

Redox Processes

Oxidation and reduction:

- Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer or change in oxidation number.
- An oxidising agent is reduced and a reducing agent is oxidised.
- Variable oxidation numbers exist for transition metals and for most main-group non-metals.
- The activity series ranks metals according to the ease with which they undergo oxidation
- The Winkler Method can be used to measure biochemical oxygen demand (BOD), used as a measure of the degree of pollution in a water sample.

Oxidation:

1. Gain of Oxygen
2. Loss of Hydrogen

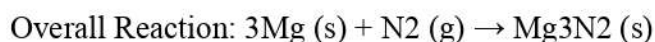
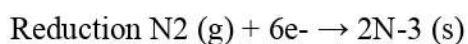
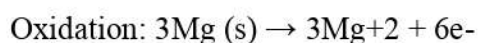
Reduction:

1. Loss of Oxygen
2. Gain of Hydrogen

Oxidation and reduction occur during chemical change when there is a shift in electron density from one atom to another.

Oxidation is Loss, Reduction is Gain

Redox reactions are interdependent: If reactant “A” is oxidised then reactant “B” must be reduced. Reduction and Oxidation reactions occur simultaneously, depicted using half equations:



Oxidation numbers:

- The apparent charge that an atom has in a molecule or ion.
- A measure of the electron control or possession it has relative to the atom in the pure element.
- Oxidation is the increase in oxidation state
- Reduction is the decrease in oxidation state

Assigning Oxidation States:

Elements not combined with other elements have an oxidation state of 0

- Na, Mg, O₂, N₂

Oxidation state is equal to charge of ions in ionic compounds

- (NaCl: Na⁺, Cl⁻), (CaCl₂: Ca⁺², Cl⁻)

The oxidation states of all the atoms in a neutral compound must add up to 0

- H₂SO₄ (H = +1, O = -2, S = +6)

In simple ions, the oxidation state is the same as the charge on the ion

- Mg⁺² (+2), Cl⁻ (-1),

The oxidation states of all the atoms in a polyatomic ion must add up to the charge on the ion:

- SO₄²⁻ (O = -2, S = +6)

Element	Usual oxidation state	Exceptions	Explanation
Li, Na, K	+1		
Mg, Ca	+2		
F	-1		there are no exceptions because F is the most electronegative element
O	-2	peroxides such as H_2O_2 , where it is -1; OF_2 , where it is +2	
H	+1	metal hydrides such as NaH , where it is -1	H is more electronegative than Na and so gains electron control
Cl	-1	when it is combined with O or F	Cl is less electronegative than O and F, and so loses electron control

Variable Oxidation States:

Use Roman numerals to indicate oxidation state when naming compounds:

- $FeCl_2$: Iron (II) Chloride (Fe = +2)
- $FeCl_3$: Iron (III) Chloride (Fe = +3)
- $K_2Cr_2O_7$: Potassium Dichromate (VI) (Cr = +6)
- Cr_2O_3 : Chromium (III) Oxide (Cr = +3)

Balancing Redox Reactions:

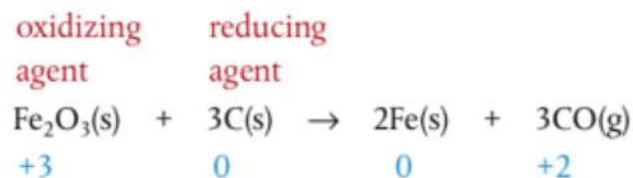
- Balance in terms of charge and number of atoms
- Balance oxygen with H_2O
- Balance hydrogen with H^+
- Balance electrons with e^-

Oxidising and Reducing Agents:

- Oxidising agents are readily reduced.
- O_2 , O_3 , H^+/MnO_4^- , $H^+/Cr_2O_7^{2-}$, F_2 , Cl_2 , Conc. HNO_3 , H_2O_2

- Reducing agents are readily oxidised. • H₂, C, CO, SO₂, reactive metals.

For example, in the reaction where iron (Fe) is extracted from its ore (Fe₂O₃):



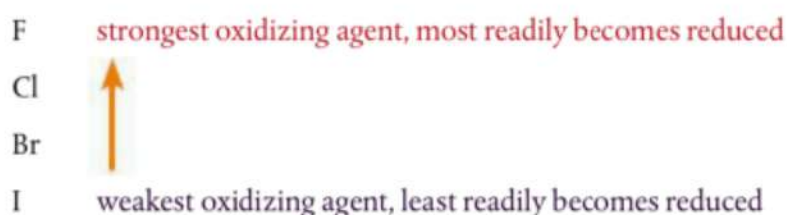
The Activity Series:

- Metals have a tendency to lose electrons and form positive ions, so they will act as reducing agents.
- More reactive metals lose their electrons more readily and thus are stronger reducing agents than less reactive metals.



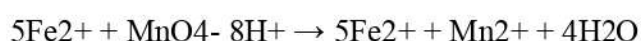
Zinc acts as a reducing agent, therefore it is the more reactive metal. If reaction is reversed with Copper in solution of Zinc ions, there would be no reaction as Cu is not a strong enough reducing agent to reduce Zn²⁺.

- More reactive non-metals are stronger oxidising agents
- Tendency to gain electrons decreases down the group, thus reactivity increase up the group



Redox Titrations & the Winkler Method:

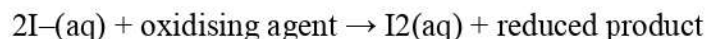
- Iron and Manganate (VII)



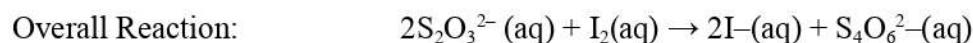
MnO₄⁻ is purple but Mn²⁺ is colourless

- Iodine–thiosulfate reaction

Oxidising agents react with excess iodide ions to form iodine.



The iodine is then titrated with sodium thiosulfate, Na₂S₂O₃, with a starch indicator



Starch indicator means the solution is initially dark blue, but the solution turns colourless as an equivalence point is reached.

- **The Winkler Method**

Dissolved Oxygen:

An indicator of the quality of water. As pollution increases, the dissolved oxygen content generally decreases as oxygen is used by bacteria in decomposition reactions.

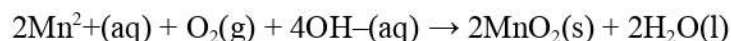
Biological Oxygen Demand:

A measure of pollution in water. The amount of oxygen used to decompose the organic matter in a sample of water over a specified time period, usually five days at a specified temperature. Measured in PPM (milligrams per decimeter cubed)

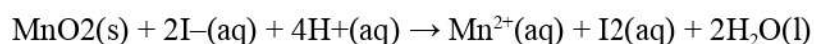
High BOD indicates a greater quantity of degradable organic waste in the water, which means a lower level of dissolved oxygen.

BOD is calculated by the Winkler method:

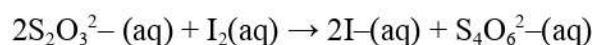
1. Extract water sample and add a manganese (II) salt such as MnSO_4 . The salt will be oxidised to a higher oxidation state by O_2 in basic solution:



2. Acidified iodide ions (I^{-}) are added and oxidised by Mn(IV) to I_2 :



3. Produced iodine is titrated with sodium thiosulfate:



Electrochemical cells:

- The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K.
- The standard electrode potential (E°) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE.
- Solute concentration is 1 mol dm^{-3} or 100 kPa for gases. E° of the SHE is 0 V.

Voltaic (Galvanic) cells:

- Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy.
- Oxidation occurs at the anode (negative electrode) and reduction occurs at the cathode (positive electrode) in a voltaic cell.
- A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit.
- The EMF is termed the cell potential (E°).

$\Delta G = -nF E^\circ$. When E° is positive, ΔG is negative indicative of a spontaneous process.

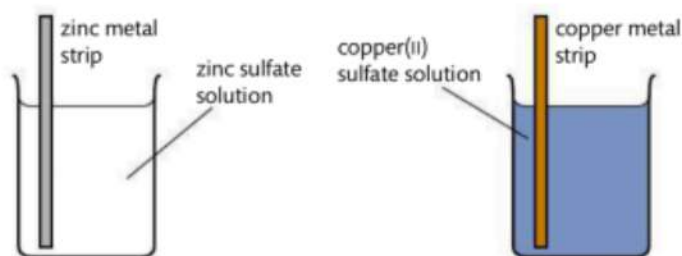
When E° is negative, ΔG is positive indicative of a non-spontaneous process. When E° is 0, then ΔG is 0.

Electrolytic cells:

- Electrolytic cells convert electrical energy to chemical energy, by bringing about non-spontaneous processes.
- Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode) in an electrolytic cell.
- When aqueous solutions are electrolysed, water can be oxidised to oxygen at the anode and reduced to hydrogen at the cathode.
- Current duration of electrolysis and charge on the ion affect the amount of product formed at the electrodes during electrolysis.
- Electroplating involves the electrolytic coating of an object with a metallic thin layer.

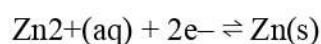
Voltaic Cells:

- Generate electricity from spontaneous redox reactions
- Separate half reactions into two half cells
- A metal in contact with an aqueous solution of its own ions.



Zinc and Copper half cells

Zinc atoms, release e^- to form zinc ions, the surface of the metal will be negatively charged relative to the solution. There is thus a charge separation, known as the electrode potential. Ions in solution will gain e^- to form Zn atoms, forming the equilibrium:

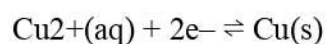


Position of equilibrium determines size of electrode potential and is dependent on the reactivity of the metal.

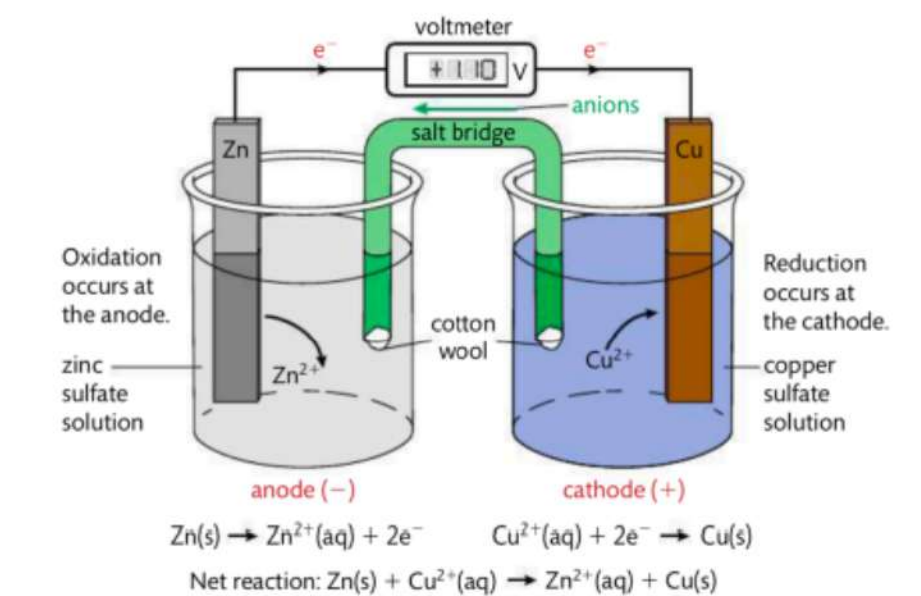
Copper is less reactive, thus it is less readily reduced than Zn.

The equilibrium will thus lie more to the right.

It will have fewer electrons on the surface of the Cu strip, thus it has a higher electrode potential than Zn.

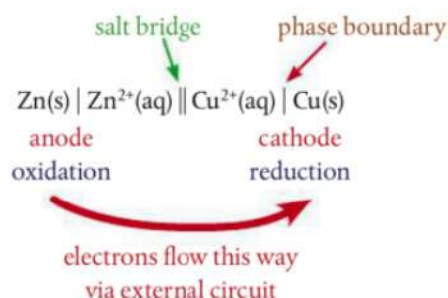


- Two connected half-cells make a voltaic cell
- Electrons flow from Zn Half-Cell (electrode) to Cu through external wire due to difference in electrode potential.
- The more reactive the metal, the greater the negativity of its electrode potential in its half-cell.
- Anodic Oxidation, Cathodic Reduction
- Needs external electronic circuit connected to each electrode (voltmeter to record voltage)
- Needs Salt bridge to complete circuit, salt bridge is a glass tube or strip of absorptive paper that contains an aqueous solution of ions (KNO_3).
- Anions move in the salt bridge from the cathode to the anode, which opposes the flow of electrons in the external circuit. Cations move in the salt bridge from the anode to the cathode.



- The greater the difference between the reactivity of the metals, the greater the voltage (EMF).
- $\text{Zn} + \text{Ag} > \text{Zn} + \text{Cu}$


- Cu + Ag (Cu is reduced due to greater reducing power) Cell Diagram Conversion:
- Single line: Phase boundary
- Double Line: Salt Bridge
- Aqueous solutions of each electrode are placed next to the salt bridge;
- Anode on the left, Cathode on the right



Standard Electrode Potentials:

- Acts as a reference point so that comparisons can be made between different electrodes
- Potential difference generated by voltaic cell known as electromotive force (EMF)
- Electrode/Cell potential (E) generated as e⁻ flow from cell with more negative potential to cell with more positive potential
- The magnitude of E depends on the difference between the tendencies of both half cells to undergo reduction.
- The electromotive force (EMF) of a voltaic cell is the greatest potential difference that it can generate
- Standard hydrogen electrode (SHE) acts as a reference point for individual half cells.
- Platinum used as electrode as it is inert
- Platinum is in contact with 1 mol dm⁻³ H⁺ and H₂ gas at 100 kPa.
- Assigned arbitrary electrode potential of 0 Volts.
- Standard Electrode Potential (E^o) is the voltage of the reduction half-equation relative to SHE at STP.
- All solutions must have a concentration of 1.0 mol dm⁻³;
- All gases must be at a pressure of 100 kPa
- All substances used must be pure;
- temperature is 298 K
- E^o > 0, half cell has greater tendency to be reduced than H⁺, e⁻ flow from H⁺ half cell.
- E^o < 0, half cell has lower tendency to be reduced than H⁺, e⁻ flow to the H⁺ half cell.

- E° values refer to reduction reactions
- E° values don't depend on the number of electrons, thus are not affected by stoichiometric coefficients.
- The more positive the E° value is, the more readily it is reduced (cathode)
- The more positive the E° value is, the more readily it is oxidised (anode)

	Oxidized species		Reduced species	$E^\circ / \text{V, at 298 K}$
increasing tendency to occur as reduction 	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	$\text{Zn}(\text{s})$	-0.76
	$\text{H}^+(\text{aq}) + \text{e}^-$	\rightleftharpoons	$\frac{1}{2}\text{H}_2(\text{g})$	0.00
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	$\text{Cu}(\text{s})$	+0.34
	$\text{Ag}^+(\text{aq}) + \text{e}^-$	\rightleftharpoons	$\text{Ag}(\text{s})$	+0.80

Calculating E°_{Cell} :

- Calculate the EMF of a voltaic cell for any two half-cells

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}$$

- Must use reduction potentials, do not reverse values
- The E° values do not have to be multiplied according to the stoichiometry of the redox equation as they are intensive values

Determining the Spontaneity of a Reaction:

- If E°_{Cell} is positive, reaction is spontaneous
- If E°_{Cell} is negative, reaction is non-spontaneous, reverse reaction is spontaneous

Electrode potential and free energy change (E_{cell} and ΔG)

$$\Delta G = -nFE^\circ$$

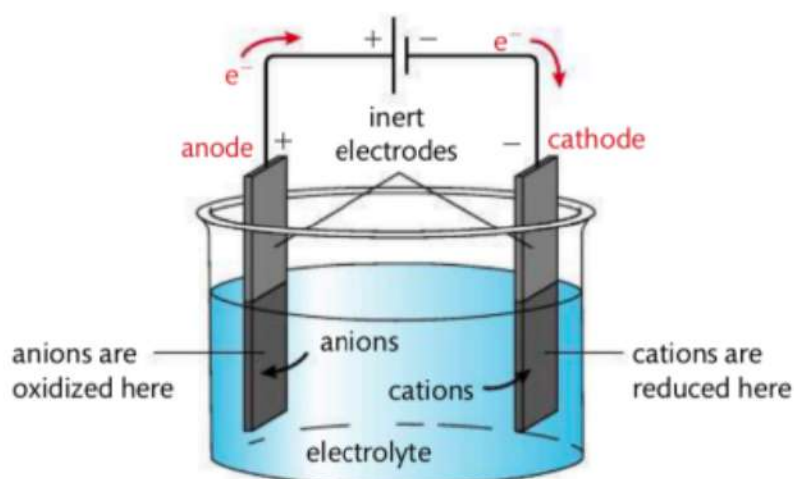
- n = number of moles of electrons transferred
- F = Faraday's constant
- If E° is positive, ΔG is negative, reaction is spontaneous
- If E° is negative, ΔG is positive, reaction is nonspontaneous
- If $E^\circ = 0$, $\Delta G = 0$, Reaction is in equilibrium

- More positive E^\ominus values mean ΔG is more negative, meaning the reaction is more energetically favourable. In a voltaic cell the half-cell with the greater E^\ominus will be reduced, whilst the half-cell with the lower E^\ominus value will be oxidised.

	Oxidized species		Reduced species	E^\ominus / V	
increasing strength as oxidizing agent ↓	$Zn^{2+}(aq) + 2e^-$	\rightleftharpoons	$Zn(s)$	-0.76	↑ increasing strength as reducing agent
	$H^+(aq) + e^-$	\rightleftharpoons	$\frac{1}{2}H_2(g)$	0.00	
	$Cu^{2+}(aq) + 2e^-$	\rightleftharpoons	$Cu(s)$	+0.34	
	$\frac{1}{2}I_2(s) + e^-$	\rightleftharpoons	$I^-(aq)$	+0.54	
	$\frac{1}{2}Cl_2(g) + e^-$	\rightleftharpoons	$Cl^-(aq)$	+1.36	

Electrolytic Cells:

- Uses an external source of electrical energy to bring about a redox reaction that would otherwise be non-spontaneous
- Reactants known as electrolytes • Redox reactions occur at electrodes
- Ions are discharged



Electrolytic Cell contains:

- Source of electric power source ||, longer line represents positive terminal, shorter line represents negative terminal
- Inert electrodes are submerged in electrolyte

- Electrical wires connect electrodes to power source
- Power source pushes electrons towards the cathode where they enter the electrolyte
- Electrons are released at the anode and returned to the source
- Current passed through electrolyte by mobile ions
- Reactions at each electrode remove ions from solution
- Electrons flow clockwise

Redox reactions occur at the electrodes:

- Ions in electrolyte migrate to electrodes by attraction of opposite charges
- Anions migrate to anode, cations migrate to cathode
- In aqueous solutions, water is

oxidised to oxygen at anode, and reduced to hydrogen at the cathode

Cathode (negative electrode): $M^+ + e^- \rightarrow M$

Anode (positive electrode): $A^- \rightarrow A + e^-$

	Voltaic cell		Electrolytic cell	
Anode	oxidation occurs here	negative	oxidation occurs here	positive
Cathode	reduction occurs here	positive	reduction occurs here	negative

The electrolysis of molten salts:

- No solvent, only the compound itself.
- Usually only one ion migrates to each electrode

Electrolysis of aqueous solutions:

- Water can be oxidised or reduced
- At the cathode, H₂O can be reduced to H₂: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
- At the anode, H₂O is can be oxidised to O₂: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

When solute A-M⁺ is in aqueous solution:

- At the cathode, H₂O is reduced or M⁺ is reduced
- At the anode, H₂O is oxidised or A⁻ is oxidised

Discharge of ion at electrodes depends on:

- The relative E° values of the ions

- Smallest absolute value is oxidised/reduced
- The relative concentrations of the ions in the electrolyte
- If one of the ions is much more concentrated than another ion then it may be preferentially discharged.
- The nature of the electrode.
- Consider electrolysis of CuSO_4 (aq)
- Cu^{+2} (reduced at cathode), SO_4^{2-} (oxidised at anode)

Carbon Electrodes (Inert):

- Cathode: • Cu^{+2} or H_2O
- Cu^{+2} preferentially reduced
- Anode: • SO_4^{2-} or H_2O
- H_2O preferentially oxidised

Copper Electrodes:Cathode:

- Cu^{+2} or H_2O • Cu^{+2} preferentially reduced

Anode:

- Cu electrode is itself oxidised, supplying electrons and forming Cu^{+2} ions
- $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$
- So the net reaction is the movement of Cu^{2+} (aq) from where it is produced at the anode to the cathode where it is discharged as Cu(s) .

Factors affecting the amount of product in electrolysis:

Charge = Current x Time Amount of product depends on:

- Size of current
- Time used
- Charge of ion