

OCR A Chemistry A-level

Module 5.2: Energy

Detailed Notes

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5.2.1 Lattice Enthalpy

Lattice Enthalpy

Lattice Enthalpy ($\Delta_{LE}H$)

Lattice enthalpies are used for **ionic substances**. Lattice enthalpy is a measure of the strength of ionic bonding in a giant ionic lattice.

Lattice **dissociation** enthalpy is defined as:

The enthalpy change when one mole of a solid ionic compound is completely dissociated into its gaseous constituent ions under standard conditions.

This is an **endothermic process**.

Lattice **formation** enthalpy is defined as:

The enthalpy change when one mole of a solid ionic compound is formed from its gaseous constituent ions under standard conditions.

This is an **exothermic process**.

Lattice enthalpy cannot be measured directly. It is calculated using experimental values for other enthalpy changes in a cycle called a **Born-Haber cycle**.

Atomisation Enthalpy ($\Delta_{at}H$)

This is defined as:

The energy required for the formation of one mole of gaseous atoms from an element under standard conditions.

Enthalpy of Electron Affinity ($\Delta_{ea}H$)

This is defined as:

The enthalpy change when one mole of electrons is added to a mole of gaseous atoms to form one mole of gaseous 1- ions under standard conditions.



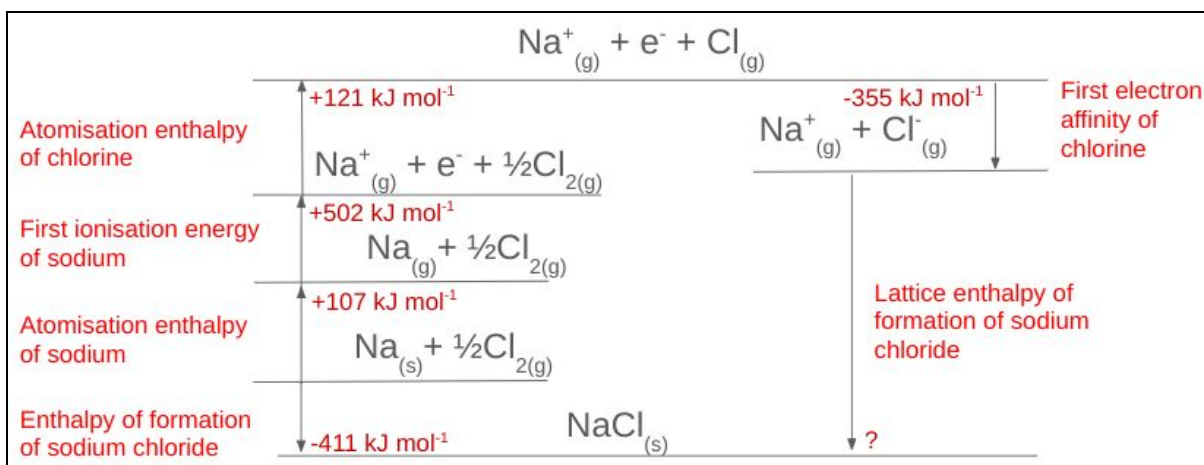


Born-Haber and Related Enthalpy Cycles

Born-Haber cycles are similar to the cycles used with **Hess's Law**. Note, Hess's law states that the **enthalpy change** of a reaction is **independent** of the **route** taken. Born-Haber cycles allow **enthalpy changes** to be determined when they cannot be measured directly.

The different enthalpy changes can be **combined** to produce a **Born-Haber cycle**. In a similar way to Hess's Law, the arrows represent a reaction and they are treated like vectors. If the cycle **counters the direction** of the arrow, the sign of the enthalpy change represented by that arrow is **reversed**.

Example:



In this example, lattice enthalpy of formation ($\Delta_e H$) is calculated by following anticlockwise rotation around the cycle: $\Delta_e H = [-(-355) - (121) - (502) - (107) + (-411)] = -786 \text{ kJ mol}^{-1}$

This cycle, derived from **empirical** data, will produce a different value for lattice enthalpy compared with the theoretical value predicted using **electrostatic theory**. This theory assumes a **'perfect ionic model'**. Therefore, experimentally derived lattice enthalpies can be used as indicators of **the degree of covalent bonding** in a lattice.

Perfect Ionic Model

It is often assumed that the ions are **'perfectly ionic'**.

The perfect ionic model assumes that:

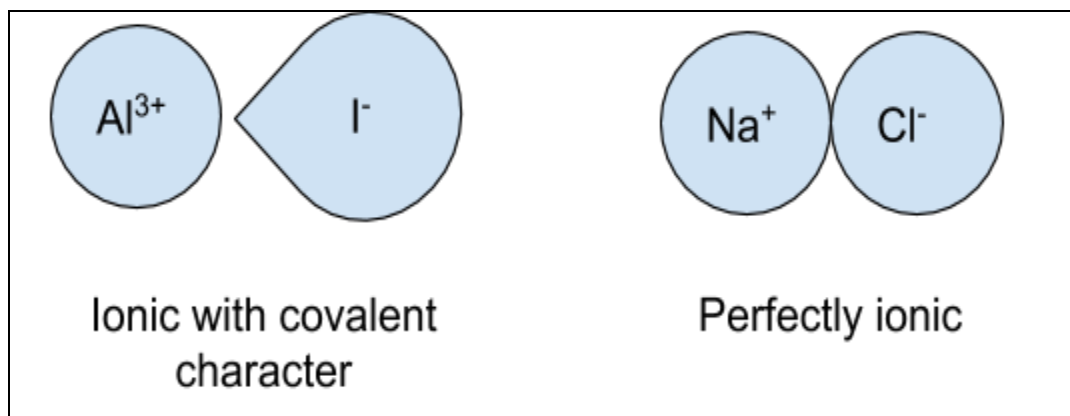
- All the ions are **perfectly spherical**.
- **Charge** is distributed **evenly** throughout the ion.
- The ions display **no covalent character**.





Covalent character occurs in ions when two bonded ions have **varying sizes or charges**, meaning the distribution of charge is **not even**. This **polarisation** of anions by cations creates **covalent character**.

Example:



Enthalpies of Solution ($\Delta_{\text{sol}}\text{H}$) and Hydration ($\Delta_{\text{hyd}}\text{H}$)

Enthalpies of solution and hydration can be used as another way of measuring lattice enthalpies **indirectly**. They are combined using a similar idea to Hess's Law.

Enthalpy of **solution** is defined as:

The enthalpy change when one mole of ionic solid is dissolved in water to infinite dilution so that the ions no longer interact under standard conditions.

Enthalpy of **hydration** is defined as:

The enthalpy change when one mole of gaseous ions is dissolved in water to form one mole of aqueous ions under standard conditions.

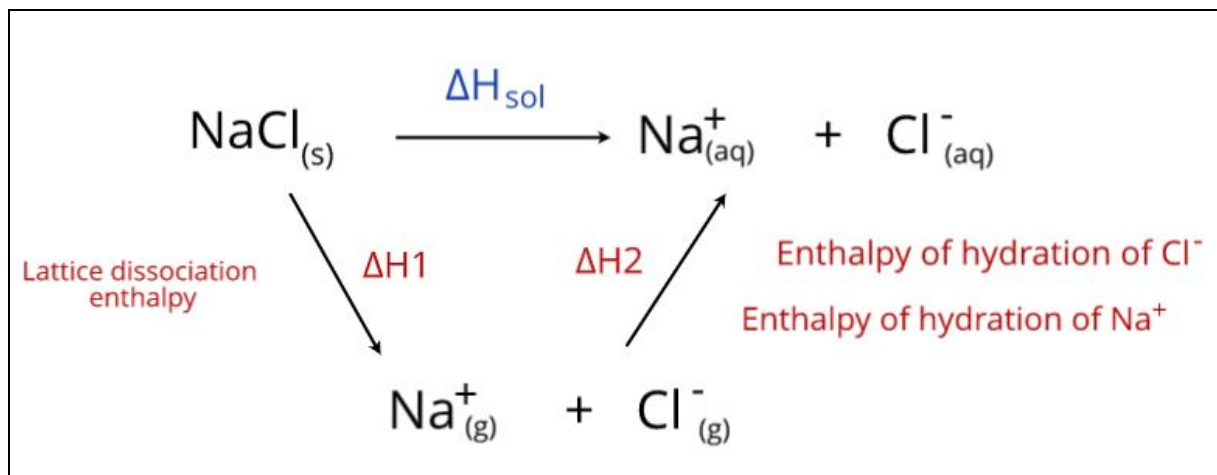
Enthalpy of hydration is nearly always **negative** as water molecules have **$\delta+$ regions** that naturally **attract** negative ions.

The enthalpy of solution and the enthalpy of hydration are combined in the following way to form an **energy cycle**.





Example: Calculating the lattice dissociation enthalpy of sodium chloride



$$\Delta H1 = \Delta H_{\text{sol}} - \Delta H2$$

Factors Affecting Enthalpy of Hydration and Lattice Enthalpy

Enthalpy of hydration is a measure of the attraction between ions (that were in a lattice) and water molecules in solution. **Positive ions** will be attracted to the **δ- oxygen atoms**, and **negative ions** will be attracted to the **δ+ hydrogen atoms**.

Attractions are stronger with **smaller ions** and with ions of a **greater charge**. This explains why hydration enthalpies **decrease** as you move **down a group** and why Na^+ ions have a lower enthalpy of hydration than Mg^{2+} ions.

Lattice dissociation enthalpy also **increases** in magnitude with **decreasing ionic radius** and **increasing charge**. This is because the ions form **stronger attractions** and so the energy required for dissociation is greater.

5.2.2 Enthalpy and Entropy

Entropy

In chemistry, things tend towards a state of **disorder**. Entropy, ΔS , is a **measure of disorder**. It is a measure of the dispersal of energy in a system, which is greater the more disordered a system is.

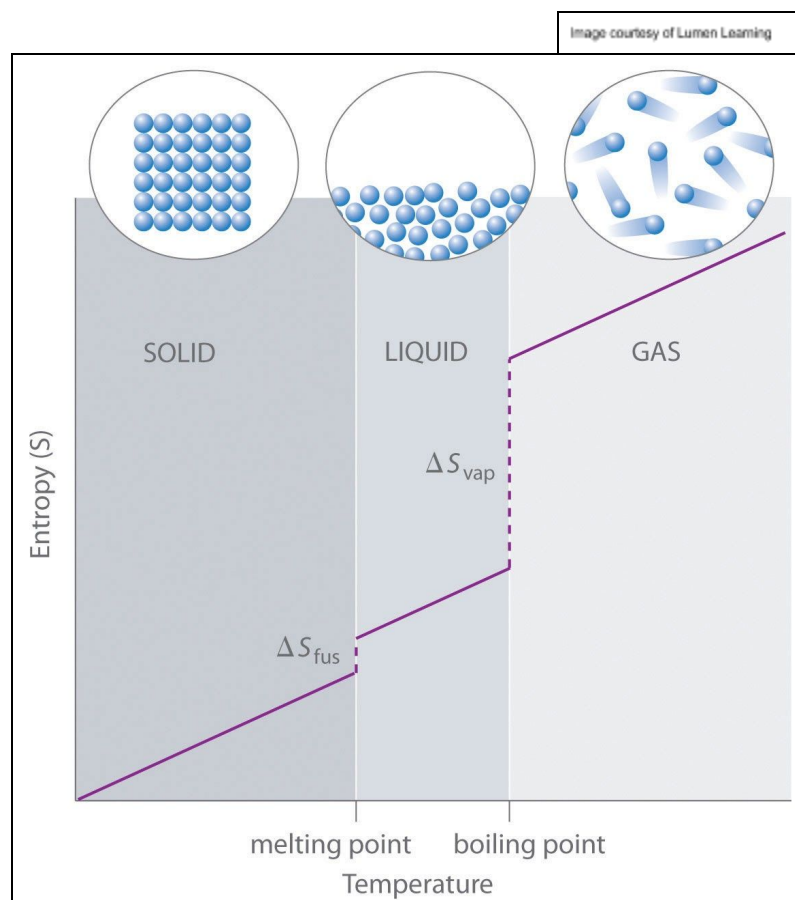




Some **endothermic reactions** are able to occur **spontaneously** at room temperature. This shows how enthalpy is not the only driver of chemical reactions. **Entropy** is also key.

Entropy increases as temperature increases because the particles **gain energy** and move **faster and further apart**. In other words, the particles become less ordered.

Gases have the **greatest entropy** compared to solids and liquids.



When a substance melts or evaporates, there is a **sudden increase** in entropy. The entropy change of vaporisation is much greater than that of fusion as a **gas is much more disordered** than a liquid or a solid.

Another case where there is a sudden increase in entropy is in a reaction when there are **more moles of gaseous product** than reactants. In this case there is an **increase in disorder**.

When a **lattice is dissolved** in solution, there is an increase in entropy. This is because the ions that make up the lattice are **dissociated** and can **move** in the solution, as opposed to being held in their position by strong bonds. This freedom of movement causes an **increase in disorder**.





The overall entropy change for a reaction can be calculated. It is measured in $\text{J K}^{-1} \text{mol}^{-1}$:

The entropy change for a reaction within a system can be calculated by finding the difference between the standard entropies of the **products** and the **reactants**:

$$\Delta S_{\text{total}} = \sum \Delta S_{\text{products}} - \sum \Delta S_{\text{reactants}}$$

If the entropy change for a reaction is **positive**, the products are **more disordered** than the reactants.

If the entropy change for a reaction is **negative**, the products are **less disordered** than the reactants.

Generally, you will only calculate the entropy change within a system. However, it is important to understand that the **natural direction of change** is towards a more disorderly state overall, which is a **positive change** in entropy. An example of this is the natural and spontaneous spreading of gas throughout a room, or the expansion of the universe.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Free Energy

Gibbs free-energy quantifies the balance between entropy and enthalpy in a system, acting as an **indicator of reaction feasibility**. It also allows ΔS to be found without needing to measure the effects on the surroundings:

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

Gibbs free-energy is measured in kJ mol^{-1} so it is important that ΔH and $T\Delta S$ are used in the same, **standard units**.

This equation also takes the form ' **$y = mx + c$** ', meaning it can be represented graphically as a straight line graph of ΔG (y-axis) against T (x-axis).

ΔG is **less than or equal to zero for all spontaneous reactions**. The minimum temperature at which a reaction is spontaneous can be found by putting **ΔG equal to zero**.





A reaction becomes feasible when $\Delta G = 0$.

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

$$0 = \Delta H - T\Delta S$$

Rearranging gives $T\Delta S = \Delta H$

Therefore, the temperature at which the reaction becomes feasible:

$$T = \frac{\Delta H}{\Delta S}$$

Changing the temperature or the type of reaction occurring will **change the feasibility** of the reaction happening.

Since ΔG is dependent on both the enthalpy and the entropy, if the entropy change for a reaction is positive and large enough, a reaction with a positive ΔH (**endothermic reaction**) could still have an overall **negative ΔG** and occur **spontaneously**.

Kinetics vs. Thermodynamics

Although a reaction may be thermodynamically feasible, it still may not be able to occur due to **kinetic factors**. A reaction may be thermodynamically feasible but kinetic factors may lead it to occur at **such a slow rate** that, in practice, it does not appear to occur at all.

Another example of this is **activation energy**. A reaction may require a large activation energy that is not provided by the reaction conditions. Therefore, it will not occur spontaneously.

5.2.3 Redox and Electrode Potentials

Redox

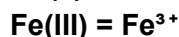
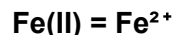
Oxidation is the loss of electrons and **reduction is the gain** of electrons. This can be remembered by the acronym **OILRIG** - Oxidation Is Loss, Reduction Is Gain.

Oxidation results in the **oxidation number** becoming more positive, whereas reduction results in the oxidation number becoming more negative.

Blocks of the periodic table, such as the s-block and d-block, indicate the orbital of the **outer electron**. During reactions, s-block, d-block and some p-block species tend to undergo **oxidation** whereas most p-block elements (further to the right of the periodic table) tend to undergo **reduction**.



The **oxidation number** of a species tells you the oxidation state that it is in. This is indicated by roman numerals. *Example:*



Redox Titration Calculations

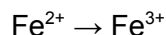
Method for balancing half equations:

1. Balance all atoms except for oxygen and hydrogen.
2. Add H_2O to balance **oxygens** (if needed).
3. Add H^+ ions to balance **hydrogens** (if needed).
4. Add e^- to balance **charges** (if needed).

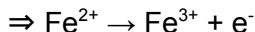
Example:

Write the full half equations for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$ and then combine the half equations.

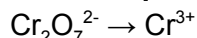
Step 1: Write the full half equation for iron.



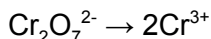
[The only thing that isn't balanced are the **charges**.]



Step 2: Write the full half equation for chromium.



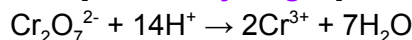
[Balance **chromium**]



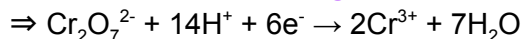
[Balance **oxygen**]



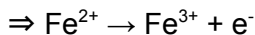
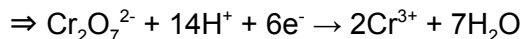
[Balance **hydrogen**]



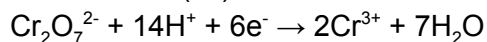
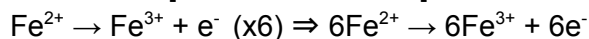
[Balance **charges**]



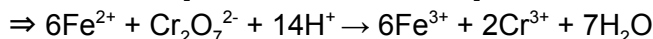
Step 3: Combine the two half equations.



[Balance **electrons**]



[**Cancel** the **electrons**]

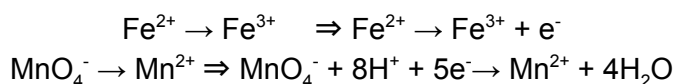




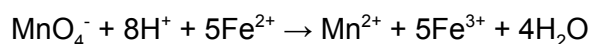
Redox Titrations

Reaction between Iron ions and Potassium Manganate

In the redox titration between iron ions and manganate ions, the **iron ions are oxidised** while the **manganate ions are reduced**. Their half equations can be found using the method described above.



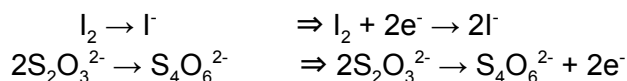
These **half equations** can be combined to give the overall **redox** equation:



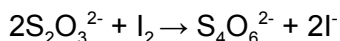
The iron solution is measured into a conical flask using a pipette and pipette filler. The endpoint of the titration is indicated when the solution in the conical flask has a permanent **pale pink colour**. At this point there is an excess of manganate ions.

Reaction between Iodine and Sodium Thiosulphate

In the redox titration between iodine and thiosulphate ions, the **thiosulphate ions are oxidised**, while the **iodine is reduced**. Their half equations can be found using the method described above.



These **half equations** can be combined to give the overall **redox** equation:



The same principles can be applied to any redox system.

Electrode Potentials

Electrochemical Cells

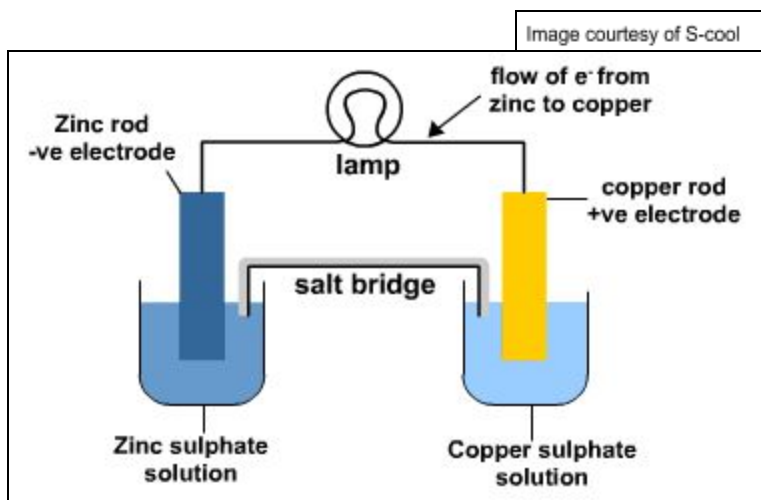
Electrochemical cells use **redox reactions** since the **electron transfer** between products creates a flow of electrons. This flow of charged particles is an **electrical current** that flows between **electrodes** in the cell. A **potential difference** is produced between the two electrodes which can be measured using a voltmeter.





Most electrochemical cells consist of **two solutions, two metal electrodes** and a **salt bridge**. A salt bridge is a tube of **unreactive ions** that can move between the solutions to carry the flow of charge, whilst not interfering with the reaction. The salt bridge is crucial as it creates a closed loop for the circuit.

Example: Electrochemical cell setup - the position of the lamp is where the voltmeter can be placed to measure the potential difference.



Each electrochemical cell contains two **half-cells** which make up the full chemical cell. These half-cells each have a **cell potential** which indicates how it will react, either in an oxidation or reduction reaction.

Cell Potentials (E^\ominus)

If measured under **standard conditions**, cell potentials are measured compared to the **Standard Hydrogen Electrode (SHE)** to give a numerical value for the half-cell potential. SHE is an electrode used for **reference** on all half-cell potentials, so, by definition it has a standard electrode potential of **zero**.

Positive potentials mean the substances are more easily **reduced** and will **gain electrons**. **Negative** potentials mean the substances are more easily **oxidised** and will **lose electrons** to become more stable.

Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode is the **measuring standard** for half-cell potentials. It has a cell potential of **0.00V**, measured under **standard conditions**. These conditions are:

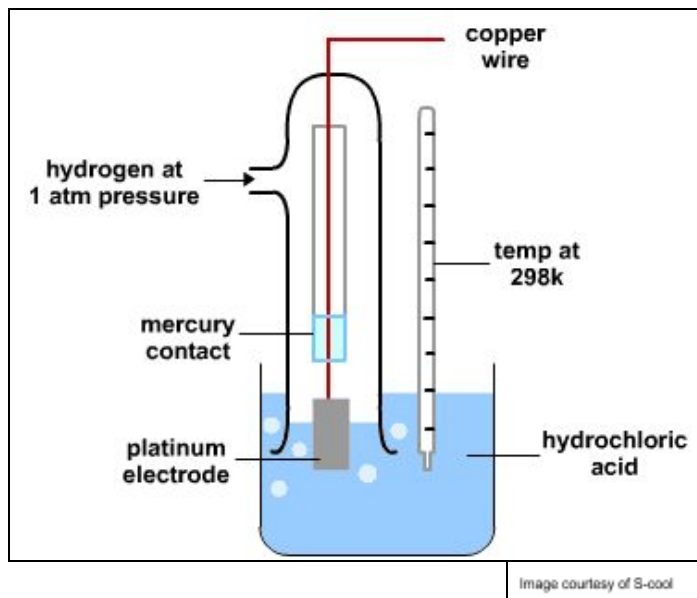
- Solutions of **1.0 mol dm⁻³** concentration
- A temperature of **298K**
- **100 kPa** pressure





The cell consists of **hydrochloric acid solution**, **hydrogen gas** and **platinum electrodes**. Platinum electrodes are chosen as they are **metallic**, so will conduct electricity, but **inert**, so will not interfere with the reaction.

Example:

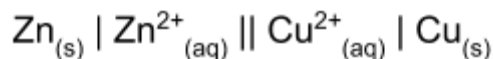
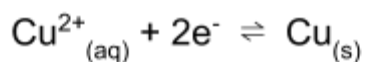
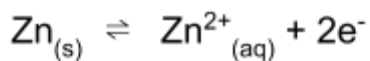


Conventional Cell Representation

Cells are represented in a simplified way so that they don't have to be drawn out each time. This representation has **specific rules** to help show the reactions that occur:

- The half-cell with the **most negative** potential goes on the **left**.
- The **most oxidised** species from each half-cell goes **next to the salt bridge**.
- A salt bridge is shown using a **double line**.
- **State symbols** are always included.

Example: Compared to copper, zinc has the most negative potential so is placed on the left and undergoes oxidation.





Calculating Cell Emf

Standard cell potential values are used to calculate the **overall cell emf**. This is always calculated as the **potential of the right of the cell minus the potential of the left** of the cell, when looking at the conventional cell representation.

$$E_{\text{cell}} = E^{\circ}_{\text{(right)}} - E^{\circ}_{\text{(left)}}$$

It can also be remembered as the **most positive potential minus the most negative potential**.

If the overall cell potential is a **positive** value, the reaction taking place is **spontaneous and favourable**. The more positive the potential, the more favourable the reaction.

The cell emf can be calculated for electrochemical cells containing **different metals or non-metals** in contact with their ions, or alternatively, for electrochemical cells involving two half cells containing **the same element but in different oxidation states**.

For example, a Fe^{2+} half cell and a Fe^{3+} half cell could be combined to make up an electrochemical cell.

E°_{cell} and Entropy

The standard emf of a cell is **directly proportional** to both $\ln(K)$, where K is the equilibrium constant of the reaction, and the **total entropy change, (ΔS_{total})**. This means that a positive E°_{cell} value will have an overall positive entropy change.

Limitations

There are **limitations** to both calculating a standard cell potential using the SHE and using the calculated value to determine reaction **feasibility**.

Although the cell emf value will tell you if a reaction is thermodynamically feasible or not, it does not take into account the **kinetics** of the reaction. Even if a reaction is feasible, it may occur at such a **slow rate** that, in practice, it does not actually occur.

The standard cell potential relies on conditions being **standard** throughout the experiment, when in reality, the system may **deviate** from standard conditions.





Oxidising and Reducing Agents

Standard electrode potentials can also be referred to as **standard reduction potentials** and can be ordered into a series known as the **electrochemical series**. In this series, all half reactions are written in the reduction direction.

Electrode potentials that are very **positive** are better **oxidising agents** and will oxidise those species more negative than themselves.

Species that are very **negative** are better **reducing agents** and will reduce those species less negative than themselves.

Image courtesy of Quora

Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

↑ stronger oxidizing agent ↓ stronger reducing agent

Disproportionation

In a **disproportionation reaction**, a species is both oxidised **and** reduced. This is indicated by both an increase and decrease in the oxidation number for that species.

Electrode potentials can be used to assess whether a species will undergo disproportionation. If the overall E^\ominus_{cell} value is **positive**, then the disproportionation reaction is **feasible**.

Example:

Will Cu^+ ions undergo disproportionation into Cu^{2+} ions and copper?

Reaction	E^\ominus_{cell}
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52

The disproportionation of Cu^+ ions involves the second and third half reactions.

$$E^\ominus_{\text{cell}} = +0.52 - (+0.15) = +0.37V$$

This value is positive, therefore the reaction is **thermodynamically feasible**.



Storage and Fuel Cells

Commercial Cells

Electrochemical cells can be a useful **source of energy for commercial use**. They can be produced to be **non-rechargeable, rechargeable or fuel cells**.

Fuel Cells

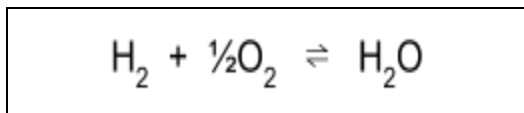
Fuel cells are a type of **electrochemical cell** which continuously produces a voltage when supplied with a fuel and oxygen. The fuel donates electrons at one electrode and oxygen gains electrons at the other electrode. The energy released is used to **generate a voltage**.

The most common type of fuel cell is the **hydrogen fuel cell**, which uses a **continuous supply** of hydrogen and oxygen from the air to generate a **continuous current**. Other common fuels include **hydrogen-rich compounds** like methane.

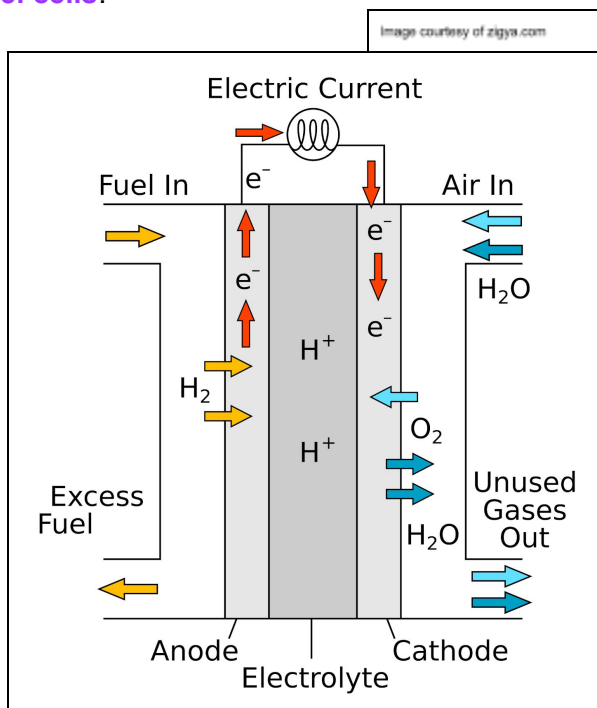
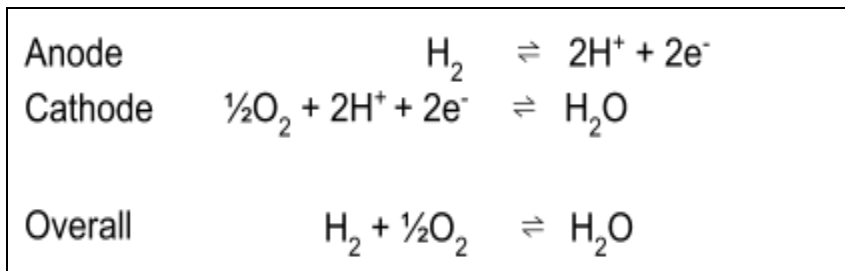
The reaction that takes place in a hydrogen fuel cell produces **water** as the only waste product, so the hydrogen fuel cell is seen as being relatively **environmentally friendly**.

The downsides to hydrogen fuel cells include the **high flammability of hydrogen** and that they are **expensive to produce**, meaning they are not yet commonly used.

The hydrogen fuel cell can be carried out with either an **acidic** or an **alkaline electrolyte**. The overall equation in both systems is the same:

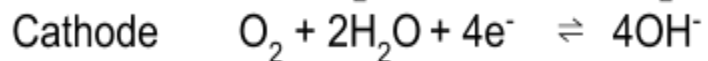
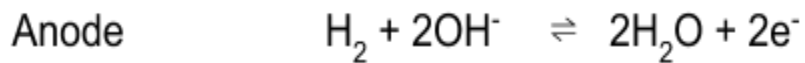


In an acidic electrolyte, such as H_2SO_4 , there are **H^+ ions in solution**. The half equations are as follows:





In an alkaline electrolyte, there are **OH⁻ ions in solution**. The half equations are as follows:



Lithium ion batteries are a commonly used example of an electrochemical cell. They are rechargeable, however, their benefits are counteracted by risks of toxicity and fire.

