

Redox Notes

- Redox involves transfer of electrons
- **Oxidised** \Rightarrow loses electrons
- **Reductions** \Rightarrow gains electrons
- **Reduced species** \Rightarrow oxidising agent/oxidant
- **Oxidised species** \Rightarrow reducing agent/reductant
- Redox reaction only occurs if there is a transfer of electrons
- Oxidation numbers shows which atoms are reduced or oxidised

GENERAL RULE WHEN DETERMINING OXIDATION NO		
Group	Oxidation No	
1	+1	
2	+2	
13	+3	
14-17	Varies	
	Usually	Exceptions
Oxygen	-2	Peroxides (-1); Ex. H_2O_2 ; Na_2O_2 F_2O : O(+2)
Hydrogen	+1	Metal hydrides (-1); Ex: NaH ; KH

- Sum of oxidation numbers = net charge
- Oxidised species increase in oxidation number
- Reduced species decrease in oxidation number (reduced \Rightarrow become smaller)
- Species which do not change in oxidation numbers are spectators

Types of Redox Reactions

- Metal-metal ion displacement \Rightarrow electrons transfer from more reactive metal to less reactive metal ions (more reactive metal is oxidised, less reactive reduced)
- Halogen-halide ion displacement \Rightarrow halogen (group 17) becomes reduced, halide ions of less reactive halogen oxidised
 - o It is more convenient to use halogen reagents in aqueous solution form
- Combustion \Rightarrow oxidation of fuel and reduction of oxygen gas
- Corrosion \Rightarrow Metal is oxidised, and oxygen gas is reduced
 - o More reactive metals have greater tendency to corrode
 - o Some metals naturally form a thin protective oxide coating which forms when exposed to air, hence protecting underlying metal from corrosion

Half Equations

- Half equations show individual reactions of oxidised and reduced species
- Oxidisation half equations have electrons as product
- Reduced half equations have electrons as reactant
- When both half equations are combined, electrons cancel out and redox reaction is remaining

HOW TO BALANCE HALF EQUATION

Step	What to do?
1	Balance Metal or Non-metal other than H and O
2	Balance O (using H_2O)
3	Balance H (using H^+)
4	Count charge each side
5	Add e^- to the BIGGER SIDE
6	Simplify (if needed)
7	DOUBLE CHECK TO ENSURE CHARGE IS MATCHING BOTH SIDES

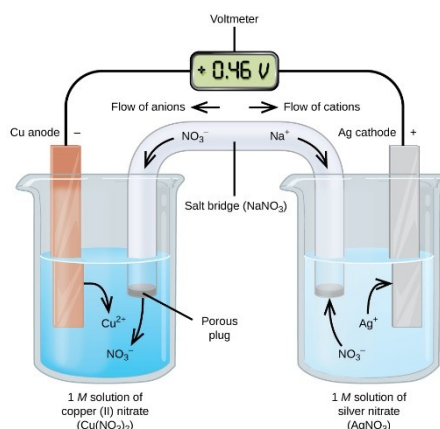
- In simply stage, if H_2O or H^+ are on both sides, subtract coefficient on both sides by smallest number

Predicting Spontaneity

- Total E^0 can be used to predict spontaneity
- If $E^0 > 0$, reaction is spontaneous \Rightarrow reaction will only occur in forward direction
- If $E^0 < 0$, reaction is not spontaneous \Rightarrow reaction will only occur in reverse direction

Galvanic Cells

- Galvanic cells/electrochemical cells \Rightarrow batteries
- Galvanic cells use redox reaction to produce a voltage (potential difference) and current
- They work by allowing redox reaction to occur without direct contact between agents
- **Anode \Rightarrow loses electrons/oxidised/reducing agent**
- **Cathode \Rightarrow gains electrons/reduced/oxidising agent**
- Galvanic cell uses metal cathode and anode in aqueous solution (reducing and oxidising agents) of respective ions of metals
- Anodes and cathodes are connected, and salt bridge made of non-reactive electrolyte solution connects solutions



- Anode \Rightarrow oxidation occurs. Electrode contacts reductant and labelled -ve terminal
- Cathode \Rightarrow reduction occurs. Electrode contacts oxidant and labelled +ve terminal
- Electrolyte \Rightarrow electrodes (metal nodes) are immersed in electrolyte solution
 - o Ions in electrolyte conduct charge in the solution to prevent build-up of charge
 - o May become oxidised or reduced
- Salt Bridge \Rightarrow contains a non-reactive electrolyte solution
 - o Prevents direct contact between redox agents, while allowing ions to flow between them
 - o Anions flow towards anode
 - o Cations flow towards cathode
 - o Salt bridge is essential to prevent build-up of electrical charge
 - o If no salt bridge, there will be no potential difference in charge between nodes, therefore, no current
- Oxidation half-cell \Rightarrow where oxidation occurs
 - o Consists of anode and surrounding electrolyte
- Reduction half-cell \Rightarrow where reduction occurs
 - o Consists of cathode and surrounding electrolyte

Strength of Oxidants

- Voltage is a measure of strength of oxidant
- Back of data sheet (table of standard reduction potentials) ranks strength of oxidising agents
- SRP is ability of a substance to be reduced by H_2 gas
- Test is same as galvanic cell, but hydrogen gas node in H^+ electrolyte is used against tested substance
- Therefore, voltage produced against hydrogen as tested substance is 0V, as no potential difference exists
- SRPT shows potential for reaction to occur
- Equations at bottom of the table are least likely to occur

Predicting Equations

- Do determine if a reaction will occur and spontaneity, look at SRPT
- SRPT half equations are ranking in order of ability to be reduced
- Substances at the top of the table have a higher electronegativity and are good oxidants
- Substances at the bottom have a low electronegativity and are good reductants
- Each half equation is reversible
- Left \Rightarrow right is reduction
- Right \Rightarrow left is oxidation
- All reduction potentials are relative to hydrogen ions
- Do not use values in explanations, unless comparing two half equations
- Predicting:
 1. List all species on reactant side of the potential reaction \Rightarrow don't list products

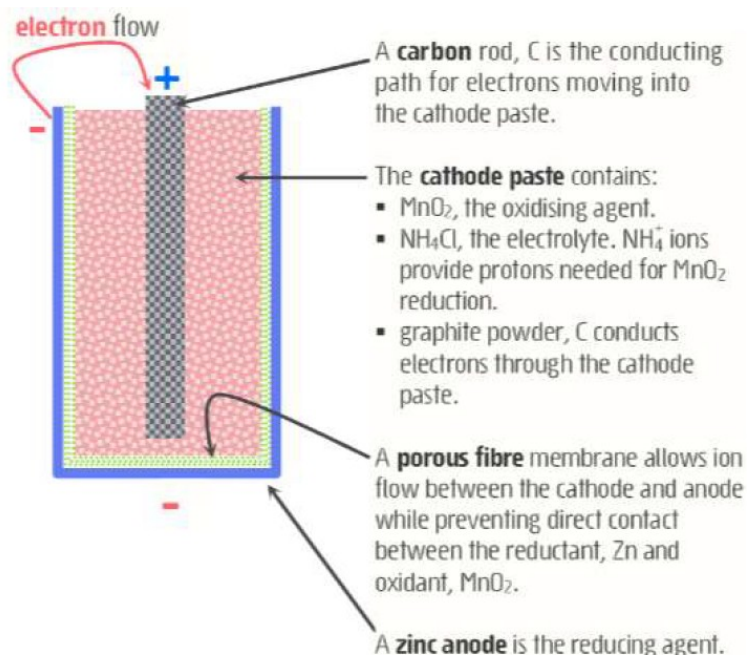
2. Species which appears first from the top is oxidising agent
 3. Species which appears second from the top is reducing agent
 4. Ignore all other species
- If oxidant is above reductant, reaction is spontaneous, otherwise, there's no reaction
 - Negative slope \Rightarrow reaction occurs
 - Positive slope \Rightarrow no reaction occurs
 - If half equation is not on the chart, spontaneity cannot be predicted unless further information is not provided
 - Non-chart equations \Rightarrow ranks equations from information given
 - Phases:
 - o Ensure phases in questions are phases being used \Rightarrow not phases in chart
 - o RTQ to ensure correct phases
 - All reactions in SRPT is at standard conditions \Rightarrow 25°, 1.00M and 1atm
 - o Predictions become unreliable if not at these conditions

Fuel Cells

- Primary Cells
 - o Non rechargeable galvanic cells
 - o Fixed amount of oxidants and reductants (fixed amount of reactant) and cannot be replaced
 - o Alkaline cells \Rightarrow devices that require higher current (cd players, torches, radios etc)
 - o Silver oxide button cells \Rightarrow steady constant voltage and small size (watches, pacemakers, hearing aids)
 - o Lithium cell \Rightarrow very flammable, non-toxic and high energy density
 - o Dry Cell
 - Advantages:
 - Cheap
 - Portable
 - Disadvantages:
 - Low energy to mass ratio
 - Voltage decreases slowly over time (due to disintegration of reactants)
 - Max V = 1.5V, however this decreases with time ([reactants] decrease)
 - Large quantities of toxic Zn waste may enter groundwater and soil in disposal in landfill
 - Can be attached in series to add voltage

Figure 5 The dry cell uses zinc as the reducing agent and manganese(IV) oxide, MnO_2 as the oxidising agent. A graphite rod, C and powdered graphite, C conduct electrons to the surface of individual MnO_2 particles within the cathode paste. Ammonium chloride is also incorporated into the cathode paste and serves as a salt bridge as well as providing protons (NH_4^+ is a weak acid) needed in the reduction of MnO_2 .

However, the use of ammonium ions is problematic, as over time their acidic nature causes the zinc anode to dissolve forming Zn^{2+} ions. For this reason dry cells have a low shelf life of around a year.



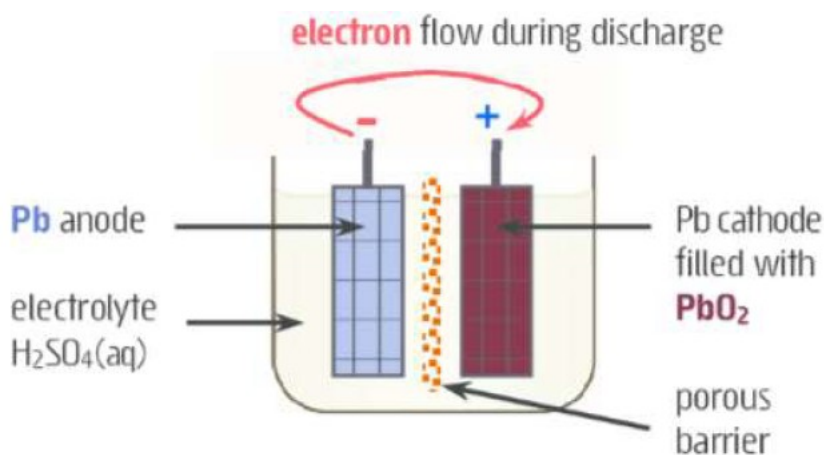
The overall cell reactions for a dry cell are:

Anode half-reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

Cathode half-reaction: $2\text{MnO}_2(\text{s}) + 2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)}$

Overall redox reaction: $2\text{MnO}_2(\text{s}) + 2\text{NH}_4^+(\text{aq}) + \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Mn}_2\text{O}_3(\text{s}) + 2\text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)}$

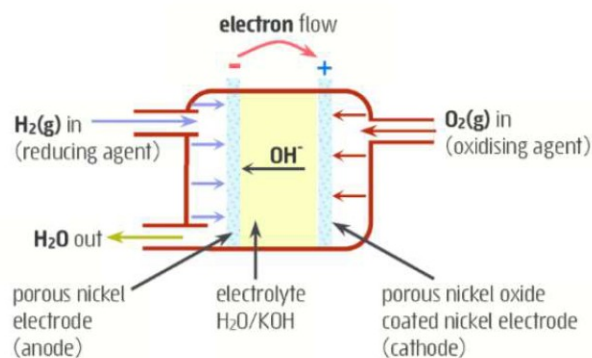
- Secondary Cells
 - o Rechargeable galvanic cells
 - o Lead-acid cell



- Each cell produces 2V and are connected in series
- Used in vehicles, solar power systems and emergency power systems
- Recharging lead acid battery is essentially electrolysis, DC current applied in opposite direction to force oxidant and reductant to reform
- Two lead grid electrodes immersed in sulfuric acid
 - Anode grid has spongy lead (Pb)
 - Cathode has powdered lead oxide (PbO_2)

- Discharge:
 - Pb oxidised to PbSO₄ in presence of H₂SO₄
 - PbO₂ solid reduced in presence of H₂SO₄
 - Recharge:
 - Other direction (anode becomes positive, cathode becomes negative)
 - Current is applied such that Voltage > 2V to ensure completion of reaction
 - Net Voltage > 0V
 - Reverse discharge reaction
 - Advantages
 - High surge current => cells maintain high power to weight ratio
 - Powdered lead components => greater surface area and reaction rate
 - Low cost
 - Can undergo many discharge/recharge cycles over many years
 - Flat => force DC current in opposite direction for spontaneous reaction and recharge
- o Lithium Ion Cell
 - Advantages
 - High energy density
 - Long shelf life
 - Many discharge/recharge cycles
 - Disadvantages
 - High cost
 - Used in technology
- Fuel Cell
 - o Galvanic cell where oxidant and reductant are continuously fed into cell and waste is expelled
 - Reductant is a type of fuel (H₂, CH₄ etc)
 - Oxidant usually O₂
 - Very long lifespan as long and operates without limit as long as reactants are continuously fed into the cell
 - Alkaline hydrogen-oxygen fuel cell
 - Used by space shuttles for energy and drinking water
 - o Advantages
 - High efficiency ~ 70%
 - No greenhouse emissions
 - o Disadvantages
 - Expensive and difficult to source H₂
 - H₂ very flammable

Figure 14 A simplified view of an **alkaline H_2/O_2 fuel cell**. The reducing agent, H_2 , diffuses into the porous Ni electrode and is oxidised forming H^+ ions and free electrons. These electrons are conducted by the Ni electrode out of the cell to the cathode. Oxygen absorbed into the cathode then gains electrons forming OH^- ions. The resulting H^+ ions and OH^- ions migrate through the electrolyte to combine and form water, the only chemical product. This cell operates at $\approx 150\text{--}200^\circ\text{C}$ with an efficiency of around 70%.



Mistakes

- Always flip E^0 value when reverse reaction
- Electrochemical cell \Rightarrow Anode is -ve, cathode positive, electrolytic \Rightarrow anode +ve, cathode -ve
- ALWAYS LOOK FOR H_2O IN ELECTROLYTIC CELLS
- **REFER TO SPONTANEITY**
- **ENSURE RHS PROPERTIES = LHS PROPERTIES IN CHEMICAL EQUATION**
- **ANOX \Rightarrow ANODE OXIDISED**
- Include equations in explaining answers where possible
- Concentration effect \Rightarrow Redox potentials are only reliable for 1M concentrations
- DON'T ignore anion
- Use word \Rightarrow DISPROPORTIONATE
- SOLID ISN'T NECESSARILY FORMED IN GALVANIC CELL (at cathode) \Rightarrow ion formed can be aqueous \Rightarrow therefore, solid doesn't necessarily gain mass
- Ions already within salt bridge move \Rightarrow use KNO_3 for salt bridge salt
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