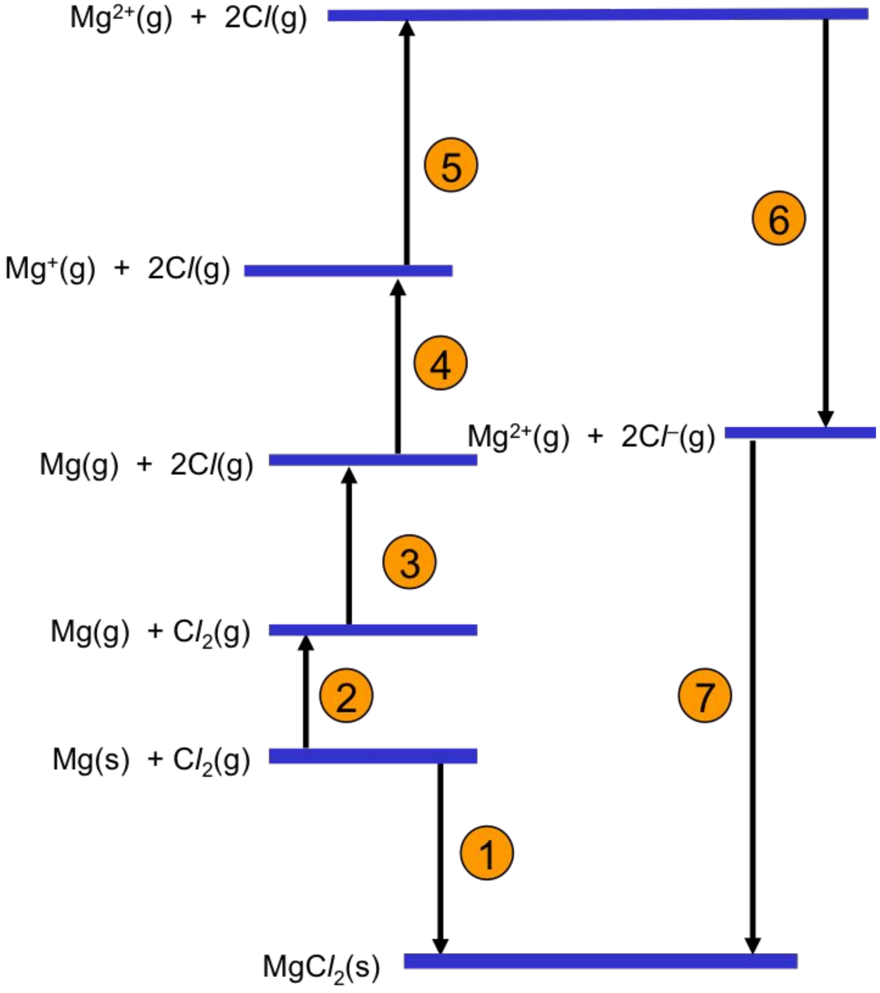
   $Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$

6. **Electron Affinity of Cl**

   $Cl(g) + e^- \longrightarrow Cl^-(g)$ x2

7. **Lattice Enthalpy of $MgCl_2$**

   $Mg^{2+}(g) + 2Cl^-(g) \longrightarrow MgCl_2(s)$



Born-Haber Cycle-NaCl

Apply Hess' Law

⑥ = - ① + ② + ③ + ④ + ⑤

The minus shows you are going in the opposite direction to the definition

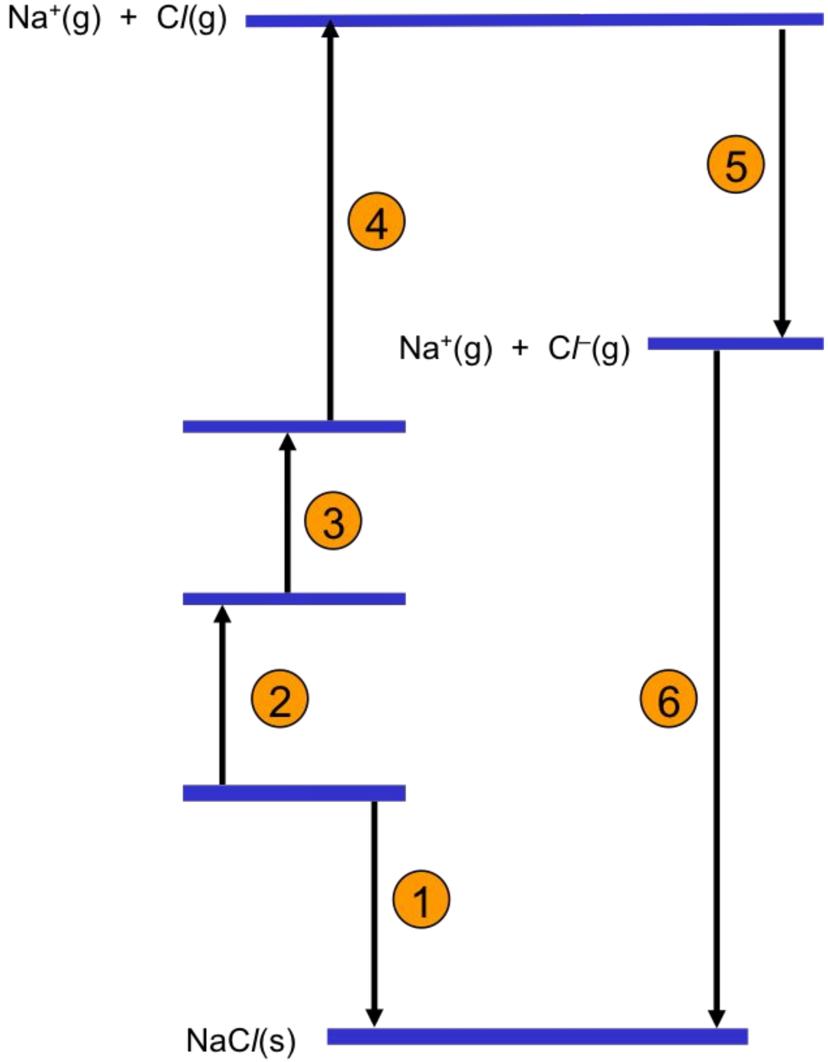
= - (411) + (108) + (121) + (500) + (364)

= - 682 kJ mol^{-1}

OR…

Ignore the signs and just use the values;

If you go up you add, if you come down you subtract the value



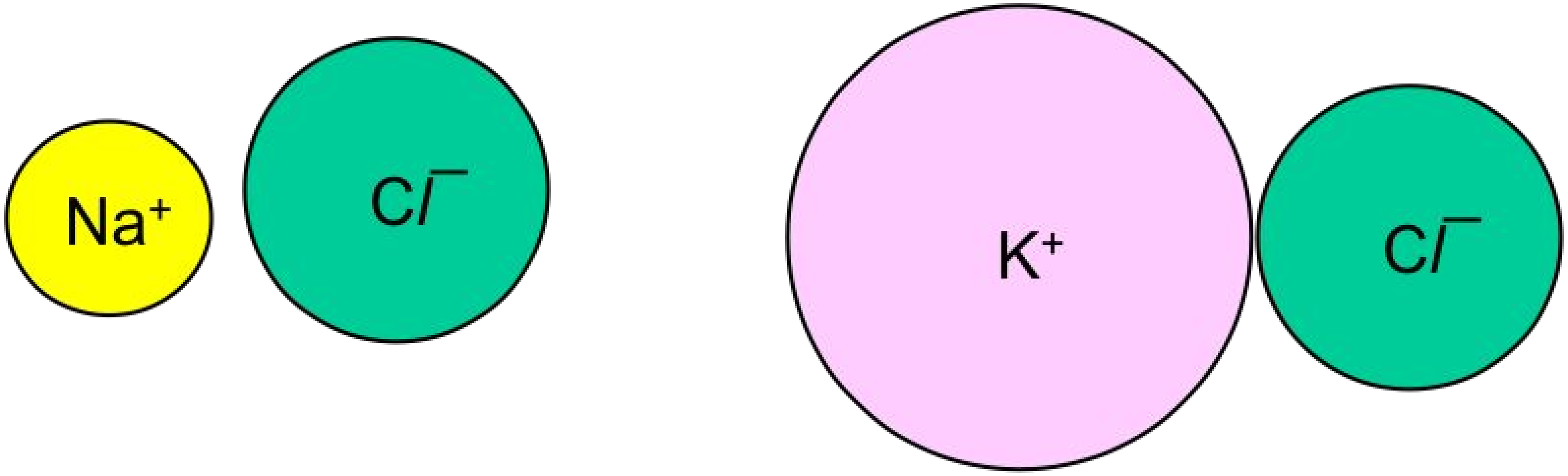
Lattice Enthalpy Values

	Cl^-	Br^-	F^-	O^{2-}
Na^+	-780	-742	-918	-2478
K^+	-711	-679	-817	-2232
Rb^+	-685	-656	-783	
Mg^{2+}	-2256			-3791
Ca^{2+}	-2259			

Smaller ions will have a greater attraction for each other because of their higher charge density. They will have larger Lattice Enthalpies and larger melting points because of the extra energy which must be put in to separate the oppositely charged ions.

Main

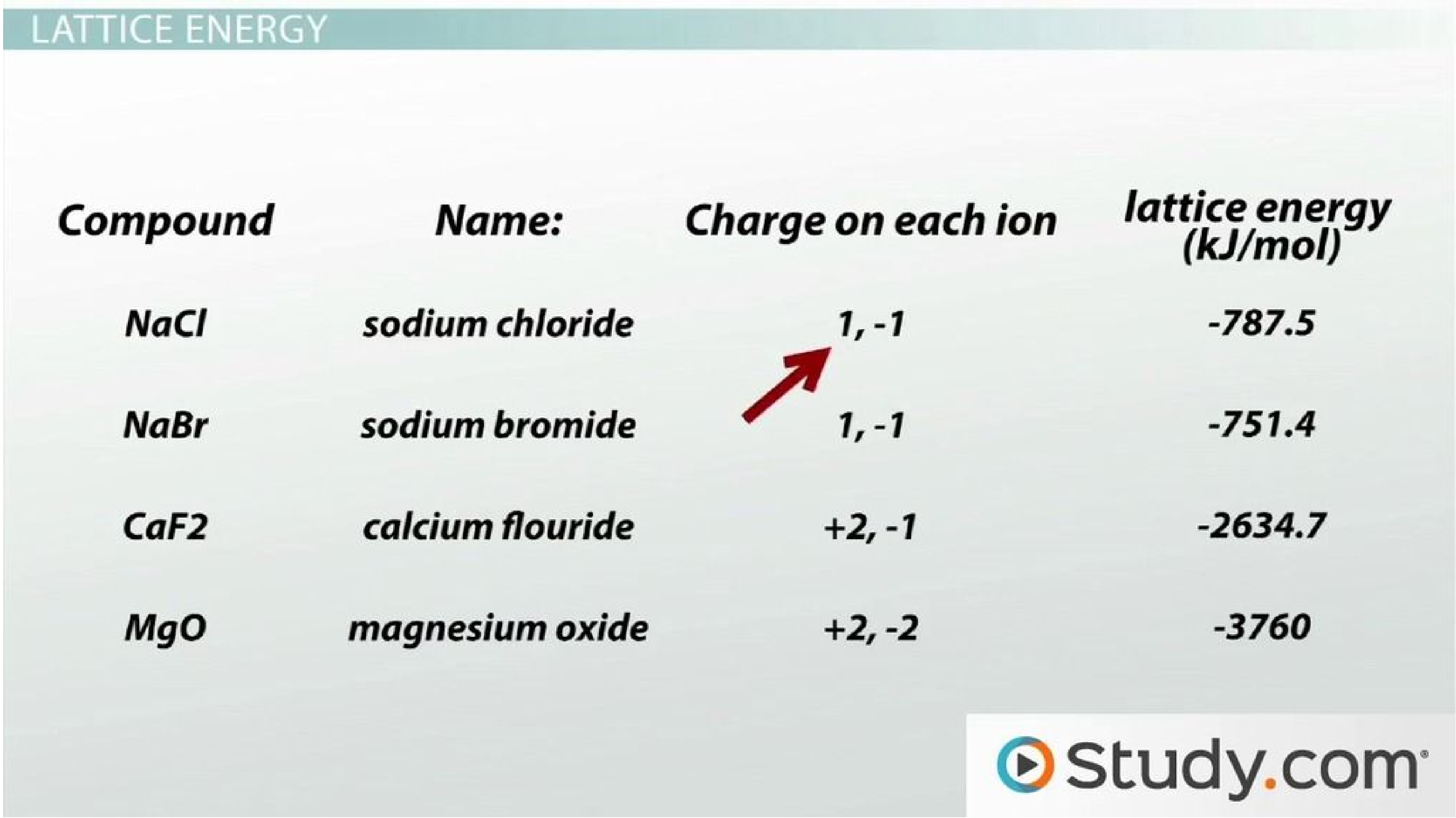
Lattice Enthalpy Values



The sodium ion has the same charge as a potassium ion but is smaller. It has a higher charge density so will have a more effective attraction for the chloride ion. More energy will be released when they come together.

Main

Lattice Enthalpy Values



LATTICE ENERGY

Compound	Name:	Charge on each ion	lattice energy (kJ/mol)
NaCl	sodium chloride	1, -1	-787.5
NaBr	sodium bromide	1, -1	-751.4
CaF2	calcium flouride	+2, -1	-2634.7
MgO	magnesium oxide	+2, -2	-3760

Standard Enthalpy Change of Solution, ΔH°_{sol}

- The standard enthalpy change of solution is the change in enthalpy when 1 mole of a substance is dissolved in a large excess of a pure solvent
  - Can have either positive or negative values

$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq) \qquad \Delta H^\circ_{sol} = +14.78\ kJ\ mol^{-1}$

$LiBr(s) \rightarrow Li^+(aq) + Br^-(aq) \qquad \Delta H^\circ_{sol} = -48.83\ kJ\ mol^{-1}$

- It is possible to calculate the enthalpy change of solution empirically, or by using an energy cycle that involves the lattice enthalpy of the ionic solid and the subsequent hydration enthalpy of the gaseous ions produced.

Main

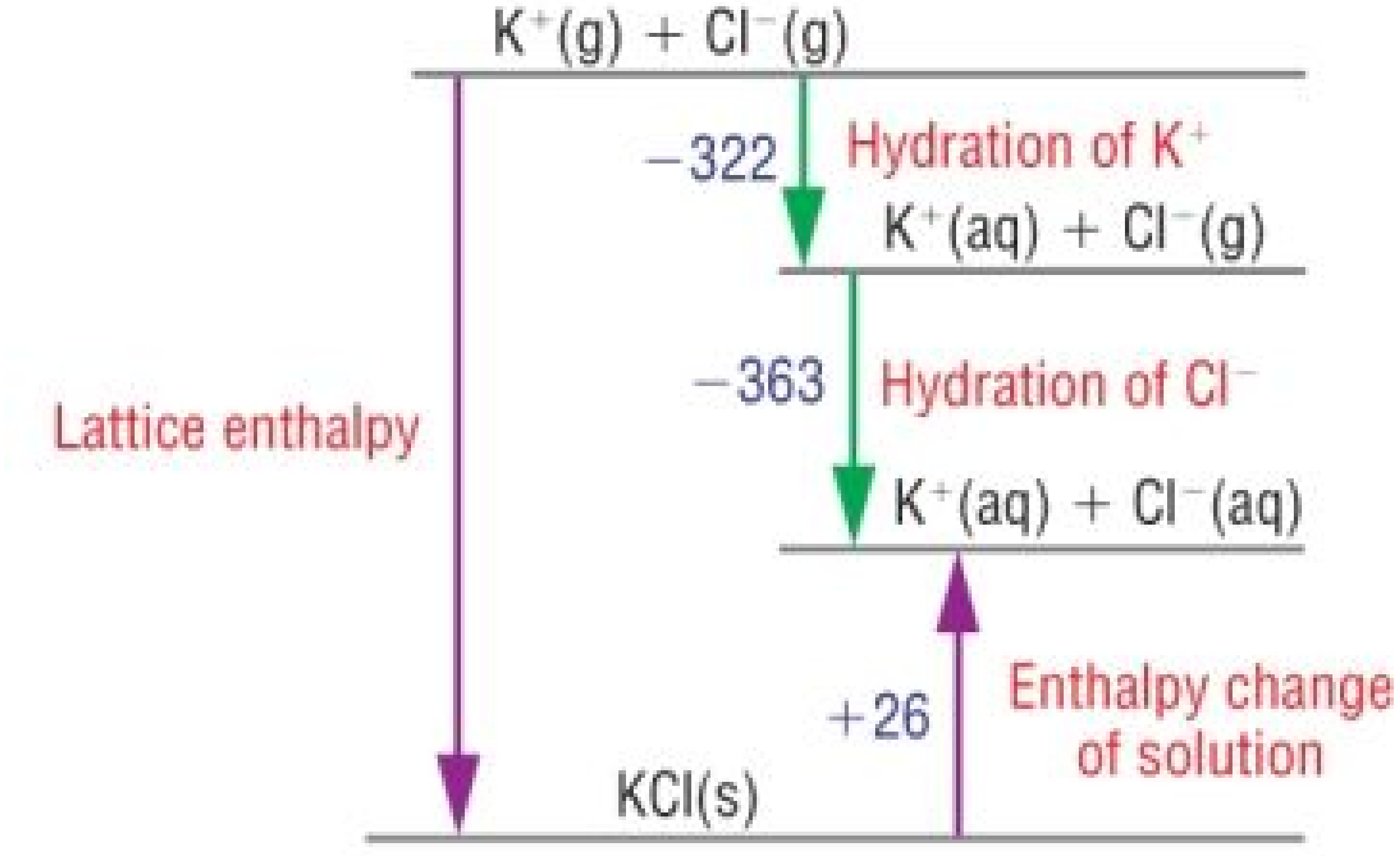
Enthalpy Change of Hydration, ΔH°_{hyd}

- The enthalpy change of hydration for an ion is the enthalpy change when 1 mole of the gaseous ion is added to water to form a dilute solution
  - The term solvaton is used in place of hydration for solvents other than water
  - The enthalpy change of hydration always has a negative value

$$M^+(g) \rightarrow M^+(aq) \qquad \Delta H^\circ_{hyd} = -\ \mathrm{kJ\ mol^{-1}}$$

$$X^-(g) \rightarrow X^-(aq) \qquad \Delta H^\circ_{hyd} = -\ \mathrm{kJ\ mol^{-1}}$$

Enthalpy Change of Solution



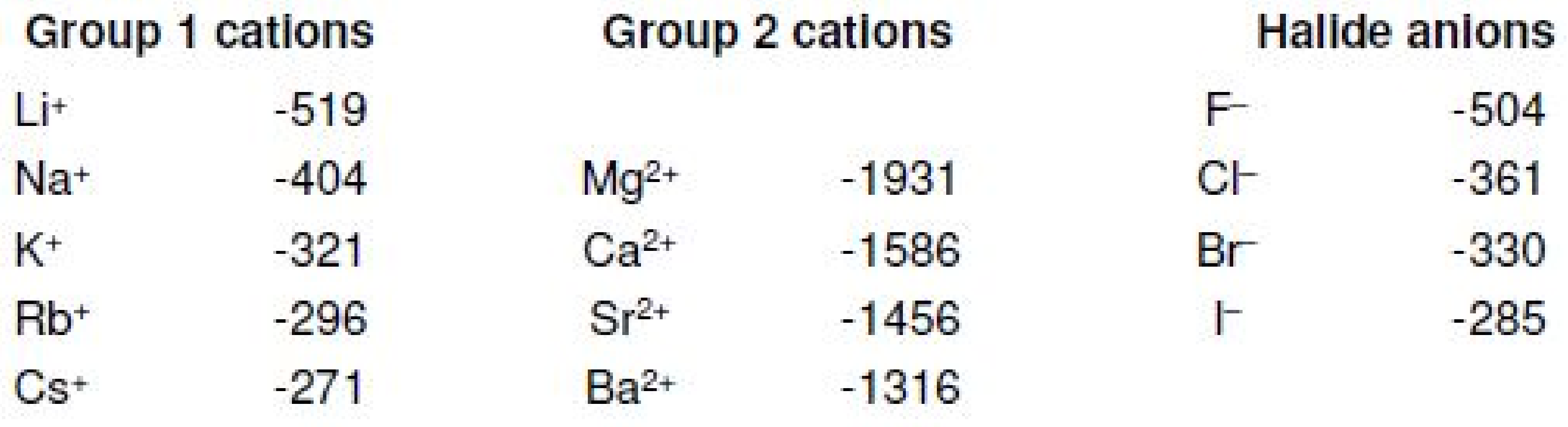
Enthalpy of Hydration

- The enthalpy of hydration is a way of quantifying the amount of energy released during the process of solvation
    - Solvation is described as any stabilizing interaction of a solute and the solvent or a similar interaction of solvent with groups of an insoluble matter.

- The magnitude of the enthalpy of hydration is influenced by the charge and size of the ion.
    - Table 20 in the Data Booklet

Main

Enthalpy of Hydration



Group 1 cations		Group 2 cations		Halide anions	
Li^+	-519			F^-	-504
Na^+	-404	Mg^{2+}	-1931	Cl^-	-361
K^+	-321	Ca^{2+}	-1586	Br^-	-330
Rb^+	-296	Sr^{2+}	-1456	I^-	-285
Cs^+	-271	Ba^{2+}	-1316		

- As you move down a group in the periodic table the enthalpy of hydration decreases as the ionic radius increases.
- For cations, an increase in charge on the ion combined with a decrease in size results in significantly larger enthalpy of hydration.

Main

International Mindedness

The importance of being able to obtain measurements of something which cannot be measured directly is significant everywhere. Borehole temperatures, snow cover depth, glacier recession, rates of evaporation and precipitation cycles are among some indirect indicators of global warming. Why is it important for countries to collaborate to combat global problems like global warming

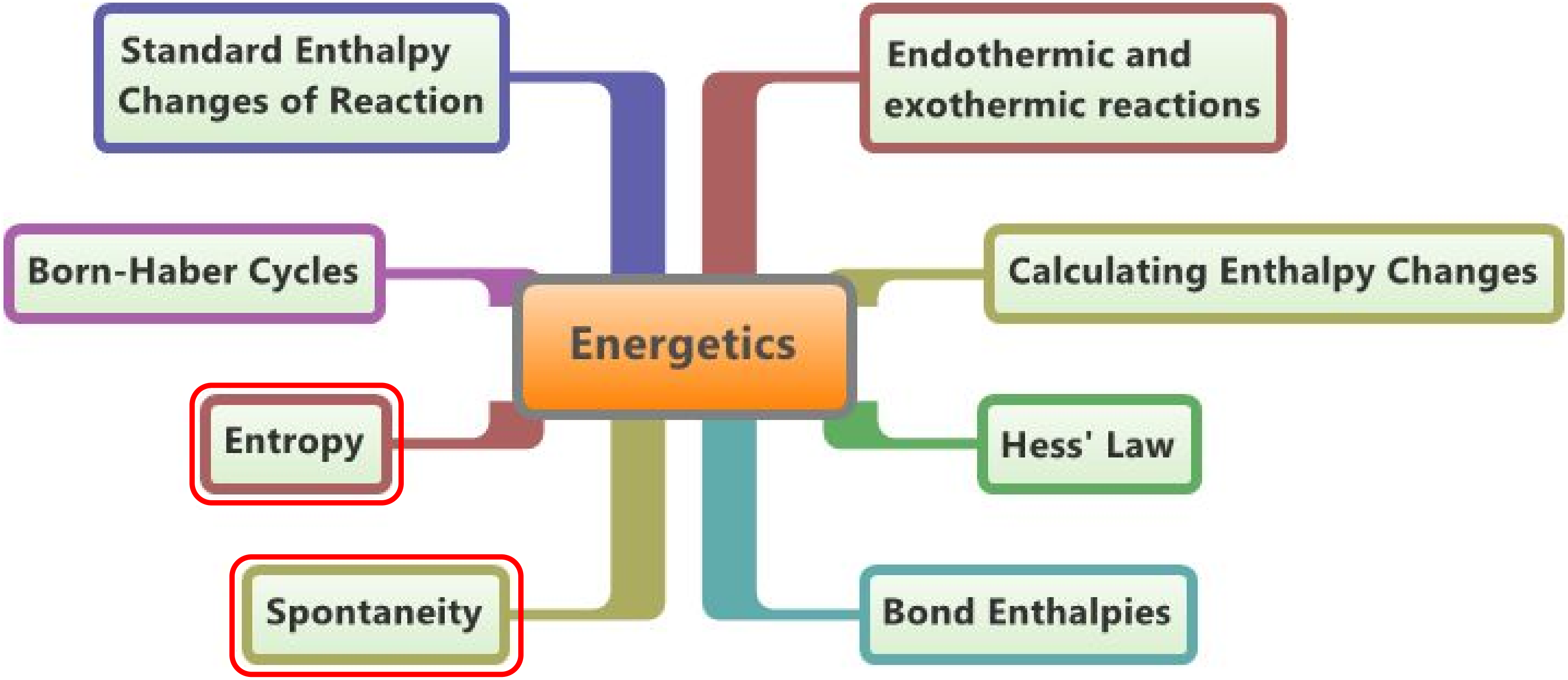
Main

Lesson 5

15.2 Entropy and Spontaneity

Main
Menu

We Are Here



Standard Enthalpy Changes of Reaction

Endothermic and exothermic reactions

Born-Haber Cycles

Calculating Enthalpy Changes

Energetics

Entropy

Hess' Law

Spontaneity

Bond Enthalpies

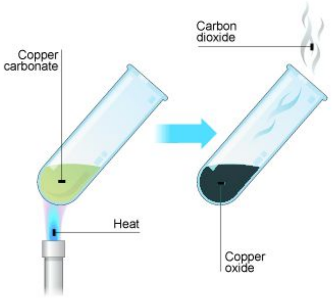
Main

Spontaneity

- A spontaneous reaction is one that keeps itself going
  - i.e. It doesn't require an external energy input
- Some reactions are spontaneous at all temperatures:
  - Although if you lower the temperature enough, the rate might be too low to matter
- Some reactions only become spontaneous above a certain temperature while others are only spontaneous below a certain temperature.
- Exothermic reactions are usually spontaneous, with some exceptions

- Burning wood is a spontaneous reaction

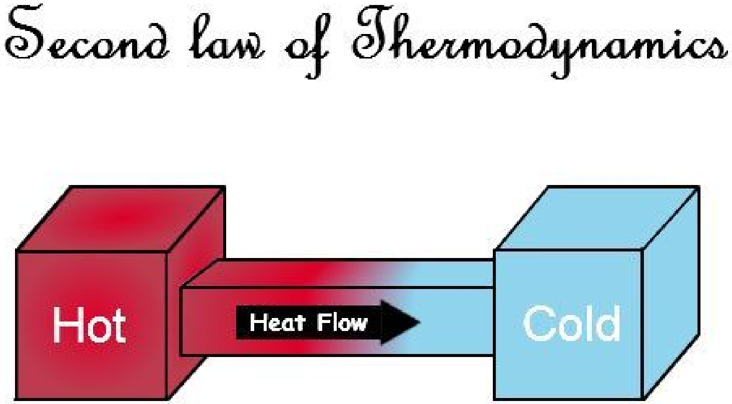
- The thermal decomposition of copper carbonate is a non-spontaneous reaction



Main

Spontaneity

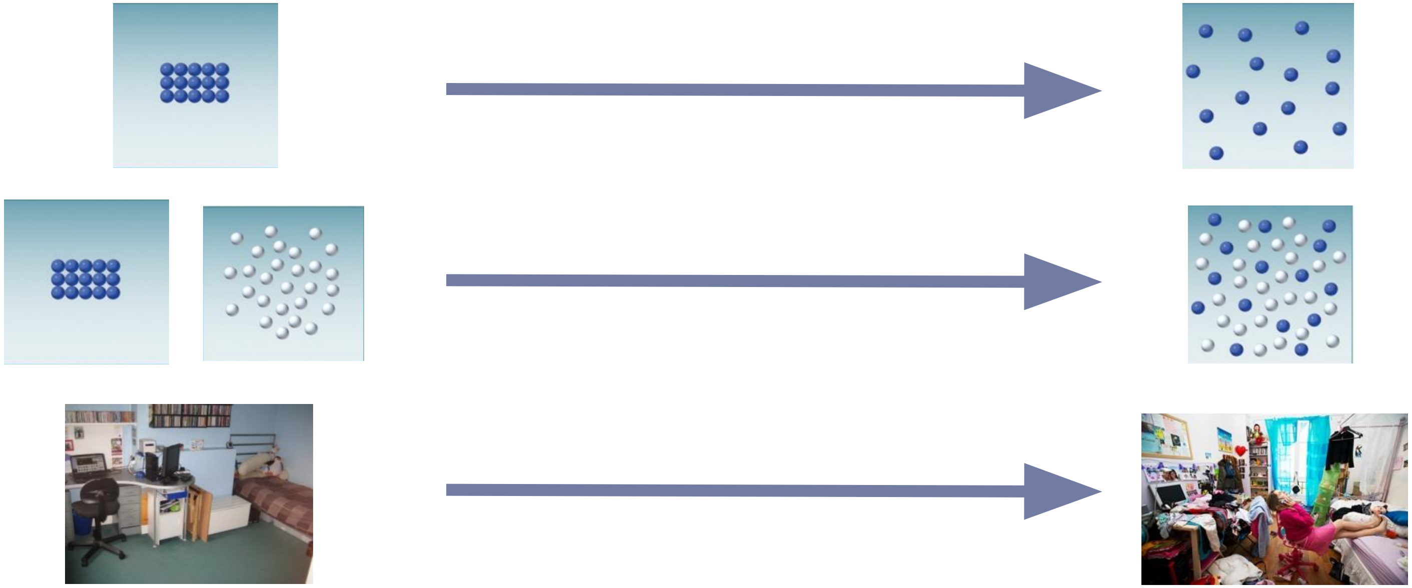
- The first and second law of thermodynamics are fundamental practical applications in chemistry
  - The first law, the law of conservation of energy, concerns energy n the physical world
  - The second law of thermodynamics focuses on entropy and the spontaneity of chemical reactions



Main

Entropy, S

- Entropy (*S*) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
  - The disorder of a system
- Units: J K^{-1} mol^{-1} (Joules per Kelvin per mole)



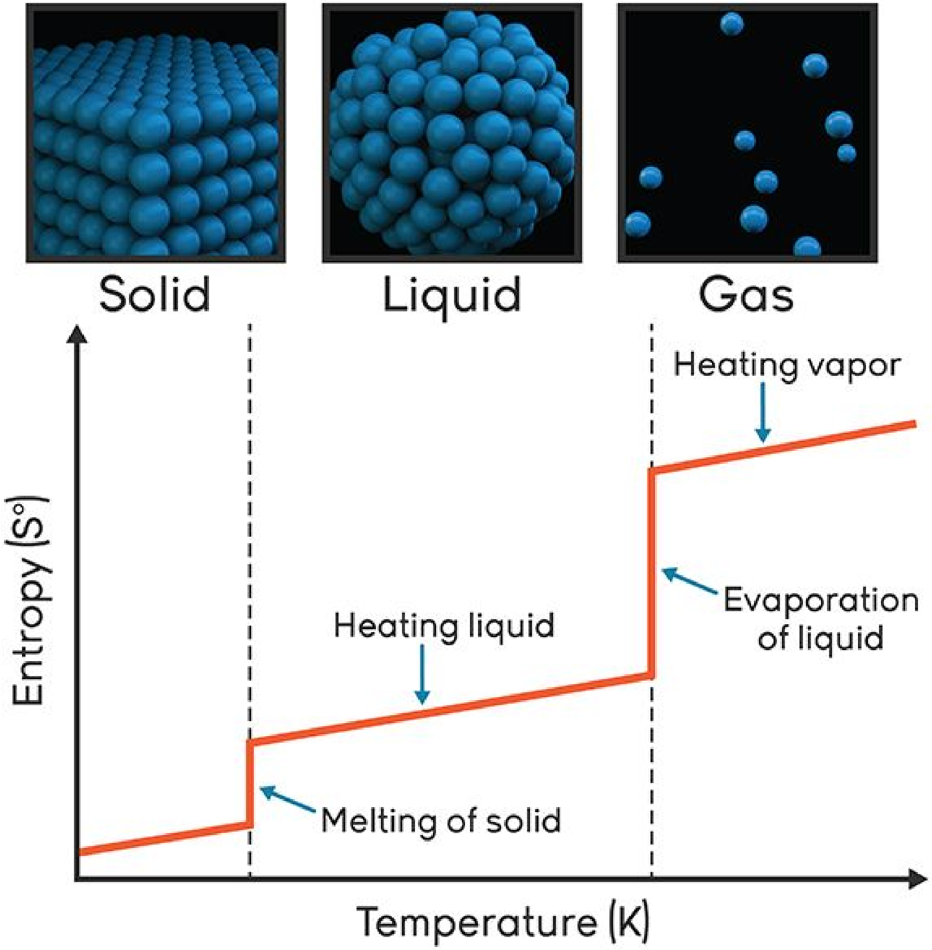
LOW ENTROPY

HIGH ENTROPY

Main

Entropy of Phases

Entropy of gas>liquid>solid under same conditions.



Main

Entropy

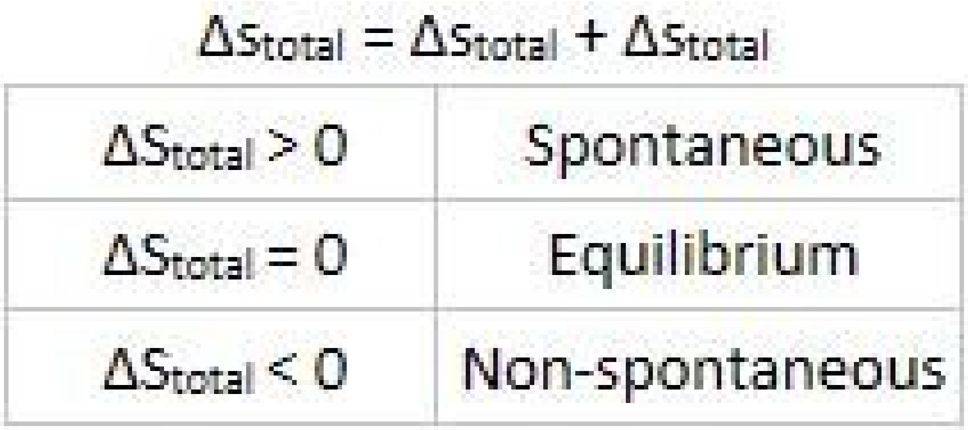
- Spontaneous reactions lead to an increase in the total entropy within the system and the surroundings
- Entropy is a state function, so a change in entropy is determined by the difference between its final and initial values

$$\Delta S_{298}(\text{reaction}) = \Sigma S_{298}(\text{products}) - \Sigma S_{298}(\text{reactants})$$

Main

Entropy

- When the overall entropy of the universe remains unchanged, the system is in equilibrium.
- If the overall entropy of the universe is found to be negative, the reaction is non-spontaneous, or spontaneous in the opposite direction



$$\Delta S_{total} = \Delta S_{total} + \Delta S_{total}$$

$\Delta S_{total} > 0$	Spontaneous
$\Delta S_{total} = 0$	Equilibrium
$\Delta S_{total} < 0$	Non-spontaneous

Main

Entropy

- An increase in enthalpy within the system will result in increased movement of the particles, leading to greater disorder and an increase in the entropy of the system
- The changes in both enthalpy and entropy affect the spontaneity of a chemical reaction
  - Exothermic reactions are more likely to be spontaneous, as this leads to a reduction in enthalpy and greater stability of the reaction products
  - An increase in entropy makes reactions more likely to be spontaneous, as greater disorder leads to more uniform distribution of energy within the system

Main

Entropy

- Lower Entropy:
  - Pure substances
  - Slow moving particles
  - Particles close together
  - Fewer particles
  - Solids

- Higher Entropy
  - Mixtures of substances
  - Fast moving particles
  - Particles spread out
  - More particles
  - Gases

Main

Factors Affecting Entropy

- An increase in the number of moles of gas
  - ΔS: positive; Entropy: increases

- A decrease in the number of moles of gas
  - ΔS: negative; Entropy: decreases

- An increase in temperature
  - ΔS: positive; Entropy: increases

- An increase in pressure
  - ΔS: positive; Entropy: increases

Main

Calculating Entropy Change, $\Delta S^\ominus$

- For example:
  - Calculate the standard entropy change when pentane ($S^\ominus$=261 $JK^{-1}mol^{-1}$) is ‘cracked’ to form propane ($S^\ominus$=270 $JK^{-1}mol^{-1}$) and ethene ($S^\ominus$=220 $JK^{-1}mol^{-1}$) :

  - $C_5H_{12}(l) \rightarrow C_2H_4(g) + C_3H_8(g)$
  - $\Delta S^\ominus$ = (270 + 220) – 261 = **229 J K^{-1} mol^{-1}**
  - The positive nature of this result should be expected, as you have increased the number of molecules, and changed state from liquid to gas

Calculate $\Delta S^\ominus$ for:

For each one, explain why $\Delta S^\ominus$ has the sign it does

$\Delta S^\ominus$ are written underneath the formula if not in data booklet.

- $C_6H_{14}(l) \rightarrow C_2H_4(g) + C_4H_{10}(g)$
- $CH_4(g) + 2\underset{205}{O_2}(g) \rightarrow \underset{214}{CO_2}(g) + 2\underset{189}{H_2O}(l)$
- $6\underset{214}{CO_2}(g) + 6\underset{189}{H_2O}(l) \rightarrow \underset{209}{C_6H_{12}O_6}(s) + 6\underset{205}{O_2}(g)$

Main

Gibbs Free Energy, G

- GIbbs free energy is a state function
- ΔG is a convenient way to take into account both the direct entropy change resulting from the transformation of the chemicals, and the indirect entropy change of the surroundings as a result of the gain/loss of heat energy
- The combination of enthalpy, entropy, and temperature of a system can be used to determine Gibbs free energy

Main

Gibbs Free Energy: Measuring Spontaneity

- Spontaneity is measured by Gibbs Free Energy:
  - -ve means spontaneous
  - +ve means non-spontaneous

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

$$\Delta G_f^{\ominus} = \Sigma\Delta G^{\ominus}_f\ \text{(products)} - \Sigma\Delta G^{\ominus}_f\ \text{(reactants)}$$

Main

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

- Is the reaction of ethene with hydrogen (to form ethane), spontaneous at room temperature (298K)?
  - $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
    - $\Delta H^\ominus = -137$ kJ mol^{-1}
    - $\Delta S^\ominus = -121$ J K^{-1} mol^{-1}
  - Calculate Gibbs Free Energy
    - $\Delta G = \Delta H - T\Delta S$
    - $\Delta G = -137 - (298 \times -121)/1000$ Divide by 1000 to convert to kJ
    - $\Delta G = -149 - (-36) = -101$ kJ mol^{-1}
  - Evaluate the answer
    - The answer is negative, which means the reaction is spontaneous at room temperature

The Effect of Changing the Temperature

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

- What happens if we increase the temperature?
  - Since ΔH and both ΔS are both negative, ΔG can be either positive or negative depending on the temperature
    - A high temperature will make the 'TΔS' term large enough to counter-balance the ΔH term
    - At any temperature below a certain point, the reaction will be spontaneous
      - □ This does not mean that the reaction will be fast, just that it will (in theory) happen

Main

Summarizing the Effect Of Temperature Changes

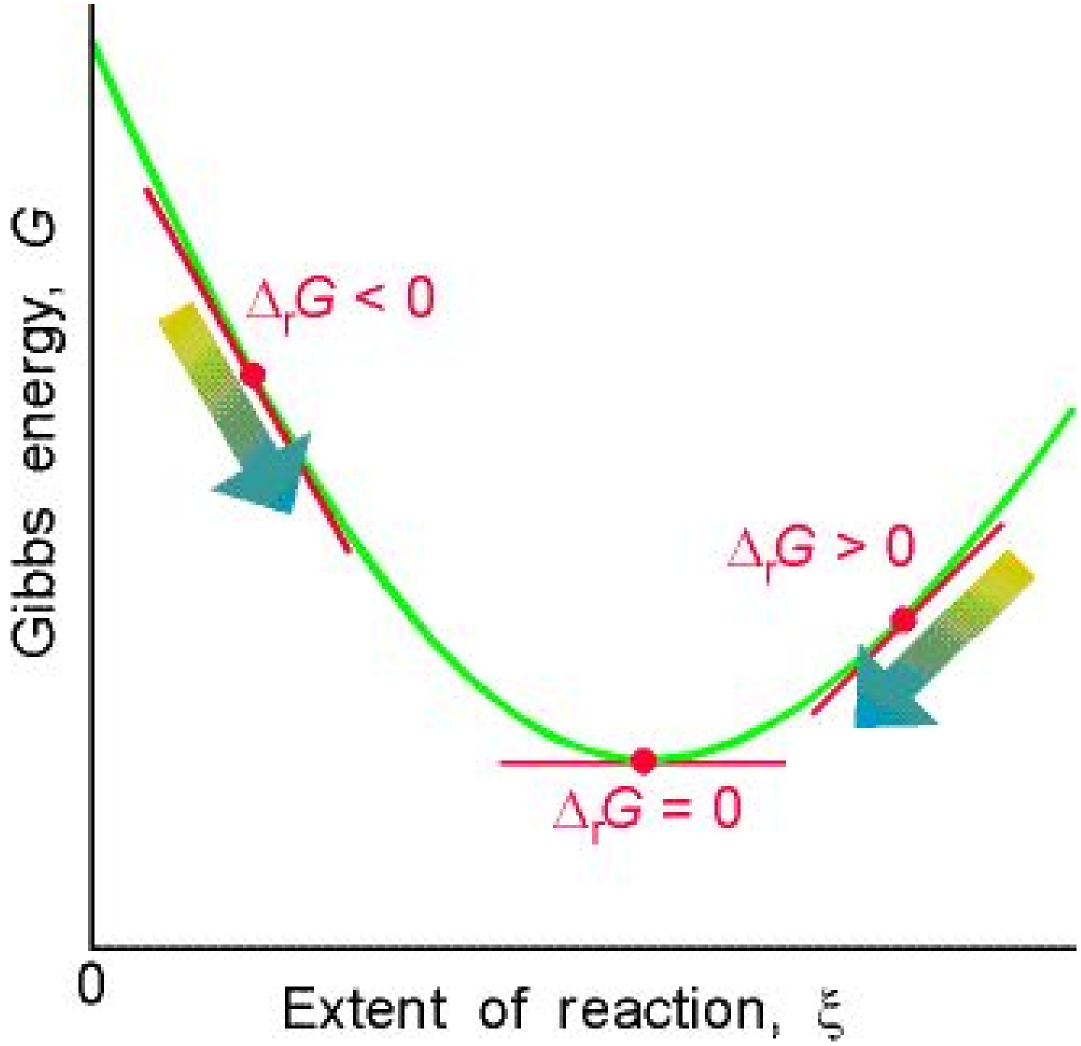
ΔH	ΔS	$-T\Delta S$	ΔG	**Spontaneity**
+	-	+	+	Nonspontaneous
-	+	-	-	Spontaneous
-	-	+	+ or -	Low Temp: Spontaneous High Temp: Nonspontaneous
+	+	-	+ or -	Low Temp: Nonspontaneous High Temp: Spontaneous

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

Use the equation to help yourself reason these through

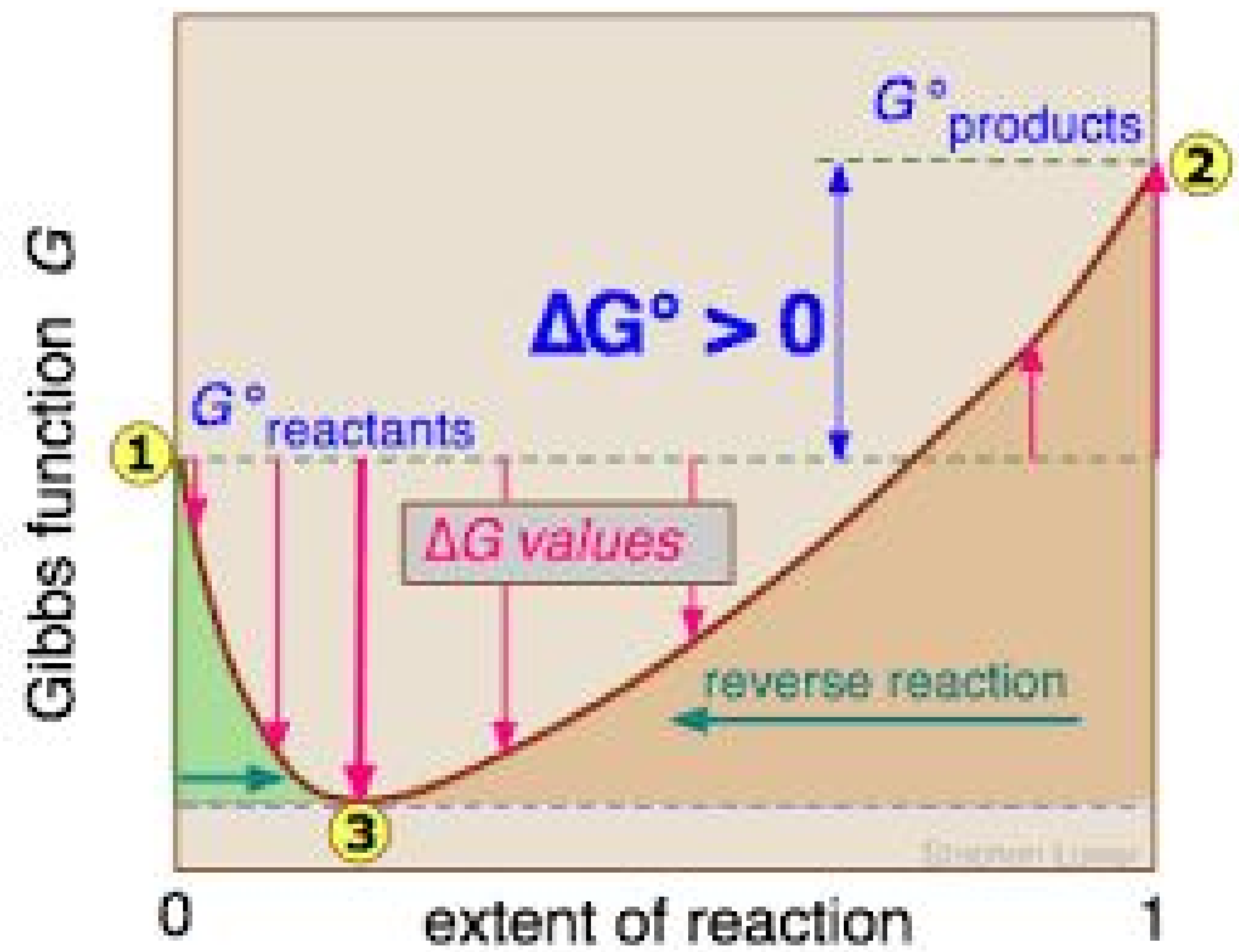
Main

Free Energy and Equilibrium



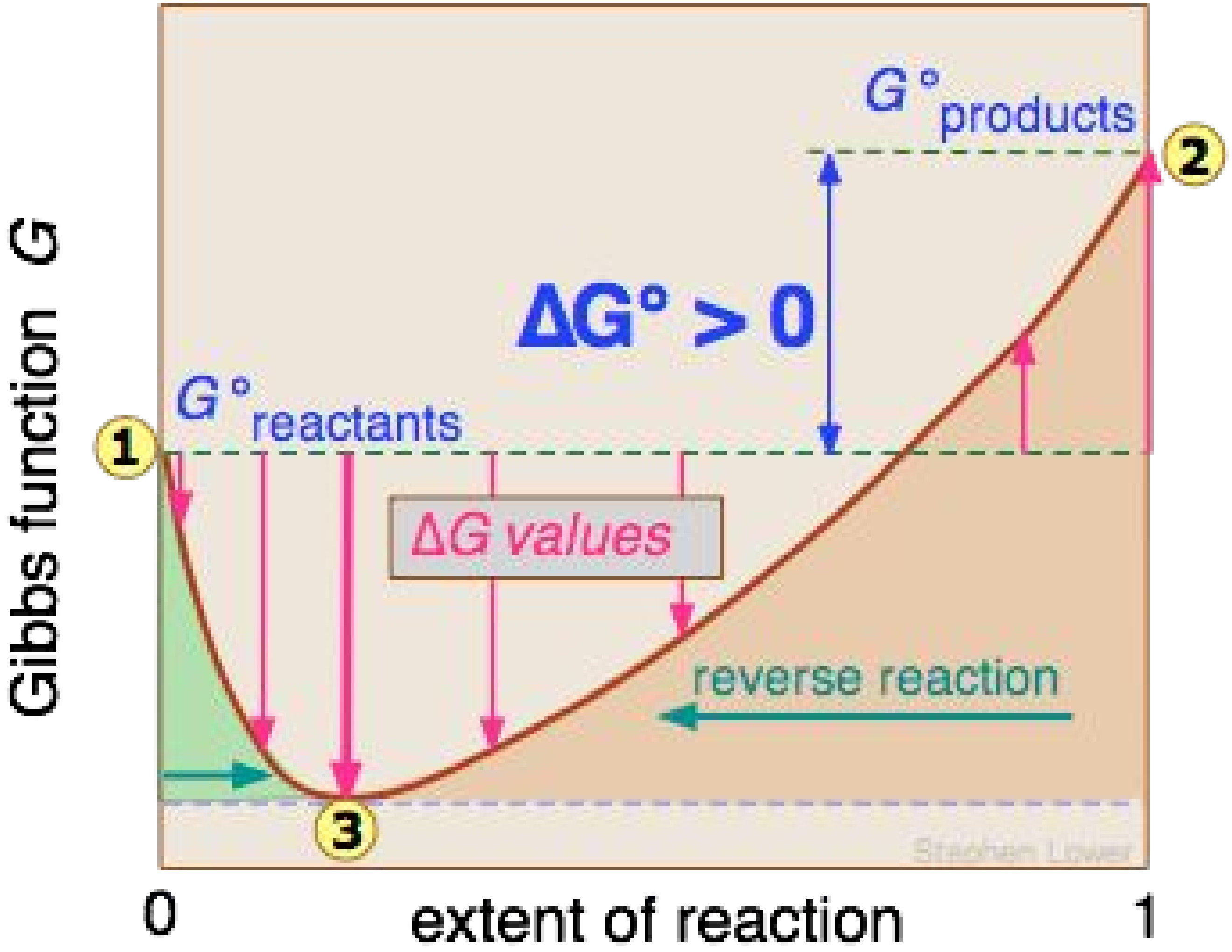
Main

Favors Reactants to Products



Main

Favors Products to Reactants



Main