

5.1 Measuring energy changes

Heat and Temperature

- Energetics is the study of heat changes in chemical reactions
 - Heat is a form of energy
- Energy can neither be created nor destroyed. Total energy is always conserved and can only be transferred
- **Heat energy always flows from a higher temperature object to a lower temperature object**
- The Kelvin scale is based on kinetic energy, so 0K means that there is no kinetic movement at all

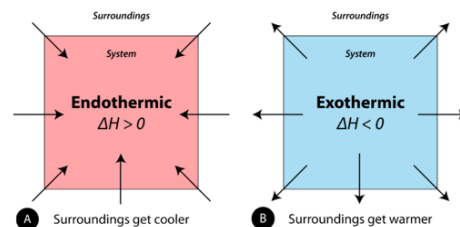
Definitions

Heat – A measure of the total kinetic energy of particles in a substance

Temperature – A measure of the average kinetic energy of particles in a substance

Enthalpy (H)

- **Enthalpy (H): The amount of heat energy contained in a substance**
- Enthalpy is stored in the chemical bonds as potential energy
- When substances react, the total enthalpy of a system cannot be measured (due to loss of heat), but it is possible to measure the difference in the enthalpy between the reactants and products
- Enthalpy is denoted as **H**, however heat change is denoted as **ΔH**
- The enthalpy change for chemical reactions is denoted kJ mol^{-1}
- The reaction mixture is called the system (the chemical reaction), which **gives heat to or takes heat from** the surroundings (anything around the system)
- Chemical reactions that involve transfer of heat between system and the surroundings are described as exothermic and endothermic



Exothermic: Heat is Released

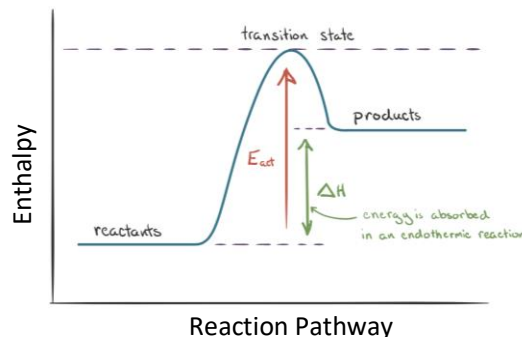
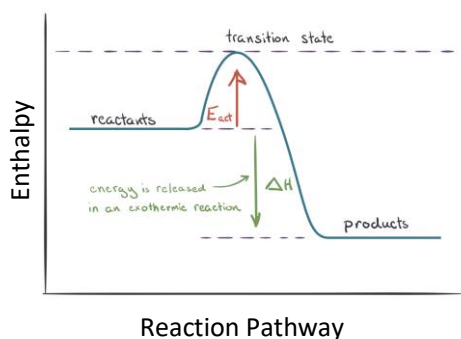
- In exothermic reactions **heat is released** to the surroundings
 - This is because more heat energy is released than what is added
 - So, the overall heat energy is released from the system, causing the surroundings to become hotter
- Exothermic reactions have **negative ΔH values**, because heat is released (thus enthalpy decreases, $-\Delta H$)
- In an exothermic reaction, the **products are more stable than the reactants** as they have a lower enthalpy
 - Less heat means more stable
- This means the reaction is downhill in terms of heat energy
- Exothermic reactions release energy (as heat)
- Examples include:
 - **Bond forming:** Removing heat brings atoms closer together, forming bonds
 - When chemical bonds are formed, heat is released (*See 5.3*)
 - Gas \rightarrow Liquid \rightarrow Solid: Heat is removed, thus these are exothermic reactions
 - Rain: The condensation of water vapor into rain releases energy in the form of heat
 - Combustion: The burning of carbon compounds uses oxygen from air, and produces CO_2 , H_2O and lots of heat

Endothermic: Heat is Absorbed

- In endothermic reactions **heat is absorbed from the surroundings**
 - This is because more heat energy is added than what is released
 - So, the overall heat energy is absorbed by the system, causing the surroundings to become cooler.
- Endothermic reactions have **positive ΔH values**, because heat is absorbed (thus, enthalpy increases $+\Delta H$)

- In an endothermic reaction, the **products are less stable than the reactants** as they have a higher enthalpy
 - More heat means less stable
- This means the reaction is uphill in terms of heat energy
- Exothermic reactions require energy (through heat)
- Examples include:
 - Bond breaking:** Adding heat separates atoms, breaks bonds (See 5.3)
 - Photosynthesis: Plants absorb heat energy from sunlight to convert CO₂ and water into glucose and oxygen
 - Solid → Liquid → Gas: Heat is added, so the reactions are endothermic

Energy Diagrams: Endothermic and Exothermic Reaction



Standard Enthalpy change: ΔH_x^θ

- Standard enthalpy change of reaction: The enthalpy change of a reaction carried out under standard with everything in its standard state
- Only ΔH^θ can be measured, not H
- Standard enthalpy change is measured in **kJ mol⁻¹**

$$\Delta H_x^\theta$$

- a) ΔH : Refers to Enthalpy change

A positive value indicates an endothermic reaction while a negative value indicates an exothermic reaction

- b) θ : Refers to standard conditions where **289K, 101.3 kPa, 1 mol dm⁻³**

Standard conditions are necessary as enthalpy changes will have different values depending on the conditions under which they are measured. Therefore, all enthalpy changes are performed under standard conditions

- c) x : Refers to the type of enthalpy change

Sometimes, bond enthalpies are average values/differ (slightly) from one compound to another so the standard enthalpy will not be the same value in the data booklet

Standard Enthalpy of Formation: ΔH_f^θ

- The standard enthalpy change of formation (ΔH_f^θ): The energy change when one mole of a compound is formed from its elements in their standard states under standard conditions
- To calculate enthalpy change from formation:

$$\Delta H^\theta = \sum \Delta H_f^\theta(\text{products}) - \sum \Delta H_f^\theta(\text{reactants})$$

- ΔH_f^θ values are found in the data booklet (remember to include coefficients) (Elements have a ΔH_f^θ value of zero)

Standard Enthalpy of Combustion: ΔH_{comb}^θ

- The standard enthalpy change of combustion (ΔH_c°): The energy released when one mole of a compound is completely **burned in excess oxygen** under standard conditions with no change in pressure
- Combustion reactions always produce CO_2 and H_2O
- **All combustion reactions are exothermic** (always negative) as heat is released during combustion process
- To calculate enthalpy change from combustion:

$$\Delta H^\theta = \sum \Delta H_{comb}^\theta(\text{reactants}) - \sum \Delta H_{comb}^\theta(\text{products})$$

Thermochemical equations

- Thermochemical equations give the balanced equation with an enthalpy charge
- State symbols must be shown, as ΔH^θ depends on the state of the reactants or products
- In order to calculate energy changes for a specific amount of a substance using the thermochemical equation:

Question

Calculate the energy released, in kJ, when 0.500kg SO_3 reacts with water



Step 1: Calculate how many moles of SO_3 there are:

$$n(\text{SO}_3) = \frac{1000\text{g}}{80.07} = 12.49\text{mol}$$

Step 2: Compare to thermochemical equation:

1 mol of SO_3 releases 129.6 kJ, therefore 12.5 mol of SO_3 releases $-x$ kJ

Step 3: Use ratios:

$$\frac{1}{12.5} = \frac{-129.6}{x} = -1618 \text{ kJ}$$

Heat changes calculations

- Heat changes (enthalpy) can be calculated from the temperature changes:

$$q = mc\Delta T$$

- q : heat change
 - m : mass (Use the mass of water unless specified)
 - c : specific heat capacity
 - Specific heat capacity (c): The energy required to raise the temperature of 1g of substance by 1K
 - ΔT : Temperature change
 - If the temperature of the compound increased, then the reaction is endothermic and q must be positive
 - If the temperature of the compound decreased, then the reaction is exothermic and q must be negative
- For calorimetry experiments take the absolute value of ΔT then:
- If the temperature of the water INCREASED, then the reaction is exothermic and q must be negative
 - If the temperature of the water DECREASED, then the reaction is endothermic and q must be positive

Enthalpy Change

- To calculate enthalpy change (ΔH), the equation below can be used:

$$\Delta H = \frac{q \text{ (energy, kJ)}}{n \text{ (mol)}}$$

- However, ΔH can be either positive or negative. Simply add a positive or negative sign to Q when:
 - The temperature of the substance INCREASED, then the reaction was endothermic and Q is positive
 - The temperature of the substance DECREASED, then the reaction was exothermic and Q is negative

Standard Enthalpy of Neutralization: ΔH_{neut}^θ

- The standard enthalpy change of neutralization ($\Delta H_{\text{neut}}^\circ$): The enthalpy change when a strong acid and base react together to form one mole of water under standard conditions
- **Neutralization reactions are exothermic** (always negative) as heat is released
- To calculate enthalpy change from combustion:
 1. Calculate the number of moles of acid and base using $n = cv$
 2. Determine the limiting reactant. This will tell you how many moles of water can be produced
 3. Add the volumes of acid and base together (where $1\text{cm}^3=1\text{g}$) to get the mass
 4. Use $Q = mc\Delta T$ to calculate enthalpy change
 5. Use $\Delta H = \frac{Q}{n}$ where n is number of moles of water produced

Calorimetry

- Calorimetry is the process of measuring the amount of heat released or absorbed during a chemical reaction
- When the reaction occurs, it is either going to give off or take in heat
- The change in heat can be measured by observing the temperature of water, as water can serve as the surroundings
- There are many ways to perform calorimetry, the most common is to use a bomb shell
- Calorimetry is performed many different ways:

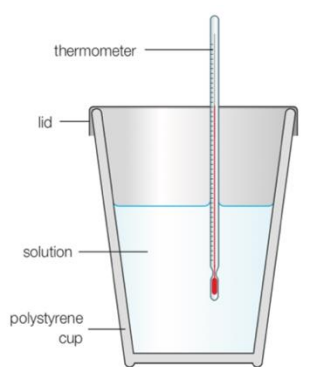


Figure 5.7 A simple calorimeter: polystyrene cup, lid and thermometer

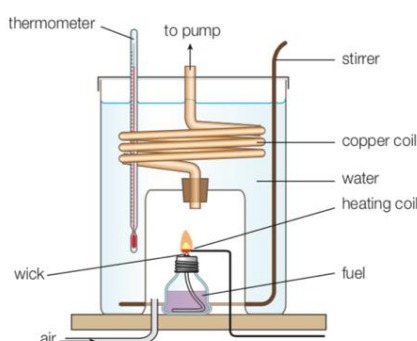


Figure 5.9 Measuring the enthalpy change of combustion of a liquid fuel using a flame combustion calorimeter

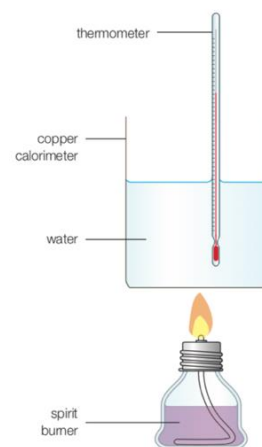
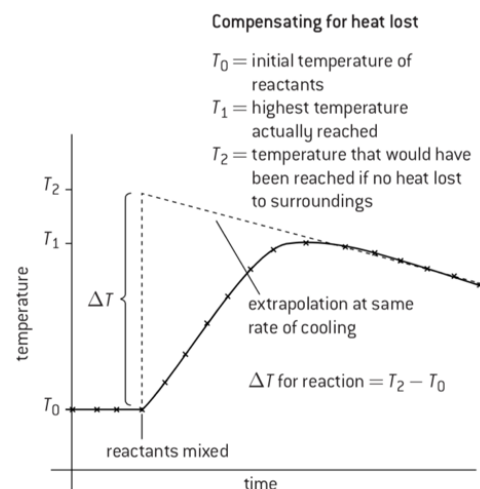


Figure 5.8 Simple apparatus used to measure enthalpy changes of combustion of

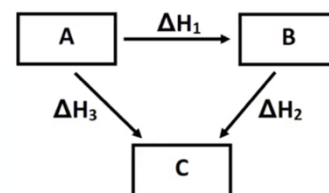
- However, when using calorimetry several assumptions are made
- This is because heat loss and incomplete combustion can lead to systematic errors in experimental results
- These assumptions are:
 1. That all the heat is transferred to the water
(Some might be transferred to the metal or is still inside the system)
 2. That all the solution has dissolved
 3. The mass of the water remained constant
 4. There was an unlimited oxygen source
 5. The experiment was under standard conditions
- **To compensate for heat lost by the water we can extrapolate the graph recorded**
- By extrapolating the graph, the temperature rise that would have taken place had the reaction been instantaneous can be calculated by taking $T_2 - T_0$



5.2 Hess's Law

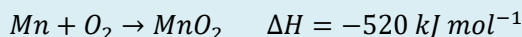
Hess's Law

- Hess's Law states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes
- This means the enthalpy change going from A to B is **the same** whether the reaction proceeds directly to A or whether it goes via A to C then B
- This is known as an energy diagram and can be written as two reactions that when combined produce the overall equation: $\Delta H_3 = \Delta H_1 + \Delta H_2$

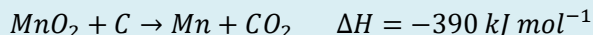


Question

Using the equation below:



Which is the enthalpy change for the following reaction?



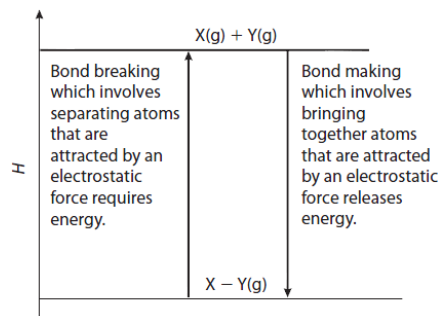
As you can see, if we reverse the second reaction (and change the sign of the enthalpy), it cancels to give the above reaction, therefore the enthalpy change is $-390 + 520 = 130 \text{ kJ mol}^{-1}$

5.3 Bond enthalpies

- 5.3.1 Bond-forming releases energy and bond-breaking requires energy
- 5.3.2 Average bond enthalpy is the energy needed to break one mol of a bond in a gaseous molecule averaged over similar compounds
- 5.3.3 Calculations of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values
- 5.3.4 Sketching and evaluation of potential energy profiles in determining whether reactants or products are more stable and if the reaction is exothermic or endothermic
- 5.3.5 Discussion of the bond strength in ozone relative to oxygen in its importance to the atmosphere

Bond enthalpy

- Average bond enthalpy: The energy required to break one mole of the same type of bond in the gaseous state averaged over a variety of similar compounds
- Energy is released through the **formation** of chemical bonds
 - **Bond forming:** Removing heat brings atoms closer together, forming bonds
 - Releases energy, ΔH negative therefore exothermic
- Energy is required when **breaking** chemical bonds
 - **Bond breaking:** Adding heat separates atoms, breaks bonds (See 5.3)
 - Requires energy, ΔH positive therefore endothermic



- The enthalpy of reaction (ΔH^θ) can be calculated using bond enthalpies
- Since there are average bond enthalpies, the calculation gives only an approximate result. To calculate:

$$\Delta H^\theta = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$

- E represents the bond energy per mol of bonds (see data booklet)
- When $\Sigma E(\text{bonds broken}) > \Sigma E(\text{bonds formed})$ the reaction is endothermic
- When $\Sigma E(\text{bonds formed}) > \Sigma E(\text{bonds broken})$ the reaction is exothermic

Question

Calculate the enthalpy of reaction of methane: $CH_4 + 2O_2 \rightarrow CO_2 + 3H_2O$

$$\text{Enthalpy of reaction} = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$

$$\text{Enthalpy of reaction} = (4(C-H) + 2(O=O)) - (2(C=O) + 6(H-O))$$

$$\text{Enthalpy of reaction} = (4 \times 414 + 2 \times 498) - (2 \times 804 + 6 \times 463)$$

$$\text{Enthalpy of reaction} = -1734 \text{ kJ mol}^{-1}$$

- However, bond enthalpies can only be used by themselves if all the reactants and products are in the gaseous state

Ozone depletion

- Oxygen is present in the atmosphere in two forms:
 - Normal oxygen: O_2
 - Ozone: O_3
- Much of the harmful UV radiation is absorbed by the ozone layer
- The ozone layer forms a protective screen which absorbed the UV light to ensure that the radiation that reaches the surface of the Earth is different from the emitted by the Sun
 - Without the ozone layer the UV radiation would have caused damage to living tissue
- The bond in oxygen and ozone are both broken when they absorb UV radiation of sufficient energy
- However, both oxygen and ozone are **broken by UV light of different wavelengths**
- This is because the bonds in oxygen, O_2 , are stronger than those in ozone, O_3
- The stronger double bond in O_2 requires higher energy UV radiation (Shorter wavelength) to break
- The wavelengths of light needed to break the bonds in ozone are calculated using a modified Planck's equation:

$$E_{\text{photon}} = \frac{h \times c}{\lambda}$$

Ozone depletion question:

The bond energy in ozone is 363 kJ mol^{-1} . Calculate the wavelength of UV radiation needed to break the bond

One mole of photons are needed to break one mole of bonds. The energy of a mole of photons is the energy of one photon multiplied by Avogadro's number (L)

$$L \times E_{\text{photon}} = 363\,000 \text{ J}$$

$$E_{\text{photon}} = \frac{363\,000}{6.02 \times 10^{23}}$$

We want to find wavelength, λ , so by rearranging Planck's equation:

$$\lambda = \frac{h \times c}{E_{\text{photon}}}$$

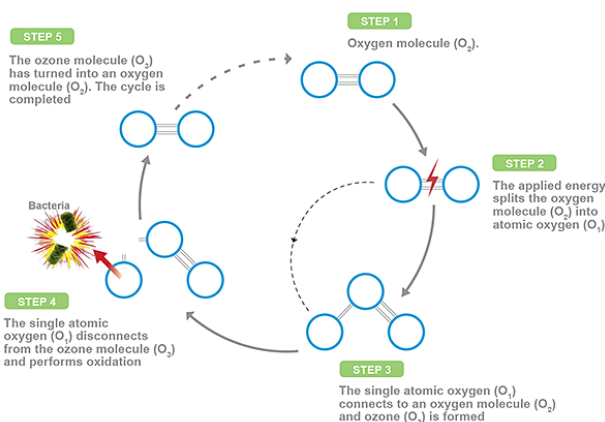
$$\lambda = 330 \text{ nm}$$

Any radiation in the UV region with a wavelength smaller than 330nm breaks the bond in ozone

- The bonds in O_3 are broken by UV radiation with a wavelength of $<330 \text{ nm}$
- The bond in O_2 is broken by UV radiation with a wavelength of $<242 \text{ nm}$

The Ozone-Oxygen Cycle

- The ozone–oxygen cycle is the process by which ozone is continually regenerated in Earth's stratosphere
- It describes how ozone is both formed and depleted by natural processes in the atmosphere (*diagram on right*)
- In the atmosphere, high-energy UV breaks the strong bonds in O_2 so that O_3 can be formed. Lower-energy UV breaks the weaker bonds in O_3**
- This cycle of reactions is significant because dangerous ultraviolet light has been absorbed and the stratosphere has become warmer



15.1 Enthalpy cycles

Born-Haber Cycle

- Born-Haber cycles are energy cycles describing the formation of ionic compounds
- Lattice enthalpy cannot be measured because gaseous ions do not combine directly to form a compound
- The Born-Haber cycle allows the experimental lattice enthalpy to be calculated from other enthalpy changes

- Hess's law can be used to find any missing value from a Born Haber cycle, not just a lattice enthalpy
- Remember the following:

Energy cycle	Definition	Equation
Ionization enthalpy ΔH_i^θ <i>First ionization energy</i>	The energy required to remove 1 mole of an electron from 1 mole of an atom in gaseous state* Since ionization always requires energy, it is always endothermic	$X(g) \rightarrow X^+(g) + e^-$
<i>Second ionization energy</i>	<i>The energy required to remove 1 mole of an electron from 1 mole of an ion in its gaseous state*</i>	$X^+(g) \rightarrow X^{2+}(g) + e^-$
Electron affinity enthalpy ΔH_e^θ <i>First electron affinity</i>	The energy change when 1 mole of an electron is added to 1 mole of an atom in its gaseous state*	$X(g) + e^- \rightarrow X^-(g)$
Lattice Enthalpy ΔH_{lat}^θ	The energy required when 1 mole of an ionic compound is formed from its gaseous ions*	$X^+(g) + Y^-(g) \rightarrow XY(s)$
Atomization Enthalpy ΔH_{atom}^θ	The energy change to make 1 mole of gaseous atoms from its elements*	$X(s) \rightarrow X(g)$

* "under standard conditions" with regarding enthalpy

- The Born-Haber cycle will contain all enthalpy cycles listed above
- By rearranging this formula, we can solve for lattice energy (Hess's Law)

Energy Cycle: Enthalpy of solution, hydration and lattice enthalpy

- Other energy cycles include the one between enthalpy of solution, hydrate and lattice enthalpy
 - Enthalpy of solution (ΔH_{sol}^θ): The enthalpy change when one mole of an ionic compound is dissolved in water to infinite dilution
 - Enthalpy of Hydration (ΔH_{hyd}^θ): The enthalpy change when one mole of gaseous ions dissolve to give an infinitely dilute solution
- The enthalpy of solution is found by (Hess's Law):

$$\Delta H_{sol}^\theta = \Delta H_{lat}^\theta + \Delta H_{hyd}^\theta$$

- First the solid ionic compound is broken down into its gaseous ions (ΔH_{lat}^θ)
- Then the gaseous ions are then hydrated by water molecules (ΔH_{hyd}^θ)

15.2 Entropy and spontaneity

Entropy

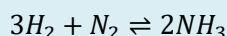
- Entropy (S) refers to the distribution of available energy among the particles in a system
 - The more ways the energy can be distributed the higher the energy
- Entropy is sometimes referred to as a measure of disorder of a system
- The change in the disorder of a system is known as the entropy change, ΔS
- The more disordered a system becomes the more positive the value of ΔS becomes
- Systems which become more ordered will have decreasing ΔS values
- Standard entropy: The entropy content of one mole of substance under a standard state
- Factors that increase the entropy of a system include:
 1. Changes of state, gas has the most entropy, solids have the least (account for coefficients)
 - Solids have low entropy values

- Gas molecules have a high entropy value
- 2. Increased number of particles (Example, increasing concentration)
- 3. Increased temperature (which increases movement of particles)
- 4. More complicated structure (or more atoms attached)
- 5. Dissolution (dissolving) of an ionic compound
- Unlike enthalpy, absolute values of entropy can be measured
- The standard entropy change for a reaction can be determined by (account for coefficients):

$$\Delta S^\theta = S^\theta_{\text{products}} - S^\theta_{\text{reactants}}$$

Entropy question:

Calculate the standard entropy for the formation of ammonia:



Step 1: Calculate the standard entropies of each molecule/compound (account for coefficients)

The standard entropies of hydrogen, nitrogen and ammonia are 131, 192 and 192 kJ mol⁻¹ respectively

$$\therefore \Delta S^\theta = S^\theta_{\text{products}} - S^\theta_{\text{reactants}} = 2 \times 192 - [(3 \times 131) + 192] = -201 \text{ kJ}^{-1}$$

- ΔS can also be calculated in a **reversible** process by: $\Delta S = \frac{q}{T}$
- The second law of thermodynamics states that the entropy of a spontaneous reaction (when not in equilibrium) will increase over time. When the system is at equilibrium will have 0 entropy

Spontaneity

- A reaction is said to be spontaneous if the system moves from a less stable to a more stable state
- Spontaneity depends both upon the enthalpy change and the entropy change
- These two factors are combined and expressed as the Gibbs energy change ΔG , often called “free energy change”
- The standard free energy change ΔG^θ is defined as:

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

- A spontaneous reaction is one that releases free energy, so ΔG must be negative if the reaction is spontaneous
 - If $\Delta G^\theta < 0$ the reaction is spontaneous
 - If $\Delta G^\theta = 0$ the reaction is at equilibrium
 - If $\Delta G^\theta > 0$ the reaction is not spontaneous
- Some reactions will always be spontaneous depending on ΔH^θ , T and ΔS^θ
- ΔH and ΔS can be either positive or negative, while T can either be a low or high value. The spontaneity can then be:

ΔH	ΔS	$-T$	ΔG	Spontaneity
+	+	Low	+	Not Spontaneous
		High	-	Spontaneous
+	-	Low/High	+	Not spontaneous
-	+	Low/high	-	Spontaneous
-	-	Low	-	Spontaneous
		High	+	Non spontaneous

- Spontaneity can also be found by substituting values into: $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
 1. Substitute 100 for ΔH and ΔS
 2. Substitute 0.1 for a low temperature, and 10 for a high temperature
 3. If ΔG is negative the reaction is spontaneous. If ΔG is positive, the reaction is not spontaneous