

NCEA Chemistry 3.4
Particles, Substances and Thermochemistry AS 91390





#### **Achievement Criteria**

This achievement standard involves describing properties of atoms, molecules, and ions, and thermochemical principles.

AS 91390 **C3.4** 

#### Properties of particles will be limited to:

- $\square$  electron configuration of atoms and ions of the first 36 elements (using *s*,*p*,*d* notation)
- periodic trends in atomic radius, ionisation energy, and electronegativity, and comparison of atomic and ionic radii
- Lewis structures and shapes (up to six electron pairs about the central atom for molecules and polyatomic ions, including those with multiple bonds), polarity of molecules
- □ attractive forces between atoms, ions, and molecules. These will include ionic bonds, covalent bonds, and intermolecular attractions due to temporary dipoles and permanent dipoles (including hydrogen bonding).

#### Properties of substances will be limited to:

- melting point, boiling point and solubility
- □ enthalpy and entropy changes associated with spontaneity in chemical reactions (entropy calculations are not required)

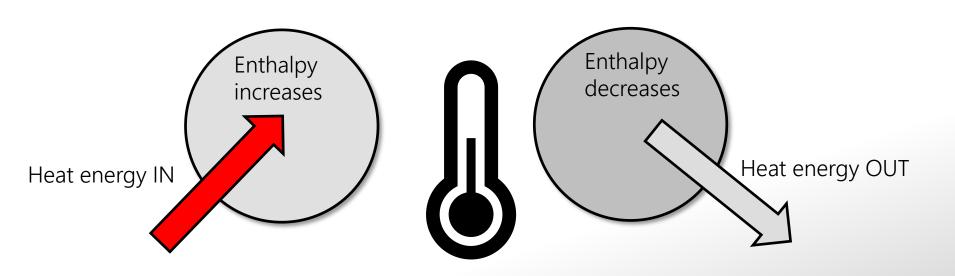
#### Thermochemical principles will include

- ☐ specific heat capacity
- $\Box \Delta_c H^\circ$ ,  $\Delta_f H^\circ$ ,  $\Delta_r H^\circ$ ,  $\Delta_{vap} H^\circ$ ,  $\Delta_{sub} H^\circ$ , and  $\Delta_{fus} H^\circ$
- $\square$  Hess's Law including application of  $\Delta_r H = \sum \Delta_f H(\text{(products)} \sum \Delta_f H(\text{reactants)})$  and related calculations.

# Enthalpy and Enthalpy change

Enthalpy (or Heat Content) is the energy in a substance due to kinetic energy of particles and potential energy in chemical bonds.

Enthalpy change  $\Delta H$  is the difference in enthalpy of products  $H_P$  and reactants  $H_R$ 



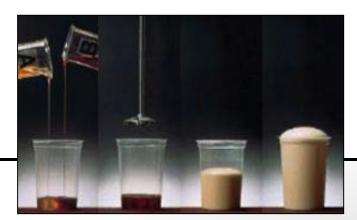
$$\Delta H = H_P - H_R$$

# **Enthalpy Changes**

 $H_p$  (products) and  $H_r$  (reactants) cannot be directly measured.

We can measure Enthalpy change ( $\Delta H$ ) by measuring energy change, normally as a change in temperature.

Released to surroundings (Exothermic Reactions)



Absorbed from surroundings (Endothermic Reactions)

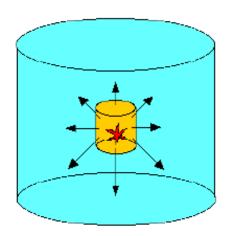


#### **Endothermic and Exothermic**

# **Exothermic Reactions**

These are reactions where **heat energy** is **released** into the surroundings.

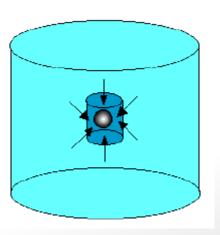
Surroundings gain heat energy. (increase in temperature)



# **Endothermic Reactions**

These are reactions where **heat energy** is **absorbed** from the surroundings.

Surroundings lose heat energy. (Decrease in temperature)



Products will have less energy than reactants.



Products will have more energy than reactants.



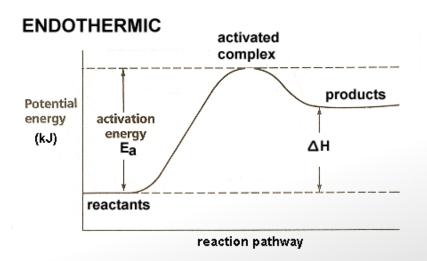
H is POSITIVE (+)

## **Enthalpy Diagrams**

Enthalpy Diagrams can be used to show the relative amounts of enthalpy of the reactants and products in a reaction, as well as the direction and relative size of enthalpy change. In endothermic reactions, the enthalpy change will be positive and in exothermic reactions, the enthalpy change will be negative.

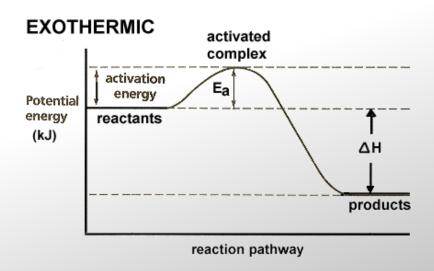
**Endothermic Reactions** e.g. Reacting methane with steam at high pressure and temp. Energy is

absorbed



#### **Exothermic Reactions**

e.g. Burning of methane in air. Energy is released

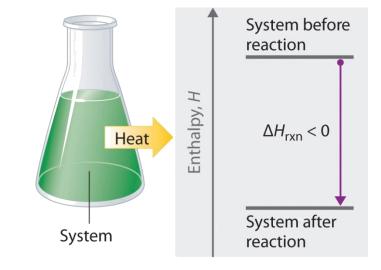


## **Enthalpy Change**

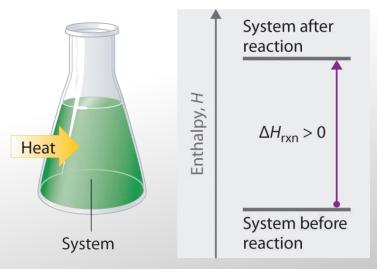
An exothermic reaction will release energy and the products will be at a lower enthalpy level than the reactants.

The reaction system will feel will feel hot to the touch as the energy is released as heat energy.

An endothermic reaction will absorb energy and the products will be at a higher enthalpy than the reactants. The reaction system will feel cool to the touch as heat energy is taken from the surroundings, including your skin, and used to break bonds in the molecules.



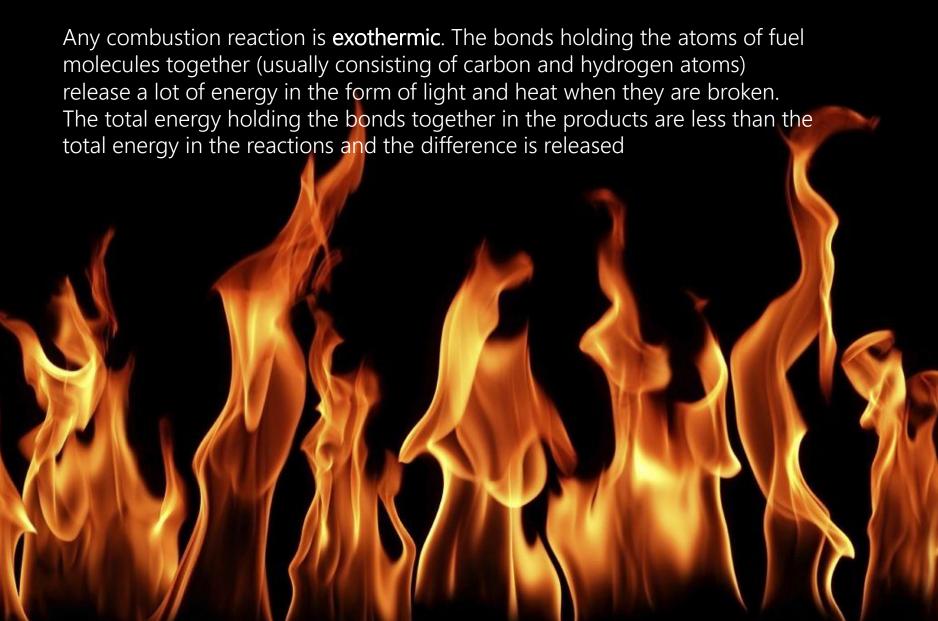
(a) Exothermic reaction



(b) Endothermic reaction



#### **Exothermic reactions**



# **Endothermic reactions**



Melting ice is an example of an endothermic reaction. The solid ice (water) atoms, that are in a fixed pattern, are barely moving and need to absorb energy in order to move faster and break the bonds to form water in a liquid state.

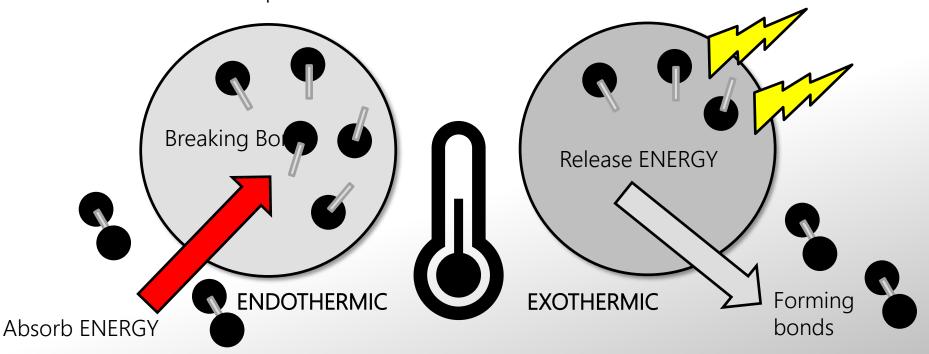


# Forming and breaking Bonds

<u>Bonds forming</u> between atoms and molecules release energy therefore **bond forming** is an exothermic reaction. Bonds are formed to form a stable molecule.

<u>Bonds breaking</u> between atoms and molecules require energy therefore **bond**<u>breaking is an endothermic reaction</u>. The input of energy (usually light or heat energy) cause the atoms and molecules to move faster and 'pull away' from each other. Each type of bond has its own specific amount of energy, called *bond enthalpy* measured in kJ, required to break its bond.

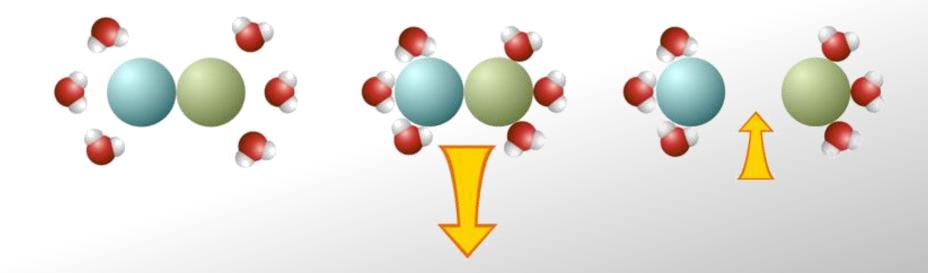
Most reactions both break and form bonds - the overall NET change in enthalpy determines whether a particular reaction is endothermic or exothermic



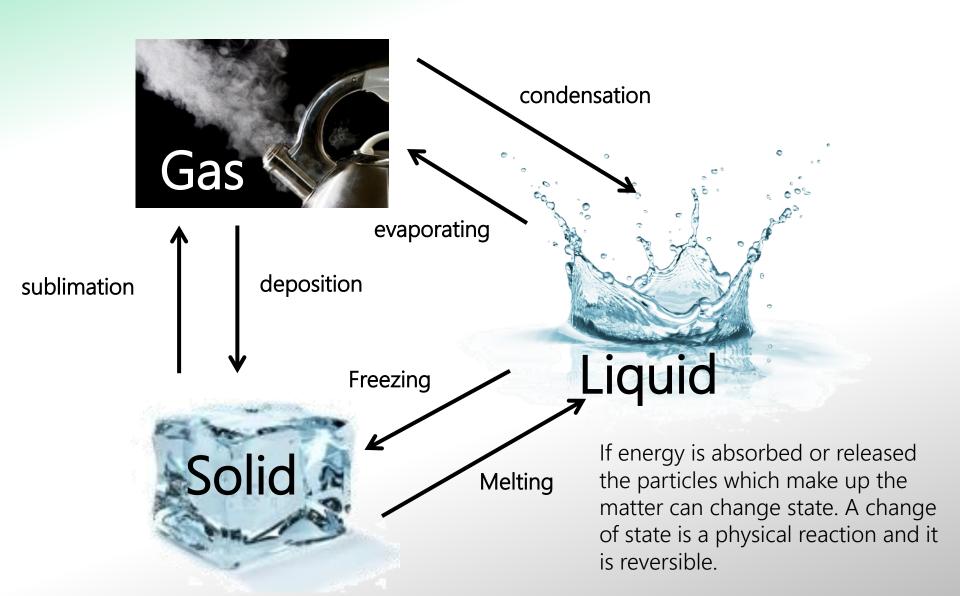
# **Enthalpy in Dissolving**

If more energy is released when water bonds to the solute than it takes to separate the solute, the dissolving is exothermic and the temperature increases. An example is adding a strong acid (such as sulfuric acid) or base (such as sodium hydroxide)

However, for some substances dissolving the reaction is **endothermic**, for example Potassium chloride in water. More energy is needed to break the bonds between this ionic salt than released when new bonds are formed with the ions and water molecules.

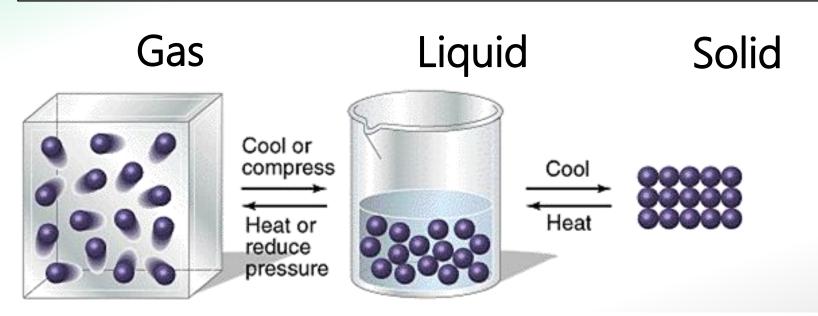


# **Enthalpy in Changes of State**



### **Enthalpy in Changes of State**

**Solid particles** are packed closely and only vibrate in a fixed position. **Liquid particles** are also packed closely but the particles move around more. **Gas particles** have a lot of space between them and move around quickly.



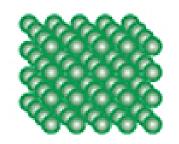
Total disorder; much empty space; particles have complete freedom of motion; particles far apart.

Disorder; particles or clusters of particles are free to move relative to each other; particles close together.

Ordered arrangement; particles are essentially in fixed positions; particles close together.

# Particles of different states have different kinetic energy levels

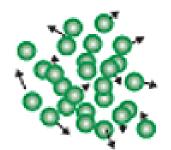
**Kinetic energy** causes particles to move. The more kinetic energy a particle has the faster it moves. Kinetic energy can be added to a particle by adding heat energy (and heats up). The heat energy is then **transformed** into the kinetic energy. Kinetic energy can also be lost from a particle, which slows it down, when it changes back into heat energy and is lost (and cools).



Energy, Heat

The first state: Solid (i.e. Ice)

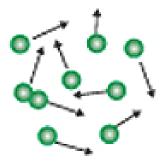
Maintains formation with a little vibration only



The second state: Liquid (i.e. water)

Energy, Heat

Movement of molecules or atoms become free and disorderly



The third state: Gas (i.e. vapor)

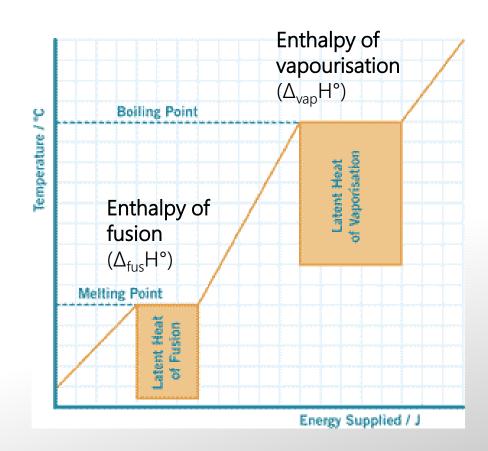
Movement of molecules and electrons become further freer

### **Enthalpy in State Change**

When heat energy is added to a solid substance at a particular temperature called the melting point, it will change state into a liquid.

Prior to this point a rise in heat energy will also show a rise in temperature. At the melting point the heat energy will be used to break the bonds in a solid – an endothermic reaction called latent heat of fusion- rather than show a temperature increase.

The same occurs at the boiling point from a liquid to a gas – an endothermic reaction called **latent** heat of vaporisation.



# **Enthalpy Changes**

Standard Enthalpy of combustion ( $\Delta_c H^\circ$ ) 1 mol of substance combusted

completely in oxygen

Standard Enthalpy of formation ( $\Delta_f H^\circ$ ) 1 mol of substance formed from

constituent elements

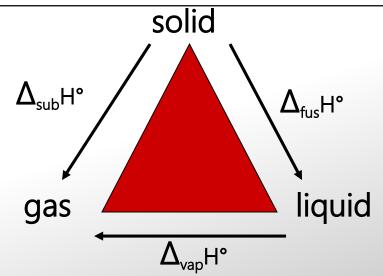
**Enthalpy of reaction** ( $\Delta_r$ H) for any given reaction

Standard conditions ( $\Delta_r$ H°) 1 atmosphere of pressure, 25°C

Enthalpy of fusion ( $\Delta_{fus}H^{\circ}$ ) 1 mol solid to liquid state

Enthalpy of vapourisation ( $\Delta_{vap}H^{\circ}$ ) 1 mol liquid to gas state

Enthalpy of sublimination ( $\Delta_{sub}H^{\circ}$ ) 1 mol solid to gas state



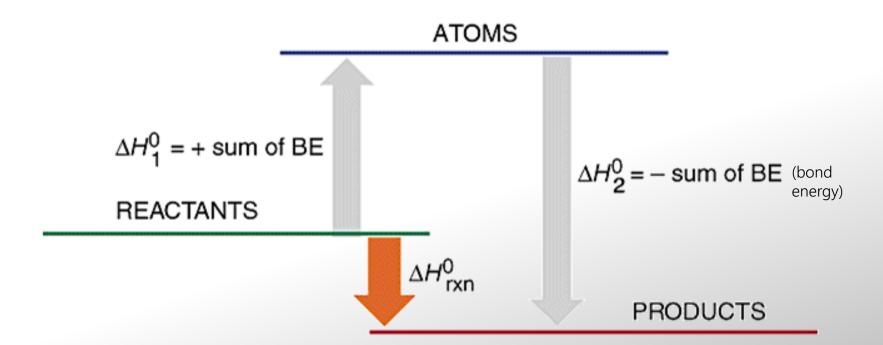
# **Enthalpy of Reaction**

Exothermic - energy released  $\Delta$  H negative

Endothermic - energy absorbed  $\Delta$  H positive

# Standard Enthalpy of Reaction △,H⊖

"The enthalpy change when products are formed from their constituent reactants under standard conditions."



# **Enthalpy of Formation**

Exothermic - energy released  $\Delta$  H negative

Endothermic - energy absorbed  $\Delta$  H positive

Standard Enthalpy of formation ( $\Delta_f H^\circ$ ) - 1 mol of substance formed from constituent elements

Example: 
$$C_3H_{8(g)}$$
 ( $\Delta_f H^{\circ}$ )

$$3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$$

# Standard Enthalpy of Formation △<sub>r</sub>H⊖

"The enthalpy change when one mole of a substance is formed from its constituent elements under standard conditions."

e.g. 
$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$
  $\Delta_f H^\circ = -74 \text{ kJ mol}^{-1}$ 

# **Enthalpy** of Combustion

Exothermic - energy released  $\Delta$  H negative

Endothermic - energy absorbed  $\Delta$  H positive

Standard Enthalpy of combustion ( $\Delta_c H^\circ$ ) – 1 mol of substance combusted completely in oxygen

Example: 
$$C_3H_{8(q)}$$
 ( $\Delta_cH^{\circ}$ )

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

# Standard Enthalpy of Combustion $\Delta_c H^{\Theta}$

"The enthalpy change when one mole of an element or compound reacts completely with oxygen under standard conditions."

e.g. 
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
  $\Delta_cH^\circ = -890 \text{ kJ mol}^{-1}$ 

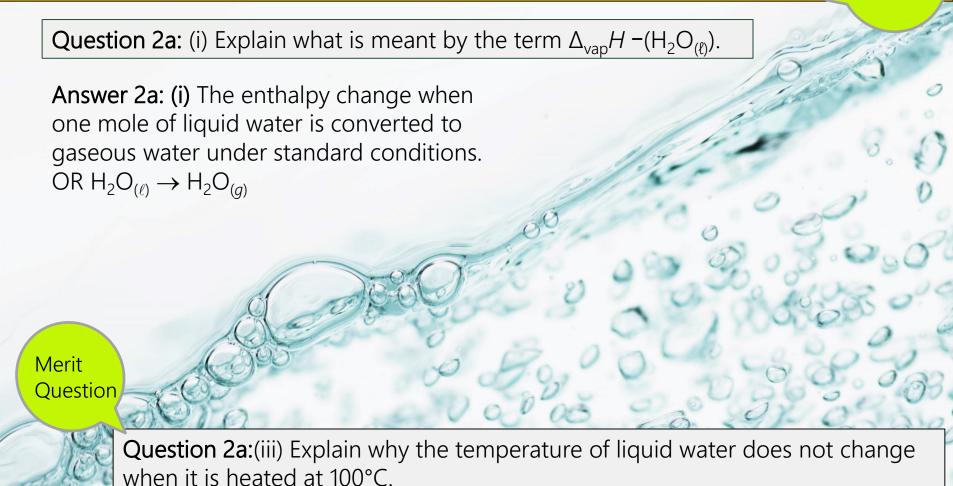
### Standard conditions



Measurements depend on conditions When measuring a enthalpy change you will get different values under different conditions. For example, the enthalpy change of a particular reaction will be different at different temperatures, different pressures or different concentrations of reactants. The values for enthalpy are given for standard conditions, indicated by the superscript  $\theta$ 

Standard conditions include: Temperature of 25°C Atmospheric pressure conditions of 1ATM Concentration of 1mol per Litre

## NCEA 2013 Enthalpy

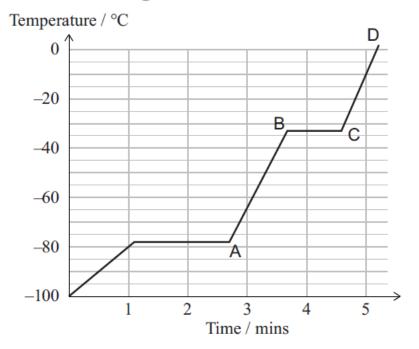


Answer 2a: (iii) At 100°C, energy is used to change liquid water to water vapour. At its boiling point, the heat energy is used to break the intermolecular forces /hydrogen bonds between the H<sub>2</sub>O molecules

#### NCEA 2014 Enthalpy

Question 2d: The following graph shows the change in temperature over a five-minute period for a sample of ammonia, where a constant amount of heat was applied per minute. Using the graph below, justify the physical changes occurring to ammonia between points A and D, in terms of the energy of the particles and the intermolecular forces of attraction.

#### Heating curve for ammonia



Answer 2d: Between A and B, molecules of ammonia are gaining kinetic energy, and hence the temperature increases. Between B and C, molecules of ammonia change from liquid to gas. Energy supplied is used to overcome the intermolecular forces rather than increase the kinetic energy of the particles; thus the temperature does not increase until all the NH<sub>3</sub> is in the gas phase.

Between C and D, the molecules of ammonia gas are again gaining kinetic energy, and so the temperature increases.

## NCEA 2015 Enthalpy

#### Question 2a (i):

The equation for  $\Delta_f H$  ° of  $H_2O_{(1)}$  is:

$$H_{2(q)} + \frac{1}{2}O_{2(q)} \rightarrow H_2O_{(l)} - 286 \text{ kJ mol}^{-1}$$

(a) (i) Write the equation for  $\Delta_c H^{\circ}$  (H<sub>2(q)</sub>).

Answer 2a (i):  $H_{2(q)} + \frac{1}{2}O_{2(q)} \rightarrow H_2O_{(\ell)}$ 

Must have states to get correct

**Question 2a(ii)**: Using the equations above, explain why  $\Delta_c H$  ° (H<sub>2</sub>) and  $\Delta_f H$  (H<sub>2</sub>O) have the same value of -286 kJ mol<sub>-1</sub>.

Achieved Question

**Answer 2a (ii):** The equation for the combustion of hydrogen is the same as the equation for the heat of formation of water.

Standard Enthalpy of combustion ( $\Delta_c H^\circ$ ) 1 mol of substance combusted completely in oxygen

Standard Enthalpy of formation ( $\Delta_f H^\circ$ ) 1 mol of substance formed from constituent elements

## NCEA 2015 Enthalpy

#### Question 2b:

The enthalpy of formation would change if the water was formed as a gas rather than a liquid.

(i) Circle the correct phrase to complete the sentence below.

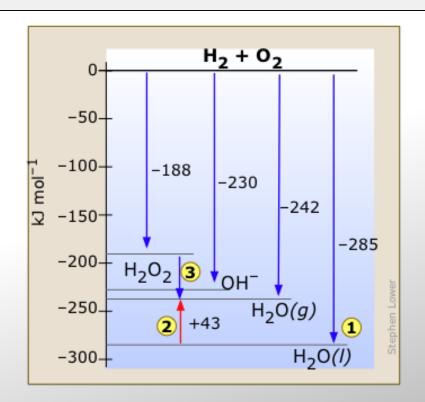
 $\Delta_f H$  °  $(H_2O_{(g))}$  is:

less negative than / the same as / more negative than  $\Delta_f H^{\circ}$  (H<sub>2</sub>O<sub>(1)</sub>).

(ii) Justify your choice.

Answer 2a (ii): The  $\Delta_f H^\circ$  (H<sub>2</sub>O<sub>(g)</sub>) will be less negative than  $\Delta_f H^\circ$  (H<sub>2</sub>O<sub>( $\ell$ )</sub>).

Making bonds releases energy. As less bonding is present in water as a gas than a liquid then less energy will be released when gaseous water is formed thus the  $\Delta_f H^\circ$  (H<sub>2</sub>O<sub>(g)</sub>) will be less negative.



Merit Question

**Question 2c (i)**: Define  $\Delta_{fus}H^{\circ}(NaCl)$ .

Enthalpy of fusion is the energy required to change 1 mol of a substance (NaCl) from a solid to a liquid

**Question 2c (ii)**: Why is  $\Delta_{\text{vap}}H^{\circ}(\text{NaCl})$  greater than  $\Delta_{\text{fus}}H^{\circ}(\text{NaCl})$ ?

Fusion of NaCl only requires sufficient heat energy to break / overcome some of the ionic bonds, whereas vaporisation requires much more heat energy to overcome all the ionic bonds, therefore the  $\Delta_{\text{vap}}H^{\circ}$  of NaCl is much greater than its  $\Delta_{\text{fus}}H^{\circ}$ .



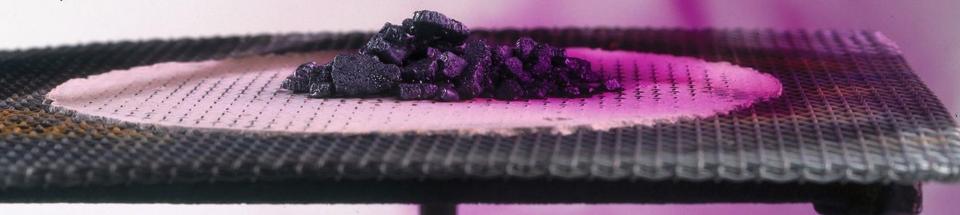
# NCEA 2017 Enthalpy

Question 3b (i): Write an equation for the sublimation of iodine below.

$$I_2(s) \rightarrow I_2(g)$$

Question 3b (ii): Define the enthalpy of sublimation for iodine.

This is the **heat energy** required to change one mole of a substance from solid state to gaseous state (at a given combination of temperature and pressure).



# NCEA 2018 Enthalpy

**Q 3a:** (i) Write an equation to represent the enthalpy of fusion (melting),  $\Delta_{fus}H^{\circ}$ , of water.

(ii) Why is the enthalpy of vaporisation of water larger than its enthalpy of fusion?

$$H_2O_{(s)} \rightarrow H_2O_{(\ell)}$$

The enthalpy of vaporisation is larger than the enthalpy of fusion since much more heat energy is required to break all the attractive forces between liquid particles to form a gas. When a solid changes into a liquid, only some of the attractive forces are overcome, so less heat energy is required.



# NCEA 2019 Enthalpy

Question 2a: The equation for the vaporisation of hexane is:

 $C_6H_{14(I)} \rightarrow C_6H_{14(g)}$ 

Circle the term that best describes this process:

**Exothermic** 

**Endothermic** 

Give a reason for your choice.

Endothermic since energy is required to break the intermolecular forces between the molecules in the liquid state.



# ent

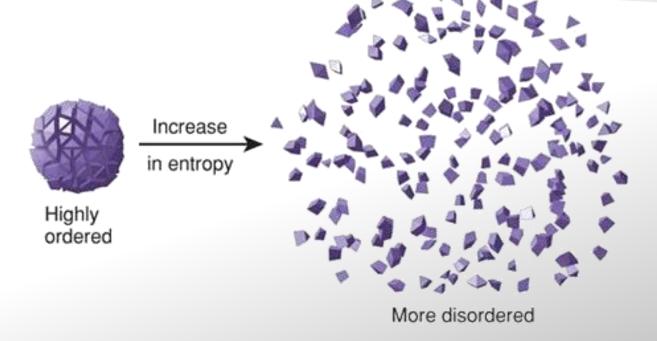
# - measure of disorder

Entropy is the measure of the disorder of a thermodynamic system, usually denoted by the letter S.

A highly ordered system has low entropy. If disorder increases, then as a result, the entropy of a system increases.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

A positive  $+\Delta S$  means Entropy has increased



### **Increasing Entropy**

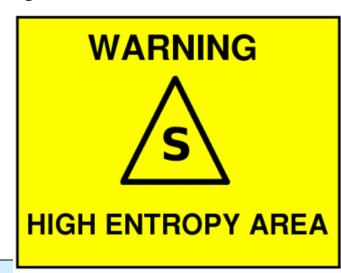
Entropy increases as temperature increases because more kinetic energy means molecules are more disorderly.

Entropy increases in a reaction if the reaction produces more product molecules than it contains reactant molecules

Especially if you are going from a solid to a liquid or to a gas.

Entropy increases when solutions are formed from pure liquids or pure solids. Because there is greater disorder in aqueous solutions then liquids that are pure or solids that are pure.

The entropy of the universe which equals the entropy of system + entropy of surrounding ΔS universe always increases.



#### Extension

If the entropy of the universe is increasing, does that mean the total enthalpy in the universe is increasing too?

Temperature effect can be explained by recognising that entropy increases with temperature and the system temperature changes significantly whereas the temperature of the "universe" is essentially invariant

# Entropy in solids, liquids and gases

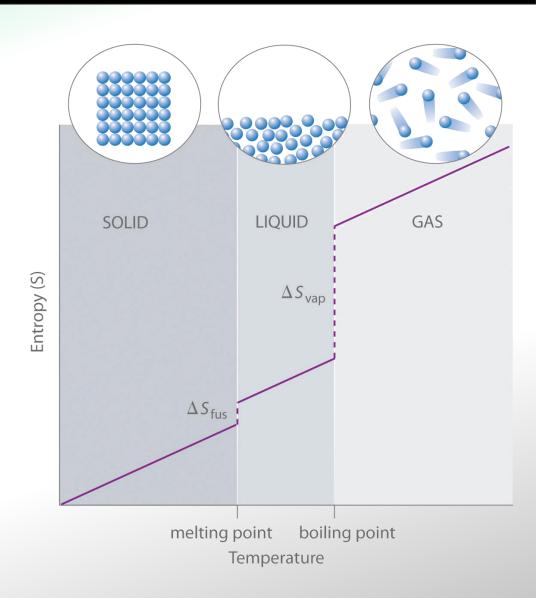
Molecules in the gaseous state have greater entropy than liquid state because there is less "order" in gaseous molecules.

Gas molecules move in random chaos without any restrictions. Therefore, going from liquid to gas you have increased the entropy of the system.

Molecules in the liquid state have a greater entropy then those in the solid state.

Molecules in the solid state are almost fixed in one spot. They are highly ordered and so liquid molecules have more disorder.

So melting increases entropy of a system.



# Entropy in solid, liquid and gas (Extension)

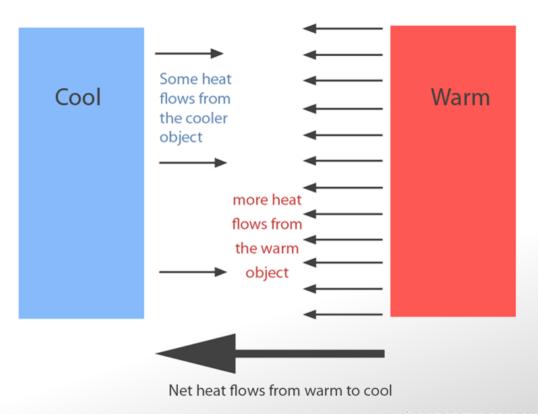


Kinetic energy increases with increasing temperature so the entropy factor becomes more important at higher temperatures. This is why equilibrium constants,  $K_c$ , (which measure the equilibrium position), change with temperature. For example in the case of melting ice, the tendency to minimum enthalpy favours the ice phase (less kinetic energy) whereas the tendency to maximum entropy favours the liquid phase (more randomness). Above the melting point of ice, the entropy factor dominates (as it increases with temperature) so spontaneous melting occurs. Below the melting point, the enthalpy factor dominates so spontaneous freezing occurs.



# Entropy and the second law of thermodynamics

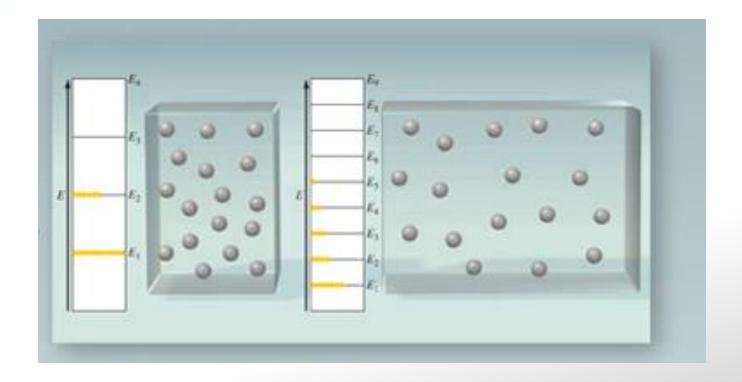
The **second law of thermodynamics** states that in a reversible process, (such as change of state) the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.



extra

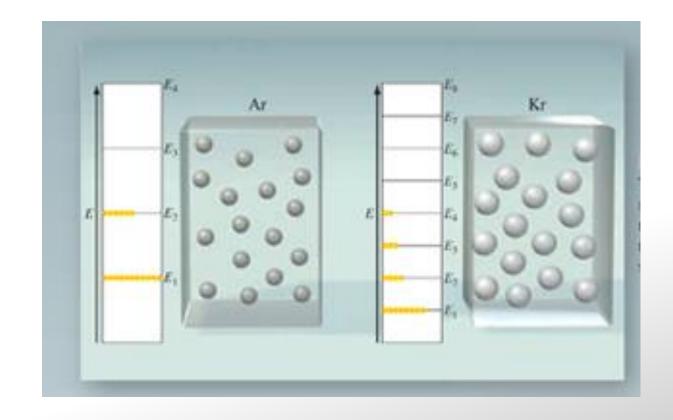
# Factors that influence the Entropy of a system – Volume Change

Volume increase causes an increase in entropy. With an increase in volume there are more energy levels available therefore energy can be dispersed more.



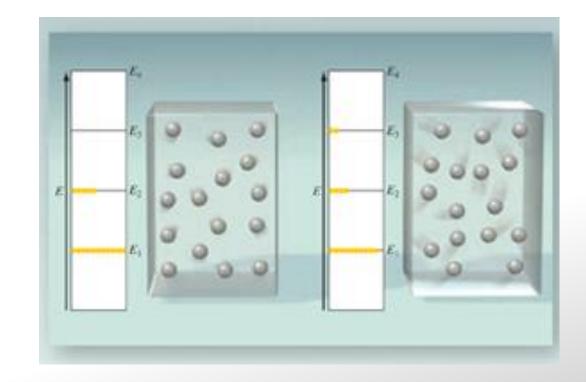
# Factors that influence the Entropy of a system – Molar Mass

Molar Mass increase causes an increase in entropy. With an increase in mass there are more energy levels available therefore energy can be dispersed more.



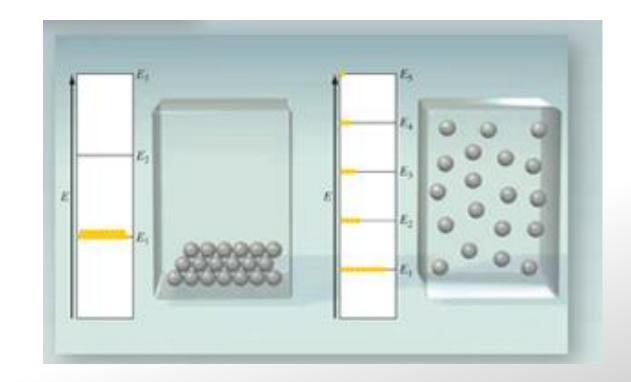
# Factors that influence the Entropy of a system – Temperature Change

Temperature increase causes an increase in entropy. With an increase in temperature the molecules have greater kinetic energy making more energy levels available therefore energy can be dispersed more.



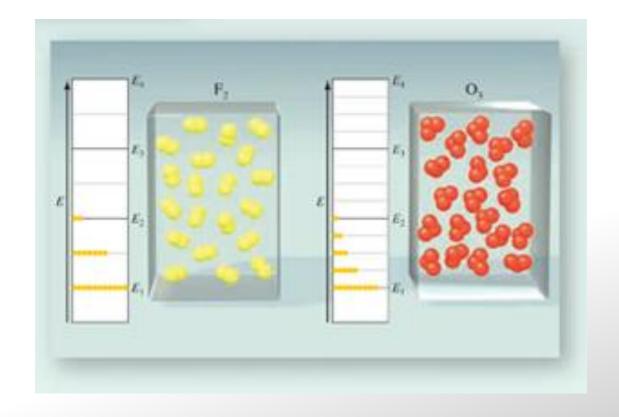
# Factors that influence the Entropy of a system – Phase Change

Phase Change from solid to liquid to gas causes an increase in entropy. With an increase in mobility of particles from solid to liquid to gas there are many more possible arrangements of particles therefore increasing randomness.



# Factors that influence the Entropy of a system – Molecular complexity

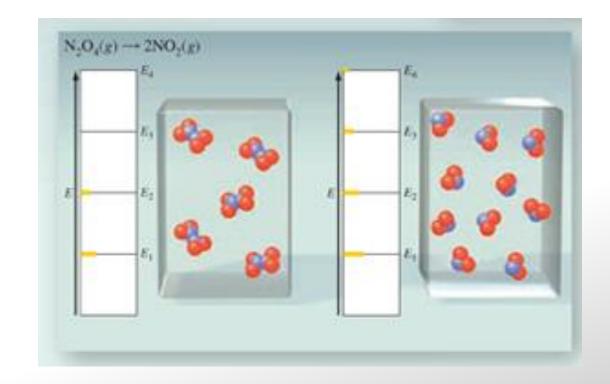
Greater complexity of molecules causes an increase in entropy. With an increase in complexity of molecules there are an increased number of ways it can rotate and vibrate between each atom therefore increasing randomness.



# Factors that influence the Entropy of a system – Number of Moles

An increase in the number of mols in a reaction causes an increase in entropy.

With an increase in the number of mols in a chemical reaction the number of different arrangements of molecules increases therefore increasing randomness.



## Entropy and spontaneous reactions

A reaction will be spontaneous if it results in the enthalpy decreasing and the entropy increasing. A reaction will not occur spontaneously if the enthalpy increases and the entropy decreases.

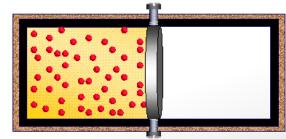
When the entropy and enthalpy oppose each other (they are both positive or both negative) then an equilibrium situation occurs. The overall result depends on the relative magnitude of the two tendencies.

Extension
Spontaneous reactions also occur when there is no increase or decrease in enthalpy but an increase in entropy occurs

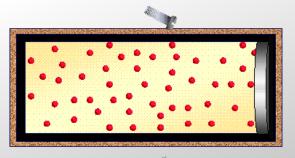
Note: An adiabatic process is a process occurring without exchange of heat of a system with its environment

#### **Energy is constant, Entropy is maximized**

The gas occupies left volume, right volume: vacuum



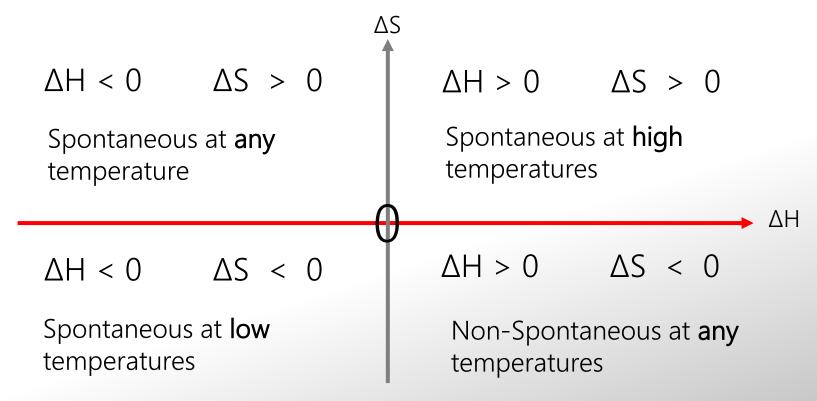
Gas expands adiabatically and irreversibly



### Enthalpy vs entropy

The majority of spontaneous reactions are exothermic due to a natural tendency towards "minimum enthalpy". Some endothermic reactions do occur spontaneously because of a different tendency towards "maximum entropy". Entropy increases the "disorderedness" of a system. For example there is more "disorder" when a solid melts or a liquid boils or a solid dissolves into a solution.

Remember; enthalpy change =  $\Delta H$  entropy change =  $\Delta S$ 



## NCEA 2013 Entropy

#### Question 3c:

Hydrazine is often used as a rocket fuel. When liquid hydrazin undergoes combustion, it forms nitrogen and water:

 $N_2H_{4(\ell)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)} \Delta cH^{\circ}(N_2H_{4(\ell)}) = -624 \text{ kJ mol}^{-1}$ Explain why liquid hydrazine readily burns in oxygen.

Your answer should consider both enthalpy and entropy changes.

**Answer 3c:** Enthalpy change: The combustion of liquid hydrazine is an exothermic process since  $\Delta_c H^\circ$  is negative. Exothermic reactions form products that have lower energy than the reactants / energy is released and this favours the spontaneous / forward reaction.

Entropy change: Exothermic reactions release heat to the surroundings, which makes the entropy change of the surroundings positive. As both the surroundings and the system gain entropy, this favours the spontaneous / forward reaction.

#### OR

The combustion reaction has more gas molecules in the products / goes from liquid to gas / increase in number of particles. Therefore the entropy of the system increases and this favours the spontaneous / forward reaction.

As both enthalpy and entropy are favoured, then hydrazine readily burns / the reaction is spontaneous.

# NCEA 2014 Entropy

#### **Question 3b:**

Ammonium nitrate is used in 'cold packs' to relieve symptoms of a sports injury. The dissolving of the solid crystals of ammonium nitrate (shown in the equation below) is spontaneous, despite being endothermic.

$$NH_4NO_{3(s)} \longrightarrow NH_4^+ (aq) + NO_3^- (aq)$$

Explain why this is so, in terms of the entropy change for the reaction system.

Answer 3b: Positive; or entropy increases. Ions in solution (generally) have higher entropy than solids as there is an increase in the dispersal of matter / degree of disorder..

# Entropy Increases with...

Melting (fusion)

 $S_{liquid} > S_{solid}$ 

Vaporization

 $S_{gas} > S_{liquid}$ 

Heating

 $S_{T2} > S_{T1} \text{ if } T_2 > T_1$ 

Dissolving (usually)

 $S_{solution} > (S_{solvent} + S_{solute})$ 

 Molecular complexity entropy more bonds, more

 Atomic complexity neutrons

more e-, protons,

## NCEA 2014 Entropy

#### Question 3c:

Ammonium nitrate dissociates in an endothermic reaction, as shown in the equation below.

 $NH_4NO_{3(s)} \rightarrow NH_{3(g)} + HNO_{3(g)}$ 

Below is a table outlining four statements about changes in entropy that may occur during any reaction.

Tick (P) to the left of any statement that is correct for the above reaction.

Tick (✓)	Entropy statement	
(P)	The entropy of the system increases.	
	The entropy of the surroundings increases.	
	The entropy of the system decreases.	
(P)	The entropy of the surroundings decreases.	

#### Answer 3c:

As a solid is converted into a gas, the **entropy of the system increases** due to the greater dispersal of matter, as the random motion of the gases is higher.

The entropy of the surroundings decreases because heat is transferred from the surroundings. This results in less random motion of the particles in the surroundings.

## NCEA 2016 Entropy

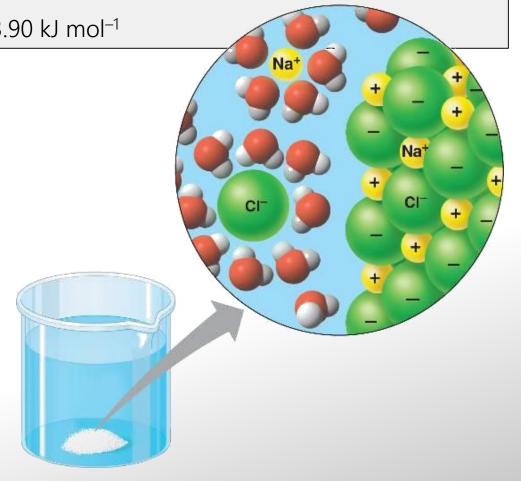
#### Question 2c (iii):

Why does NaCl readily dissolve in water, even though the process is slightly endothermic?

 $NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} \Delta_{r}H^{\circ} = +3.90 \text{ kJ mol}^{-1}$ 

#### Answer 2c (iii):

When solid NaCl dissolves in water, there is an increase in the entropy of the system since the ions in solution have greater entropy than in the solid lattice, i.e. more random / disordered arrangement. Although the ions in solution have more energy / energetically less stable than in the solid lattice (since the process is endothermic), the increase in entropy makes the process spontaneous.



## NCEA 2016 Entropy

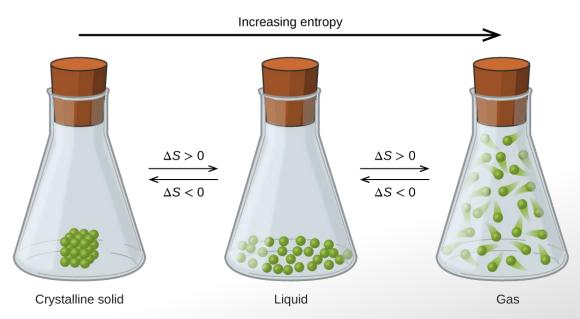
#### Question 3c (iii):

The equation for the evaporation of liquid methanol is:

 $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$ 

Explain the entropy changes of the system and surroundings for the evaporation of methanol.

There is an increase in entropy since gaseous particles are formed; gaseous particles have a more random / disordered arrangement (greater dispersal of matter) than liquid particles.



The enthalpy of the surroundings decreases as the alcohol evaporates as energy is absorbed from the surroundings to break the intermolecular forces between methanol molecules; thus the entropy of the surroundings decreases.

#### Question 2d:

The reaction for the complete combustion of hydrazine is shown in the equation below.

$$N_2H_4(I) + O_2(g) \rightarrow N_2(g) + 2O(g)$$

This is an exothermic reaction.

Explain the entropy changes associated with this reaction.

System – as the number of gaseous molecules is greater on the product side than

the reactant side, then there is an increase in disorder / the dispersal of matter / degree of randomness / dispersal of energy, thus the entropy of the system increases.

Surroundings – as the reaction is exothermic the entropy of the surroundings increases, as there is an increase in disorder / the dispersal of matter / degree of randomness / dispersal of energy.

## NCEA 2017 Entropy

#### Question 3b:

(iii) Explain why the sublimation of iodine is spontaneous, even though the enthalpy of sublimation is a positive value.

Spontaneity is determined by the total entropy change (system + surroundings). Entropy of the system increases as the solid becomes a gas because the gas particles are more disordered. The increase in entropy of the system outweighs the decreased entropy of the surroundings due to the positive enthalpy OR positive enthalpy due to the endothermic process of breaking bonds is offset by entropy changes in the system.



## NCEA 2018 Enthalpy

Q 2b (ii): The equation for the combustion of propan-1-ol is:

 $C_3H_7OH_{(I)} + 4.5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(I)}$ 

Explain how  $\Delta_c H^{\circ}$  (propan-1-ol) would differ if water was produced as a gas rather than a liquid.



The enthalpy change would be less negative / less exothermic. Energy is absorbed/required to break the intermolecular attractions when changing liquid water into gaseous water / less bonds are formed when gaseous water is produced As a result, less heat energy will be released in the reaction.

### NCEA 2018 Entropy

**Q 3c:** The dissolving of ammonium chloride in water is an endothermic process, but ammonium chloride readily dissolves in water.

$$NH_4CI_{(s)} \to NH_4^+_{(aq)} + CI^-_{(aq)}$$

Justify, in terms of the entropy changes of the system and the surroundings, why ammonium chloride readily dissolves in water.

When ammonium chloride dissolves in water, the entropy of the system increases. This is because there are more moles of particles formed / the ions / particles in the solution are more disordered than the solid / greater random movement of products particles / a greater dispersal of matter and energy.

Since the process is endothermic, the entropy of the surroundings decreases because heat energy has been transferred from the surroundings so there is decreased random motion of the / decrease in the dispersal of matter and energy.

However, since the NH4Cl readily dissolves in water / process occurs spontaneously, the total entropy change is positive / total entropy increases/increase in entropy of system outweighs decrease of entropy in the surroundings.

## NCEA 2019 Entropy

Question 3d: Ammonia reacts with oxygen according to the equation below.

 $4NH_{3(q)} + 5O_{2(q)} \rightarrow 4NO_{(q)} + 6H_2O_{(q)} \Delta_r H^\circ = -906 \text{ kJ mol}^{-1}$ 

Justify, in terms of the entropy changes of the system and surroundings, why the reaction is spontaneous.

The reaction has 9 moles of gaseous reactants and 10 moles of gaseous products. Increasing numbers of gaseous particles increases disorder, so the entropy of the system increases.

Since the process is exothermic, heat energy is released into the surroundings increasing the disorder, so the entropy of the surroundings increases.

Therefore, the total entropy increases due to an increase in both the entropy of the system and the surroundings, so the reaction is spontaneous.

# Enthalpy of Reaction using calorimetry

To measure enthalpy changes, the reaction it is carried out in an insulated container (such as a polystyrene cup) and the temperature change (in °C) is measured. Using this temperature change,  $\Delta T$ , and the value of the specific heat capacity, c, the amount of heat energy (**q**) transferred to the mass m of substance (usually water) can be calculated using the expression

$$q = m c \Delta T$$

The specific heat capacity of the water is 4.18 J °C<sup>-1</sup> g<sup>-1</sup>. Every 1mL of water can be taken as 1g due to its density

- 1. Calculate the mass of reactants record in grams (one ml liquid = one gram)
- Measure the temperature of the reactants and the temperature of the products and calculate ΔT (°C)
- 3. Calculate **q** using formula above

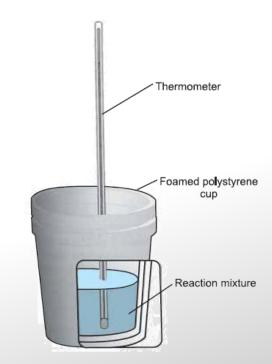


Fig. 6.8 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

# Calculating heat energy (q)

The energy change when a body of mass m experiences a temperature rise of  $\Delta T$  is given by:

$$q = m c \Delta T$$

energy change = mass x specific heat capacity x change in temperature

**Example:** Calculate the energy change when a 9 kg mass of water increases its temperature by 20 °C.

$$q = m c \Delta T$$
  
 $q = 9000g \times 4.18 \text{ kJ } \circ \text{C}^{-1}\text{kg}^{-1} \times 20 \circ \text{C}$   
 $q = 752 4000 \text{ J}$ 

Note: m is grams and q will be calculated in J. This will need to be converted to kJ for the next step to calculate  $\Delta_r H^\circ$ 

# Using Q to calculate enthalpy of reaction ( $\Delta_r H^\circ$ )

Enthalpy of reaction  $\Delta_r$ H° can be calculated from heat energy (q) in the previous step if the number of moles of one of the reactants is known, or calculated.

$$\Delta_r H^\circ = -q/n$$

Note that the q is negative and will be in kJ

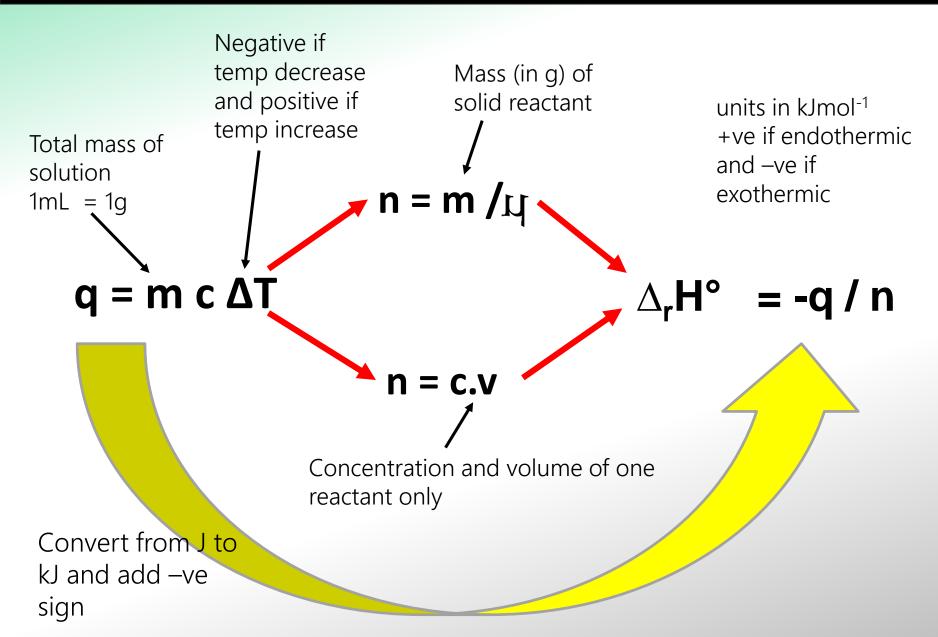
Moles (n) can be calculated from either mass of one of the reactants

$$n = m / U = molar mass (gmol-1) m = mass (g)$$

Or from the concentration and volume of one of the reactants

$$n = c.V$$
  $c = concentration (molL-1)  $v = volume (L)$$ 

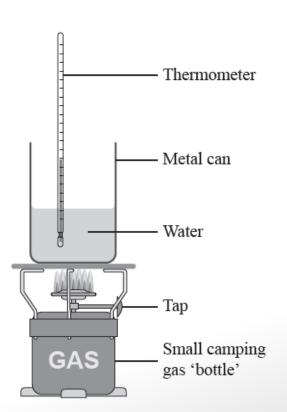
# Using Q to calculate enthalpy of reaction ( $\Delta_r H^\circ$ ) Summary



# Thermochemical Experimental data



Enthalpy change ( $\Delta_r H$ ) for a reaction, can be collected from a thermochemical investigation. Values required are masses of water in which the reaction takes place, temperature change (in °C) and the specific heat capacity value for water.



Often questions will ask why a particular investigation set up does not provide the same thermochemical data as the accepted enthalpy change.

Reasons can include errors such as:

- Some energy is used to heat the metal can and the air surrounding the experiment / the experiment was not conducted in a closed system
- 2. Incomplete combustion of butane.
- 3. Some butane may have escaped before being ignited.
- 4. The butane in the gas canister was impure.
- 5. Some water evaporated
- 6. Some energy was converted to light and sound
- 7. Not carried out under standard conditions

Therefore, not all of the energy released by the combustion of butane was transferred to heating the water

# NCEA 2013 Specific Heat Capacity

Question 2b(i): When 25.0 mL of a 1.00 mol  $L^{-1}$  hydrochloric acid solution, HCl, is added to 25.0 mL of a 1.00 mol  $L^{-1}$  ammonia solution, NH3, a temperature rise of 6.50°C is recorded, as a neutralisation reaction occurs to produce aqueous ammonium chloride and water.

Calculate  $\Delta_r H$  ° for this neutralisation reaction. The mass of the mixture is 50.0 g. Assume specific heat capacity of the aqueous ammonium chloride = 4.18 J g<sup>-1</sup> °C<sup>-1</sup>

#### Answer 2b(i):

$$q = mc\Delta T = 50 \times 4.18 \times 6.5 = 1358.5 \text{ J} = 1.3585 \text{ kJ}$$

n = c x V = 1 x 0.025 = 0.025 mol  

$$\Delta_r H^\circ = \frac{-q}{n} = \frac{-1.3585 \text{ kJ}}{0.025 \text{ mol}}$$

$$= -54.3 \text{ kJ mol}^{-1}$$

Heat capacity value always given. Use it to help you remember units

Answer 2b(ii):Conditions were not standard.

Needed to carry out under standard conditions OR

Heat lost to atmosphere / beaker / surroundings.

Insulate equipment; ensure all / as much of the energy produced as possible is collected and measured.

#### Question 2b(ii):

When the  $\Delta_r$  H° for the neutralisation above was found experimentally in a school laboratory, the value obtained was lower than the theoretical value. Account for the difference in values, and suggest how this difference could be minimised.

# NCEA 2016 Specific Heat Capacity

Question 3b (i): The enthalpy of combustion of liquid methanol,  $\Delta_c H$  °(CH<sub>3</sub>OH<sub>(I)</sub>), can also be determined by burning a known mass of methanol and measuring the temperature change in a known mass of water above the burning methanol. If 2.56 g of methanol is burned, the temperature of 500 g water increases from 21.2°C to 34.5°C.

Using these results, calculate the experimental value of  $\Delta_c H$  °(CH<sub>3</sub>OH<sub>(1)</sub>).

The specific heat capacity of water is  $4.18 \text{ J} \,^{\circ}\text{C}^{-1} \,^{\circ}\text{g}^{-1}$ .

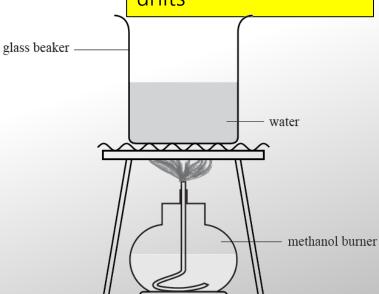
$$M(CH_3OH) = 32.0 \text{ g mol}^{-1}$$

$$q = mc\Delta T$$
  
 $q = 500 \text{ g} \times 4.18 \text{ J} \text{ °C}^{-1} \text{ g}^{-1} \times (34.5 \text{ °C} - 21.2 \text{ °C})$   
 $q = 27 797 \text{ J} = 27.797 \text{ kJ}$ 

$$n(\text{CH}_3\text{OH}) = \frac{m}{M} = \frac{2.56}{32} = 0.08 \text{ mol}$$

$$\Delta_c H = \frac{-q}{n} = \frac{-27.797}{0.08} = -347 \text{ kJ mol}^{-1}$$

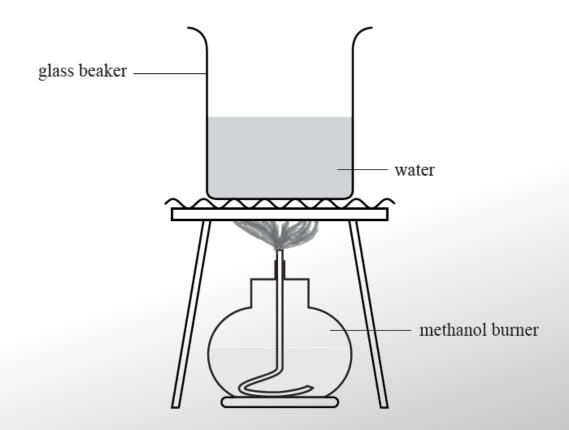
Heat capacity value always given. Use it to help you remember units



# NCEA 2016 Specific Heat Capacity

Question 3b (ii): Why is the experimental value obtained in the enthalpy of formation question less negative than the theoretical value determined in the specific heat capacity question?

Heat loss to surroundings / incomplete combustion which means the temperature of the water doesn't increase as much leading to a less negative enthalpy / the experiment wasn't insulated



## NCEA 2018 Specific Heat Capacity

**Q 3b:** When 10.6 g of ammonium chloride,  $NH_4CI$ , is dissolved in 65.0 mL of water, the temperature of the water changes from 20.9°C to 11.5°C.

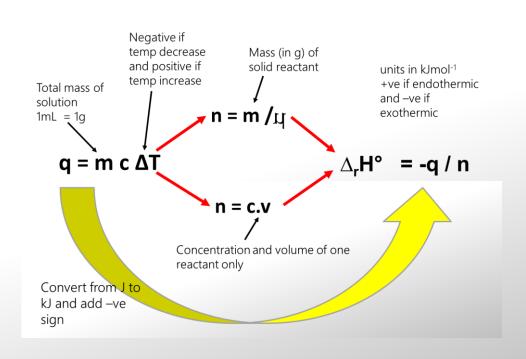
The mass of the final solution is 75.6 g

Assume specific heat capacity of aqueous ammonium chloride = 4.18 J g<sup>-1</sup> °C<sup>-1</sup>

$$M(NH_4CI) = 53.5 \text{ g mol}-1$$

Calculate the enthalpy change,  $\Delta_r H^\circ$ , for dissolving ammonium chloride in water.

$$q = mc\Delta T$$
  
 $q = 75.6 \times 4.18 (11.5 - 20.9)$   
 $q = -2970.5 J$   
 $q = -2.9705 kJ$   
 $n(NH_4Cl) = m / M$   
 $= 10.6 / 53.5$   
 $= 0.1981 mol$   
 $\Delta H = -q / n$   
 $= -2.9705 / 0.198$   
 $= +15.0 kJ mol-1$ 



## NCEA 2019 Specific Heat Capacity

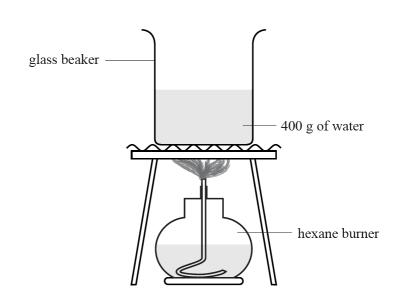
Question 2c: The enthalpy of combustion of liquid hexane,  $\Delta_c H(C_6 H_{14(l)})$ , can be determined by burning a known mass of hexane and measuring the temperature change in a known mass of water above the burning hexane.

(i) If 5.22 g of hexane is burned, the temperature of 400 g of water increases from 20.5°C to 36.7°C.

Using these results, calculate an experimental value of  $\Delta_c H(C_6 H_{14(1)})$ .

The specific heat capacity of water is 4.18 J  $g^{-1}$  °C<sup>-1</sup>.

$$M(C_6H_{14}) = 86.0 \text{ g mol}^{-1}$$



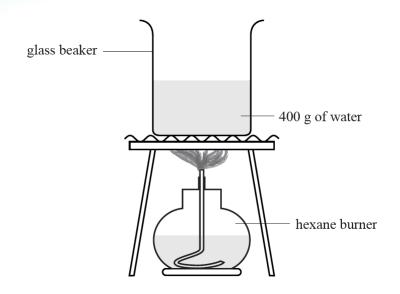
$$q = mc\Delta T$$
  
= 400 x 4.18 x (36.7 -20.5)  
= 27086 J  
= 27.086 kJ

$$n(C_8H_{14}) = 5.22/86.0 = 0.0607 \text{ mol}$$

$$\Delta$$
rH = -q/n  
=- (27.086/0.0607  
=-446 kJ mol<sup>-1</sup>

# NCEA 2019 Specific Heat Capacity

Question 2c: (ii) Explain why the experimental value obtained in part (c)(i)  $[=-446 \text{ kJ} \text{ mol}^{-1}]$  is less negative than the theoretical value of -4163 kJ mol $^{-1}$ , given in part (b).



- ☐ Less negative as a result of heat loss to the surroundings
- ☐ Some incomplete combustion occurring
- ☐ Apparatus absorbing heat
- Not done in standard conditions resulting in less energy being transferred to the water

## Calculating $\Delta_r$ H° given the standard heats of formation of reactants and products.

The standard enthalpy of any reaction can be obtained by subtraction of the standard enthalpies of formation of reactants from those of the products.

$$\Delta_r H^o = \sum_{f} n \Delta_f H^o_{products} - \sum_{f} n \Delta_f H^o_{reactants}$$

where n is the stoichiometric coefficient of each substance in the reaction equation.

#### Example

Using the standard heats of formation of  $CO_2(g)$ ,  $H_2O(l)$ , and  $C_6H_{12}O_6(s)$ , calculate the standard enthalpy of combustion of glucose.

$$\Delta_{\rm f} {\rm H}^{\rm o}({\rm C}_{6} {\rm H}_{12} {\rm O}_{6}, s) = -1268 \text{ kJ mol}^{-1}$$
  
 $\Delta_{\rm f} {\rm H}^{\rm o}({\rm CO}_{2}, g) = -394 \text{ kJ mol}^{-1}$   
 $\Delta_{\rm f} {\rm H}^{\rm o}({\rm H}_{2} {\rm O}, l) = -286 \text{ kJ mol}^{-1}$   
 $\Delta_{\rm f} {\rm H}^{\rm o}({\rm O}_{2}, g) = 0 \text{ kJ mol}^{-1}$ 

Note - Start by writing an equation for the combustion of 1 mole of glucose.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
  
 $\Delta_r H^o = \sum n\Delta_f H^o_{products} - \sum n\Delta_f H^o_{reactants}$   
 $\Delta_r H^o = (6 \times -394 + 6 \times -286) - (1 \times -1268 + 6 \times 0)$   
 $= -2812 \text{ kJ mol}^{-1}$ 

## Some $\Delta_c H^{\circ}$ can also be $\Delta_f H^{\circ}$

The combustion equations for C,  $H_2$  and S can also be the formation equations for  $CO_2$ ,  $H_2O$  and  $SO_2$  respectively

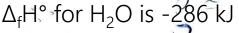
For example: Take the following combustion equation for H<sub>2</sub> with O<sub>2</sub>

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(g)}$$

 $\Delta_c$ H $^\circ$  - 286 kJ mol<sup>-1</sup>

So for one mole of H<sub>2</sub> to be completely combusted releases 286 kJ

But you can see that 1 mole of  $H_2O_{(g)}$  has been formed, so equally you could say that the



Calculating the  $\Delta_r H^{\circ}$  of a reaction using  $\Delta_f H^{\circ}$  (and some  $\Delta_c H^{\circ}$ ) is a short hand way.

But can only be used if all reactants and products in an equation have provided data.

If some do not then a longer hand calculation is required using Hess's Law

## NCEA 2013 Enthalpy of formation

#### Question 3b:

Decane is a component of petrol. Carbon dioxide and water are formed when decane burns completely in oxygen.

$$C_{10}H_{22(\ell)} + 15.5O_{2(g)} \rightarrow 10CO_{2(g)} + 11H_2O_{(\ell)}$$

Calculate  $\Delta_c H - (C_{10}H_{22})$ , given the following data:

$$\Delta_{\rm f}H - (C_{10}H_{22(\ell)}) = -250 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f}H - ({\rm CO}_{2(q)}) = -393 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H - (H_2 O_{(\ell)}) = -286 \text{ kJ mol}^{-1}$$

#### Answer 3d:

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ \text{ products} - \Sigma \Delta_f H^\circ \text{ reactants}$$
$$= [(10 \times -393) + (11 \times -286)] - (-250)$$

$$= -6.826 \text{ kJ mol}^{-1} \text{ or } (-6.830 \text{ kJ mol}^{-1})$$

## NCEA 2014 Enthalpy of formation

#### Question 2c:

An equation for the reaction of ammonia gas with hydrogen chloride gas is:

$$NH_{3(q)} + HCI_{(q)} \rightarrow NH_4CI_{(s)}$$

Calculate the standard enthalpy change,  $\Delta_r H^\circ$ , for this reaction, using the following data.

$$\Delta_{\rm f} H^{\circ} (NH_{3(q)}) = -46 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ} ({\rm HCl}_{(q)}) = -92 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ} (NH_4 CI_{(s)}) = -314 \text{ kJ mol}^{-1}$$

#### Answer 3d:

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ$$
 products  $-\Sigma \Delta_f H^\circ$  reactants  
=  $(-314) - (-46 + -92)$   
=  $-176$  kJ mol<sup>-1</sup>

Use the mole coefficients from the equation. we know it is a exothermic reaction with a Negative sign

# NCEA 2015 Enthalpy of formation

#### Question 3d:

The equation for the combustion of pentan-1-ol is:

$$C_5H_{12}O_{(I)} + 7\frac{1}{2}O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(I)}$$

Calculate  $\Delta_c H^\circ$  for pentan-1-ol, given the following data:

$$\Delta_{\rm f} H^{\circ} (C_5 H_{12} O_{(l)}) = -295 \text{ kJ mol}^{-1}$$
  
 $\Delta_{\rm f} H^{\circ} (CO_{2(g)}) = -394 \text{ kJ mol}^{-1}$   
 $\Delta_{\rm f} H^{\circ} (H_2 O_{(l)}) = -286 \text{ kJ mol}^{-1}$ 

#### Answer 3d:

$$\Delta_c H^\circ = \Sigma \Delta_f H^\circ \text{ (products)} - \Sigma \Delta_f H^\circ \text{ (reactants)}$$

$$= [(5 \times -394) + (6 \times -286)] - [-295]$$

$$= -3686 + 295$$

$$= -3391 \text{ kJ mol}^{-1}$$

Use the mole coefficients from the equation.

Because we know it is a combustion reaction check to make sure your answer is exothermic with a Negative sign

## NCEA 2016 Enthalpy of formation

#### Question 3a:

The equation for the combustion of liquid methanol is:

$$CH_3OH_{(I)} + 3/2 O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(I)}$$

Calculate the standard enthalpy of combustion of liquid methanol,  $\Delta_c H^{\circ}(CH_3OH_{(1)})$ , using the information in the table below.

Compound	kJ mol <sup>-1</sup>
$\Delta_{\mathbf{c}}H^{\circ}(\mathbf{C}(s))$	-394
$\Delta_{\rm c}H^{\circ}({\rm H_2}(g))$	-286
$\Delta_{\mathbf{f}}H^{\circ}(\mathrm{CH_{3}OH}(\ell))$	-240

This question could be calculated using  $\Delta_r H^\circ = \Sigma \Delta_f H^\circ$  products  $-\Sigma \Delta_f H^\circ$  reactants

As the combustion reactions were the same as the formation reactions

#### Answer 3a:

$$\Delta_{c}H^{\circ} = -394 + (2 \times -286) - (-240)$$

$$\Delta_c H^{\circ} = -966 + 240$$

$$\Delta_{\rm c}H^{\circ} = -726 \text{ kJ mol}^{-1}$$

O<sub>2</sub> is left out as formation enthalpy of elements is 0

Hess's Law would also have worked to calculate the enthalpy of the reaction but it would have been a longer process

# NCEA 2017 Enthalpy of formation

#### Question 2c:

Carbon dioxide and water are formed when decane burns completely in oxygen. The reaction is shown in the equation below.

$$C_{10}H_{22}(I) + 15 \frac{1}{2} O_2(g) \rightarrow 10CO_2(g) + 11H_2O(I)$$

Calculate the enthalpy of combustion for decane, given the following data:

$$\Delta_{\rm f} H^{\circ} (C_{10} H_{22}(\ell)) = -301 \, \rm kJ \, mol^{-1}$$
  
 $\Delta_{\rm c} H^{\circ} (C) = -393 \, \rm kJ \, mol^{-1}$   
 $\Delta_{\rm c} H^{\circ} (H_2) = -286 \, \rm kJ \, mol^{-1}$ 

#### Answer 2c:

10C + 11H<sub>2</sub> → C<sub>10</sub>H<sub>22</sub> −301 kJ mol<sup>-1</sup>  
C + O<sub>2</sub> → CO<sub>2</sub> −393 × 10 kJ mol<sup>-1</sup>  
H<sub>2</sub> + ½O<sub>2</sub> → H<sub>2</sub>O −286 × 11 kJ mol<sup>-1</sup>  

$$\Delta$$
H = +301 + (10 × −393) + (11 × −286)

This question could be calculated using  $\Delta_r H^\circ = \Sigma \Delta_f H^\circ$  products  $-\Sigma \Delta_f H^\circ$  reactants

As the combustion reactions were the same as the formation reactions

O<sub>2</sub> is left out as formation enthalpy of elements is 0

 $= -6775 \, \text{kl mol}^{-1}$ 

Hess's Law would also have worked to calculate the enthalpy of the reaction but it would have been a longer process

### NCEA 2018 Enthalpy of Formation

Q 2b (i): The equation for the combustion of propan-1-ol is:

$$C_3H_7OH_{(I)} + 4.5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(I)}$$

Calculate the standard enthalpy of combustion,  $\Delta_c H^\circ$ , of propan-1-ol, given the following data:

$$\Delta_f H^{\circ}(C_3H_7OH_{(1)}) = -255 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ}({\rm CO}_{2(g)}) = -394 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ}({\rm H_2O_{(1)}}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\circ = [(3 \times -394) + (4 \times -286)] - (-255) = -2071 \text{ kJ mol}^{-1}$$



# NCEA 2019 Enthalpy of Formation

Question 3c: Ammonia, NH<sub>3</sub>, reacts with methane, CH<sub>4</sub>, in the following reaction:

$$CH_{4(g)} + NH_{3(g)} \rightarrow HCN_{(g)} + 3H_{2(g)}$$

Calculate the enthalpy change,  $\Delta_r H^\circ$ , for this reaction using the following data.

$$\Delta_f H^{\circ}(NH_{3(q)}) = -45.9 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ}({\rm CH4}(g)) = -74.9 \text{ kJ mol}^{-1}$$

$$\Delta_f H^{\circ}(HCN(g)) = +135 \text{ kJ mol}^{-1}$$

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ \text{ (products)} - \Sigma \Delta_f H^\circ \text{ (reactants)}$$

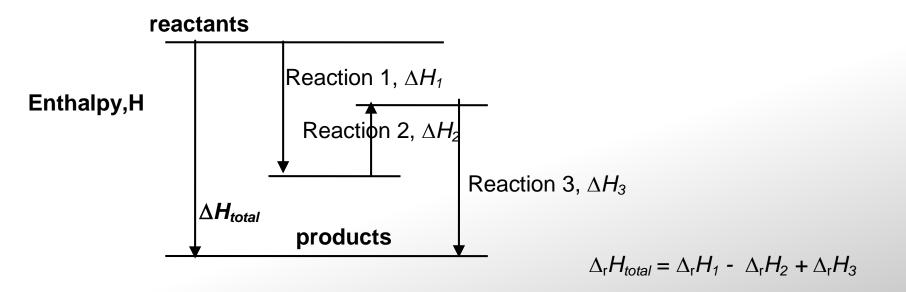
$$+ 135 - (-74.9 + -45.9)$$

$$= +256 \text{ kJ mol}^{-1}$$

#### Hess's law

If an overall reaction can be broken down into a series of two or more steps, then the corresponding overall enthalpy of reaction is the sum of the enthalpies of the individual reaction steps. None of the steps need to be a reaction that can be carried out in the laboratory.

The energy difference depends only on the **difference in energy** between the <u>reactants</u> and <u>products</u>, not on the reaction path taken.



## Application of Hess's law

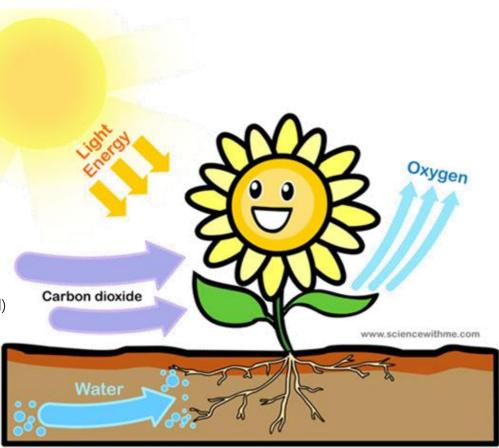
The process of photosynthesis is an endothermic process in which energy from the sun is trapped and stored in the bonds of glucose.

$$6CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(aq)} + 6O_{2(g)} \Delta rH^\circ = +2808 \text{ kJ mol}^{-1}$$

enthalpy change so using the principal of Hess's law we can more easily measure the enthalpy change for the reverse reaction, the combustion of glucose (i.e. the process of respiration). The difference between reactants and products will be the same – we only need to reverse the sign from exothermic to endothermic

$$C_6H_{12}O_{6(aq)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

 $\Delta rH^{\circ} = -2808 \text{ kJ mol}^{-1}$ 



# Application of Hess's law

All reactants and products in an equation need to be accounted for in a combination of other equations. These equations and their  $\Delta_r H^\circ$  will be provided, however for some combustion ( $\Delta_c H^\circ$ ) and formation ( $\Delta_f H^\circ$ ) values, the equation will need to be written out first.

The equations need to provide the substances in the correct number of moles (so equations may need to be multiplied or divided - in which case also multiply or divided the provided  $\Delta_r$ H° by the same factor)

The substances also need to be on the correct side of the equation. If they are not then 'flip' the reaction (reactants become products etc) and also change the sign of the  $\Delta_r H^\circ$  for that equation, from - to + or + to -.

Finally, cross off any substance (with the same amount of moles) that occurs on both sides of any of the combination of equations used - except the initial equation that you are calculating the  $\Delta_r H^\circ$  of.

Once crossing off all substnces appearing on both side you should only be left with the same reactants and products matching the initial equation - with the same number of moles, and the same side of the equation.

Finally, add up all  $\Delta_r$ H° (including  $\Delta_f$ H° and  $\Delta_c$ H°) from the equations used. Watch for - and + values. The final answer will be the  $\Delta_r$ H°

#### Steps to calculating enthalpy of reaction Hess's Law

Energy change due to a chemical reaction is independent of pathway taken

Example: calculate  $\Delta_f H^\circ$  (C<sub>3</sub>H<sub>8</sub>)

Step 1. Write out equation for reaction to calculate

$$3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$$
  $\Delta_f H^{\circ} = ?$ 

Step 2.Use given equations and rearrange until they match equation

1. 
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$\Delta_c H^\circ = -394 \text{ kJ mol}^{-1}$$

Can multiply all by 3. multiply enthalpy as well

$$3C_{(s)} + 3O_{2(g)} \rightarrow 3CO_{2(g)}$$

$$\Delta_{c}H^{\circ} = 3(-394 \text{ kJ mol}^{-1})$$

2. 
$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(l)}$$

$$\Delta_{\rm c} H^{\circ} = -286 \text{ kJ mol}^{-1}$$

$$4H_{2(g)} + 2O_{2(g)} \rightarrow 4H_2O_{(l)}$$

$$\Delta_{\rm c} {\rm H}^{\circ} = 4(-286 \text{ kJ mol}^{-1})$$

$$3.C_3H_{8(g)} + 5O_{2(g)} \rightarrow 4H_2O_{(l)} + 3CO_{2(g)}$$

$$\Delta_{\rm c} {\rm H}^{\rm o} = -2220 \; {\rm kJ \; mol^{-1}}$$

Can reverse so molecules on same side. Reverse enthalpy sign

$$4H_2O_{(I)} + 3CO_{2(g)} \rightarrow \underline{C_3}\underline{H_{8(g)}} + 5O_{2(g)}$$

$$\Delta_{c}H^{\circ} = +2220 \text{ kJ mol}^{-1}$$

#### Hess's Law

Energy change due to a chemical reaction is independent of pathway taken

Step 3. cancel out any molecules on either side.

$$\frac{3C_{(s)}}{4H_{2(g)}} + 3CO_{2(g)} \rightarrow 4H_{2}O_{(l)}$$

$$\Delta_{c}H^{\circ} = 3(-394 \text{ kJ mol}^{-1})$$

$$\Delta_{c}H^{\circ} = 4(-286 \text{ kJ mol}^{-1})$$

$$\Delta_{c}H^{\circ} = 4(-286 \text{ kJ mol}^{-1})$$

$$\Delta_{c}H^{\circ} = +2220 \text{ kJ mol}^{-1}$$

Step 4. ensurè remaining molecules match reaction equation

$$3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$$

Step 5. Add up enthalpies

$$\Delta_{\rm f}$$
H° = 3(-394 kJ mol<sup>-1</sup>) + 4(-286 kJ mol<sup>-1</sup>) + +2220 kJ mol<sup>-1</sup>  
= -106 kJ mol<sup>-1</sup>

#### NCEA 2013 Hess's law

#### Question 3a (ii):

(ii) When gaseous hydrogen and oxygen are heated in a test tube, droplets of liquid water form on the sides of the test tube. Calculate  $\Delta_f H - (H_2O_{(\ell)})$ , given the following data:

$$\Delta_{\rm f} H - ({\rm H_2O}_{(g)}) = -242 \ {\rm kJ \ mol^{-1}} \ \Delta_{\rm vap} H - ({\rm H_2O}_{(\ell)}) = +44 \ {\rm kJ \ mol^{-1}}$$

Find 
$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(\ell)}$$
  
Given  $H_2 O_{(\ell)} \rightarrow H_2 O_{(g)}$   $\Delta H = 44 \text{ kJ mol}^{-1}$  (reverse)  
 $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(g)} \Delta H = -242 \text{ kJ mol}^{-1}$   
 $\Delta_f H^o(H_2 O_{(\ell)}) = -44 + (-242) = -286 \text{ kJ mol}^{-1}$ 

If you reverse the equation then reverse the sign of the enthalpy





#### NCEA 2014 Hess's law

#### Question 3d (i):

Calculate the standard enthalpy of formation of liquid ethanol using the information given below.

Compound	kJ mol <sup>-1</sup>
$\Delta_{c}H^{\circ}\left(\mathrm{C}(s)\right)$	-394
$\Delta_{\mathbf{f}} H^{\circ} (\mathbf{H}_2 \mathbf{O}(\ell))$	-286
$\Delta_{\rm c} H^{\circ} \left( {\rm C_2 H_5 OH}(\ell) \right)$	-1367

#### **Answer 3d:**

#### Question 3d (ii):

Discuss how the value of the enthalpy change would differ if the ethanol product formed was a gas rather than a liquid. If you reverse the equation then reverse the sign of the enthalpy

The enthalpy change would be more positive.

Heat energy is absorbed when converting a liquid to a gas. Therefore if the ethanol formed were in the gaseous state, less energy would be released in its formation / products would have a higher enthalpy.

#### NCEA 2015 Hess's law

#### Question 2c:

Calculate the  $\Delta_f H$  ° for  $B_2H_{6(q)}$ , given the following data:

$$\Delta_f H \circ (B_2 O_{3(s)}) = -1255 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} H^{\circ} (H_2 O_{(1)}) = -286 \text{ kJ mol}^{-1}$$

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)} \Delta_r H^\circ = -2148 \text{ kJ mol}^{-1}$$

The melting point of boron is 2300°C.

If you reverse the equation then reverse the sign of the enthalpy

#### Answer 2c:

$$3H_2O_{(\ell)} + B_2O_{3(s)} \rightarrow B_2H_{6(g)} + 3O_{2(g)} = + 2148 \text{ kJ mol}^{-1}$$
 $2B_{(s)} + 1\frac{1}{2}O_{2(g)} \rightarrow B_2O_{3(g)} = - 1255 \text{ kJ mol}^{-1}$ 
 $3H_{2(g)} + 1\frac{1}{2}O_{2(g)} \rightarrow 3H_2O_{(\ell)} = - 858 \text{ kJ mol}^{-1}$ 
 $2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)} = + 35 \text{ kJ mol}^{-1}$ 

Expand out all equations – Formation equations require the state elements at 25° Watch that the number of mols and state is the same for the final and starting equation

# Excellence Question

#### NCEA 2018 Hess's Law

**Q 2c:** The equation for the formation of  $Al_2Cl_{6(s)}$  is:

$$2AI_{(s)} + 3CI_{2(g)} \rightarrow AI_{2}CI_{6(s)}$$

Calculate the enthalpy change,  $\Delta_r H^\circ$ , for this reaction using the following data:

$$2AI_{(s)} + 6HCI_{(aq)} \rightarrow AI_2CI_{6(aq)} + 3H_{2(q)} \Delta_r H^\circ = -1003 \text{ kJ mol}^{-1}$$

$$H_{2(q)} + Cl_{2(q)} \rightarrow 2HCl_{(q)} \Delta_r H^{\circ} = -184 \text{ kJ mol}^{-1}$$

$$HCI_{(a)} \rightarrow HCI_{(aa)} \Delta_r H^{\circ} = -72.4 \text{ kJ mol}^{-1}$$

$$Al_2CI_{6(s)} \rightarrow Al_2CI_{6(aq)}\Delta_rH^\circ = -643 \text{ kJ mol}^{-1}$$

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow Al_{2}Cl_{6(aq)} + 3H_{2(g)}$$

$$3H_{2(g)} + 3Cl_{2(g)} \rightarrow 6HCl_{(g)}$$

$$6HCl_{(g)} \rightarrow 6HCl_{(aq)}$$

$$Al_{2}Cl_{6(aq)} \rightarrow Al_{2}Cl_{6(s)}$$

$$2Al_{(s)} + 3Cl_{2(g)} \rightarrow Al_{2}Cl_{6(s)}$$

$$-1346.4 \text{ kJ mol}^{-1}$$

$$(-1350\text{kJmol}^{-1})$$

#### NCEA 2019 Hess's Law

Question 2b: The equation for the formation of liquid hexane is:

$$6C_{(s)} + 7H_{2(g)} \rightarrow C_6H_{14(l)}$$

Calculate the standard enthalpy of formation for liquid hexane,  $\Delta_f H^{\circ}(C_6H_{14(I)})$ , using the following data:

$$C_6H_{14(I)} + 9.5O_{2(g)} \rightarrow 6CO_{2(g)} + 7H_2O_{(I)} \Delta_cH^{\circ}(C_6H_{14(I)}) = -4163 \text{ kJ mol}^{-1}$$

$$\Delta_c H^{\circ}(\hat{C}_{(s)}) = -394 \text{ kJ mol}^{-1}$$

$$\Delta_{c}H^{\circ}(H_{2(q)}) = -286 \text{ kJ mol}^{-1}$$

Find 
$$6C_{(s)} + 7H_{2(q)} \rightarrow C_6H_{14(\ell)}$$

$$6C_{(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} = 6 \text{ x}' - 394 \text{ kJ mol}^{-1} = -2364 \text{ kJ mol}^{-1}$$
  
 $7H_{2(g)} + 3\frac{1}{2} O_{2(g)} \rightarrow 7H_{2}O_{(g)} = 7 \text{ 'x } -286 \text{ kJ mol}^{-1} = -2002 \text{ kJ mol}^{-1}$   
 $6CO_{2(g)} + 7H_{2}O_{(\ell)} \rightarrow C_{6}H_{14(\ell)} + 9 \frac{1}{2} O_{2(g)} = (\text{reverse}) = + 4163 \text{ kJ mol}^{-1}$   
 $\Delta_{f}H^{\circ} (C_{6}H_{14}) = -2364 + -2002 + 4163 = -203 \text{ kJ mol}^{-1}$ 

