Redox Processes

Ms. Peace

Lesson 1

9.1 Oxidation and Reduction

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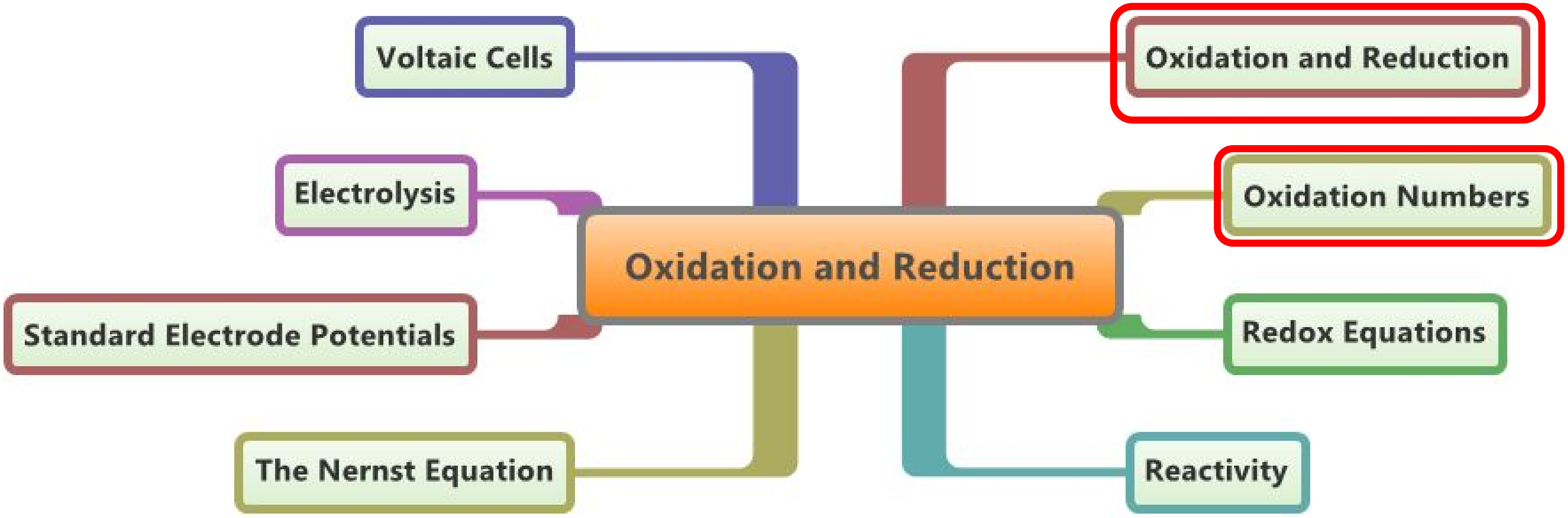

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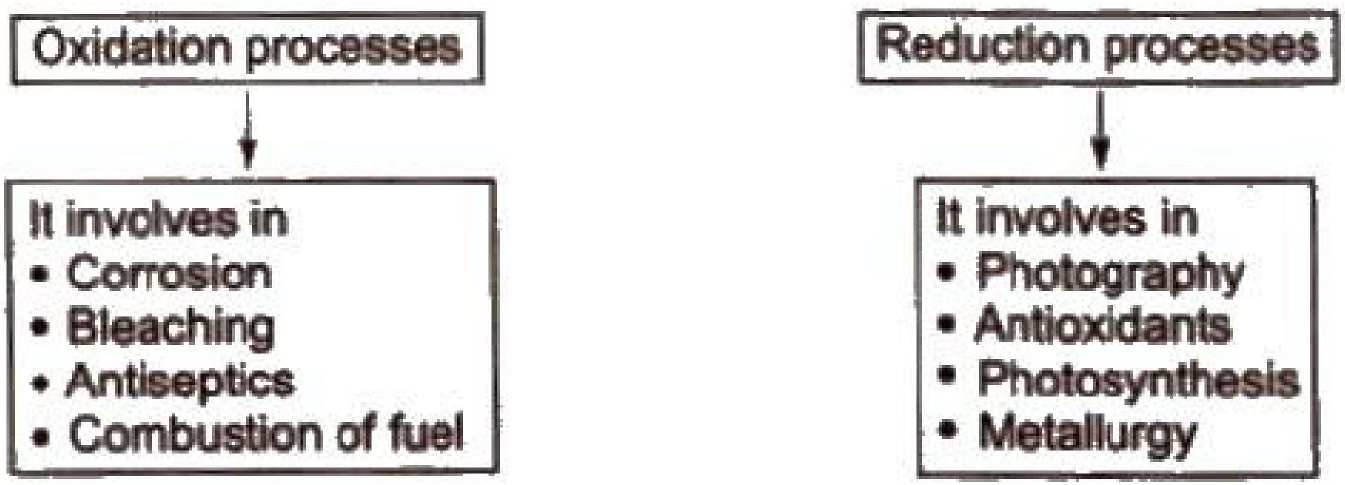
Redox Reactions

- Redox processes can be considered in terms of
  - Specific elements-oxygen and hydrogen
  - Electron transfer
  - Oxidation numbers



Oxidation processes

It involves in
- Corrosion
- Bleaching
- Antiseptics
- Combustion of fuel

Reduction processes

It involves in
- Photography
- Antioxidants
- Photosynthesis
- Metallurgy

Main

Oxidation: Addition of Oxygen or Loss of Hydrogen

- Simplest level of oxidation: a reaction in which a substance combines with oxygen
- Most common: combustion reactions

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$$

$$4Fe(s) + 3O_2 \rightarrow 2Fe_2O_3(s)$$

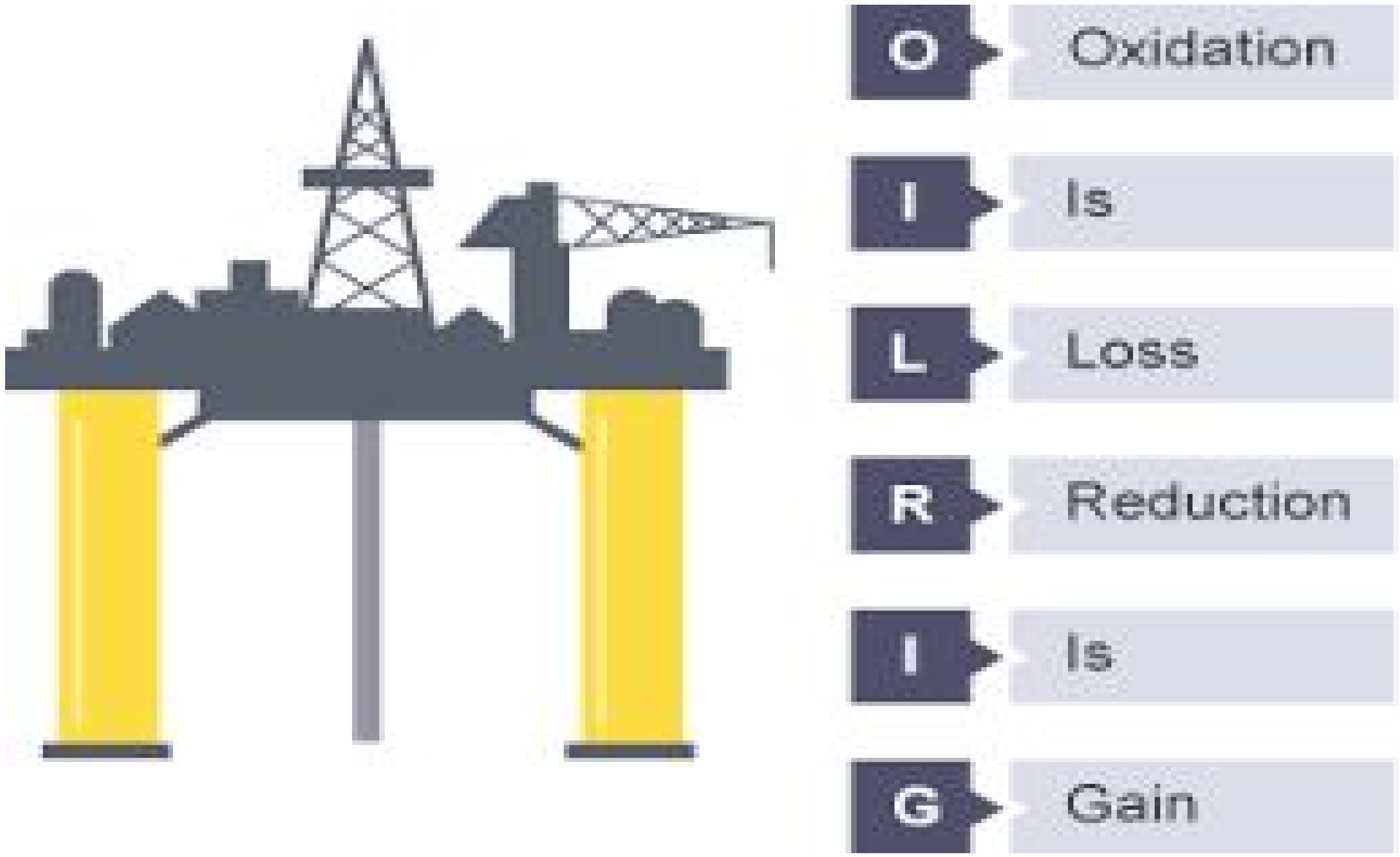
Fe_2O is rust; rusting is an example of oxidation

Reduction: Removal of Oxygen or Addition of Hydrogen

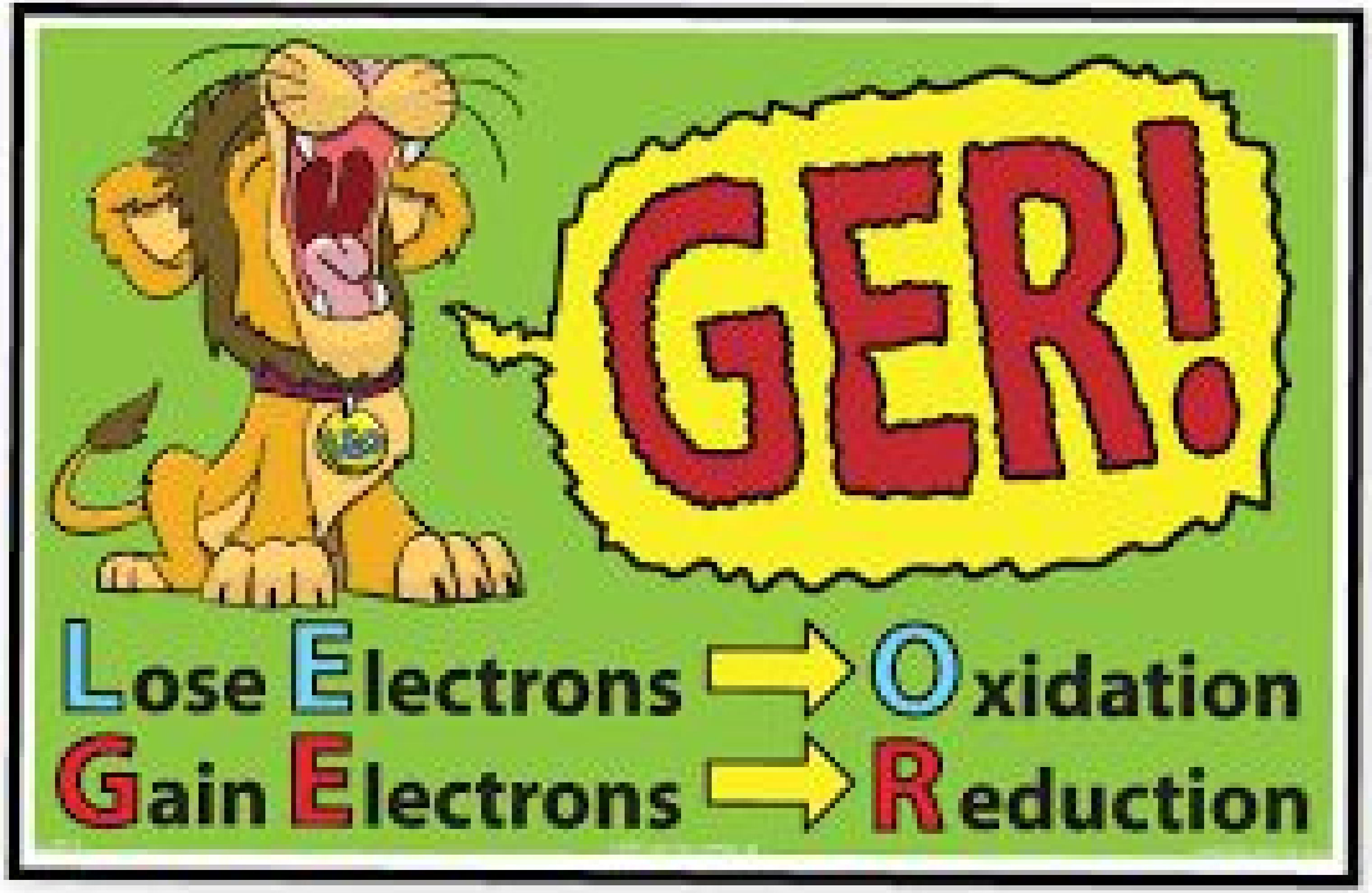
- Removal of oxygen:
  - $NiO(s) + C(s) \longrightarrow Ni(s) + CO(g)$

- Addition of hydrogen:
  - $WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(l)$

Electron Transfer



Electron Transfer

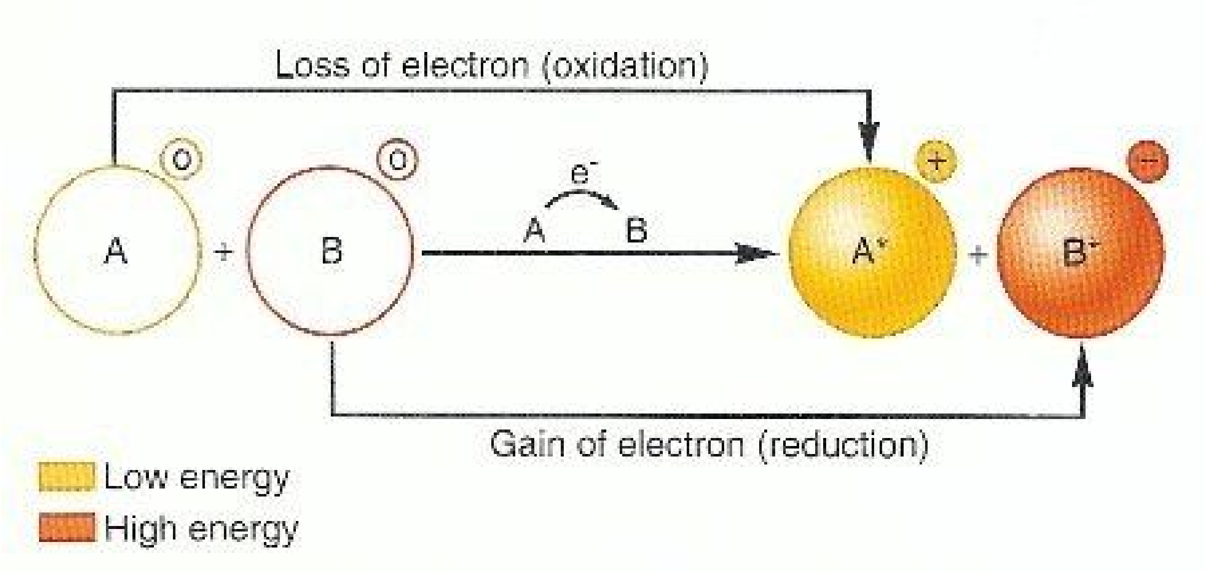


Electron Transfer

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

- $2Mg \rightarrow 2Mg^{2+} + 4e^-$
- $O_2 + 4e^- \rightarrow 2O^{2-}$

- Magnesium is oxidized because it loses electrons
- Oxygen is reduced because it gains electrons



Main

Electron Transfer

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

- Carbon dioxide is molecular, with covalent bonds, so no ionic bonds are formed

- We cannot describe this combustion reaction as a redox process in terms of electron transfer as in the theory of electrons are lost or gained and carbon dioxide is a neutral species

- The original definition is more appropriate here

Main

Oxidation States

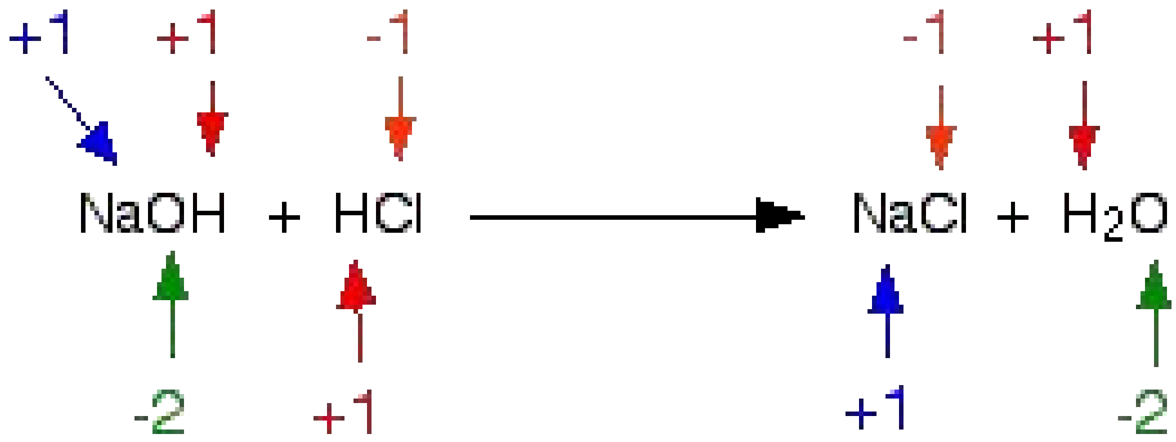
- The oxidation state is the apparent charge of an atom in a free element, molecule, or ion
- Oxidation describes a process in which the oxidation state increases
- Reduction describes a process in which the oxidation state decreases
- Oxidation numbers regard all compounds as ionic and assigns charges to the components accordingly.
- Provides a guide to the distribution of electrons and relative charges on atoms in covalent compounds and allows us to understand redox processes

Main

Rule Number	Rule	Example
1	The oxidation state of an atom in a free element is zero, 0	S_8, O_2, P_4, Na
2	Group 1 metals always have a +1 oxidation state in their ions and compounds. Group 2 elements always have a +2 oxidation state in their ions and compounds. Aluminum has an oxidation state of +3 in the majority of its compounds	NaCl CaF_2 (+1) (+2)
3	The oxidation state of hydrogen is +1 when hydrogen is bonded to a non-metal. When hydrogen is bonded to a metal, the oxidation state is -1	HCl KH (+1) (-1)
4	The oxidation state of oxygen is usually -2,. The main exception is peroxide, -O-O- , where the oxidation state of oxygen is -1	H_2O H_2O_2 (-2) (-1)
5	The oxidation of fluorine is -1 in all its compounds. For the other group 17 halogens the oxidation state is usually -1 except in combination with oxoanions and oxoacids the oxidation state is +7	HCl $HClO_4$ (-1) (+7)
6	In neutral molecules the sum of the oxidation states of all the atoms is zero. In a polyatomic ion, the sum of the oxidation states of all the atoms equals the overall charge of the ion	NH_3 (-3) + (3 x +1) = 0 NH_4^+ (-3) + (4 x +1) = +1

Oxidation States

- Oxidation states should be represented with sign given before the number
  - +2, not 2+
- The more electronegative atom in an ion assumes a negative oxidation state, the less electronegative one a positive oxidation state



For example

- Determine the oxidation states of each atom in the following:
  - CO_2
    - O, -2 -2 except with F or a peroxide
    - C, +4 to balance out the 2 lots of '-2'
  - H_2SO_4
    - O, -2 -2 except with F or peroxide
    - H, +1 +1 except in metal hydrides
    - S, +6 +6 since four lots of '-2' and two of '-1' sum to -6
  - BaO_2 (barium peroxide)
    - Ba, +2 +2 since Gp II metal
    - O, -1 -1 since peroxide
  - CO_3^{2-}
    - O, -2 -2 except with F or peroxide
    - C, +4 +4 since 3 x -2 and +4 sums to the charge, -2

Main

Determine oxidation states for each atom in:

- H_2O
- S_8
- CH_4
- H_3PO_4
- CCl_4
- $HClO$
- $KMnO_4$
- IO_3^-
- $Cr_2O_7^{2-}$
- $Cr(H_2O)_6^{3+}$

Main

Oxidation States and Names

- Stock Nomenclature uses oxidation states to name compounds
- Oxidation state of transition metals is given in Roman numerals
  - $KMnO_4$ is named potassium manganate (VII)
- ‘ate’ means an element is in a positive oxidation state
  - Usually because it is bonded with oxygen
- ‘ide’ means an element is in a negative oxidation state

Main

Oxidation States of Transition Metals

- $FeCl_2$ – iron (II) chloride
  - Iron (II) means Fe in the +2 ox. State
  - Chloride means the chlorine is in a negative oxidation state

- $FeCl_3$ – iron (III) chloride
  - Iron (III) mean Fe in the +3 ox. State

- $KClO_3$ – potassium chlorate
  - Chlorate tells you the chlorine is in a positive oxidation state

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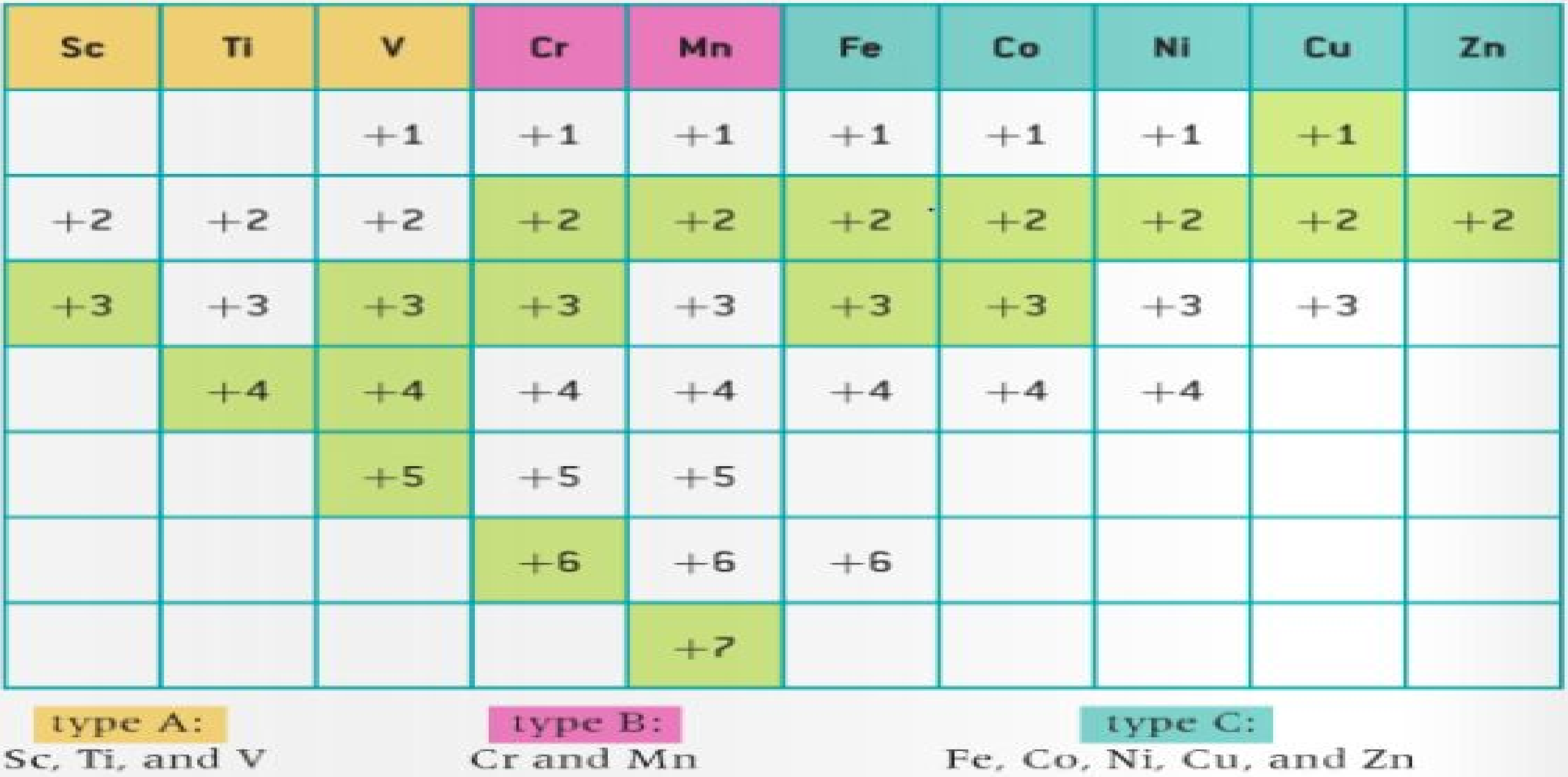
Oxidation States of Transition Metals



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
		+1	+1	+1	+1	+1	+1	+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

type A:
Sc, Ti, and V

type B:
Cr and Mn

type C:
Fe, Co, Ni, Cu, and Zn

▲ Figure 4 Oxidation states of the first-row d-block metals. The most stable oxidation states are marked in green

Name the following:

- MnO_2
- CuO
- Cu_2O
- $KMnO_4$
- $K_2Cr_2O_7$

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Lesson 2

9.1 Oxidation and Reduction

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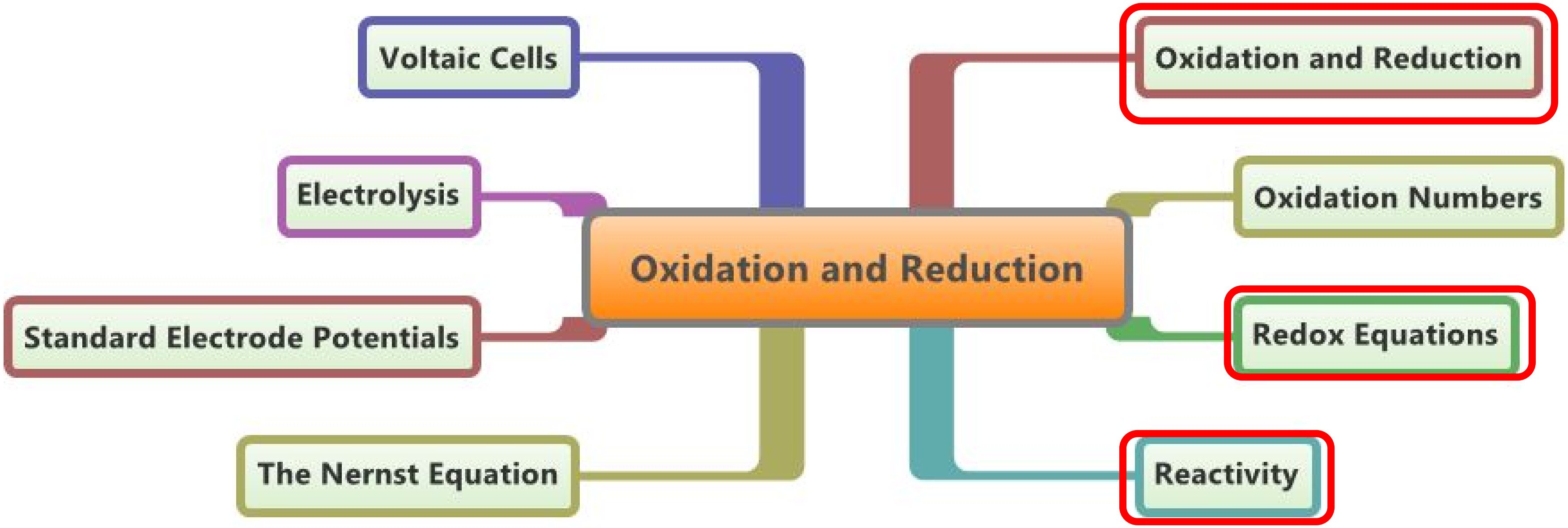

Main

Redox Reactions

- Whenever an oxidation occurs, a reduction also occurs, hence REDOX

- For example:

$$\underset{0}{Zn(s)} + \underset{+2}{Cu^{2+}(aq)} \rightarrow \underset{0}{Cu(s)} + \underset{+2}{Zn^{2+}(aq)}$$

  - Zinc is oxidized – it loses two electrons
    - Zinc is the **reducing agent** because it reduces copper

  - Copper is reduced – it gains two electrons
    - Cu^{2+} is the **oxidising agent** because it oxidises the zinc

- The number of electrons gained by species is always equal to the number of electrons lost by species.

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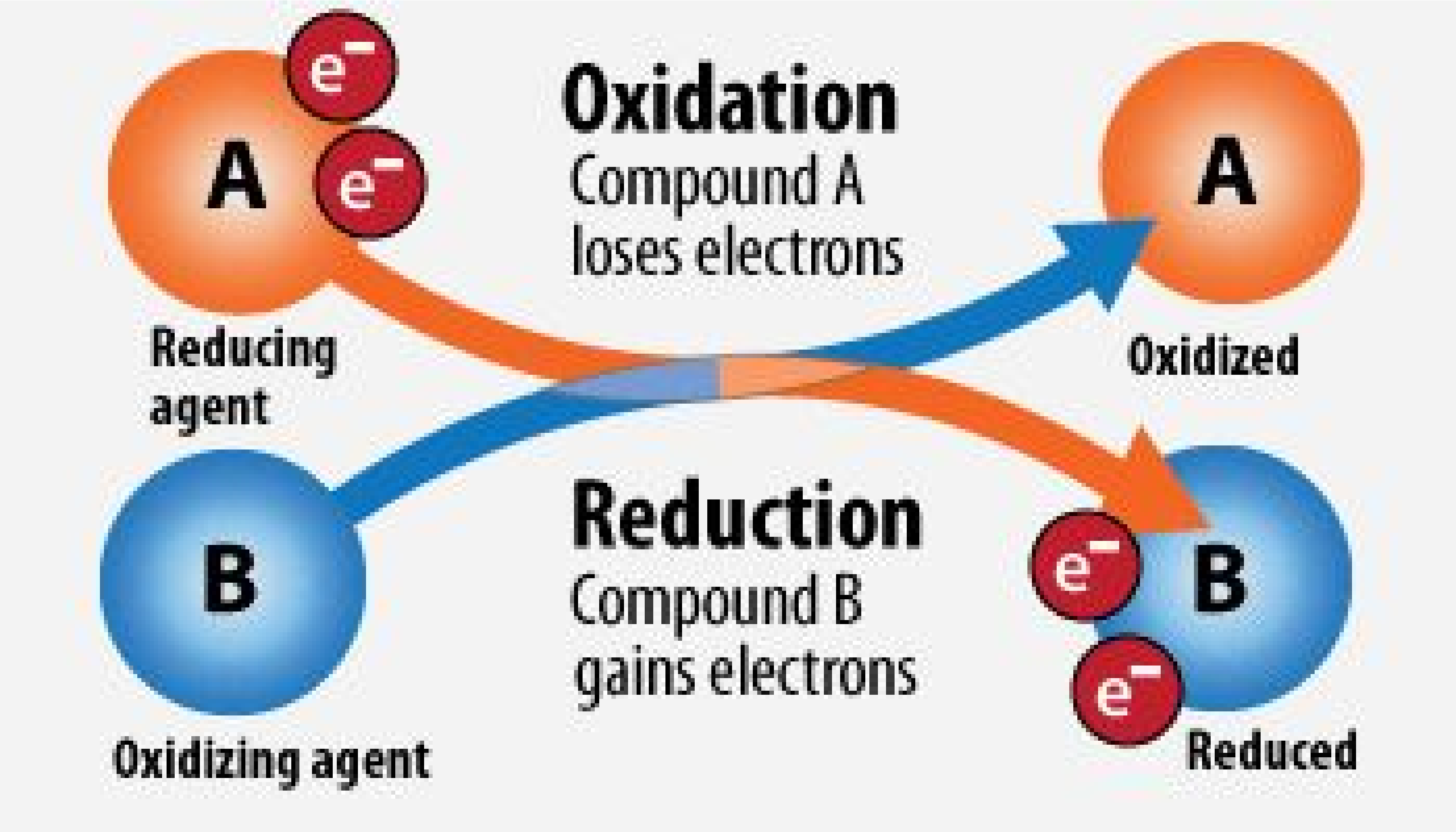
Oxidizing vs Reducing Agent



Half-Equations

- Half equations show the changes to individual species in a redox reaction.
- $Fe_2O_3 + 2\ Al \rightarrow 2\ Fe + Al_2O_3$
  - $Fe^{3+} + 3\ e^- \rightarrow Fe$ ....this is the reduction
  - $Al \rightarrow Al^{3+} + 3\ e-$ ....this is the oxidation
- A wide variety of half equations can be found in the data booklet

Half-Equations

- Step 1: Assign oxidation states for each atom in the reactants and products
- Step 2: Deduce which species is being oxidized and which species is being reduced
- Step 3: State the half-equation for the oxidation process and the corresponding half-equation for the reduction process

Main

Half-Equations

- Step 4: Balance the half-equations so that the number of electrons lost equals the number of electrons gained
- Step 5: Add the two half-equations together to write the overall redox reaction
- Step 6: Check the total charge on the reactant and product sides
- Step 7: Balance the charge and H and O by adding H^+ and H_2O to the appropriate sides

Main

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

- Step 1: Assign oxidation states for each atom in the reactants and products
  - Fe^{2+}: +2
  - Mn: +7
  - O: -2
  - Fe^{3+}: +3
  - Mn^{2+}: +2

- Step 2: Deduce which species is being oxidized and which species is being reduced
  - Fe^{2+} is being oxidized from +2 to +3
  - Mn is being reduced from +7 to +2

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

- Step 3: State the half-equation for the oxidation process and the corresponding half-equation for the reduction process
  - Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
  - Reduction: $MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq)$

- Step 4: Balance the half-equations so that the number of electrons lost equals the number of electrons gained
  - Oxidation: $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$
  - Reduction: $MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq)$

Main

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

- Step 5: Add the two half-equations together to write the overall redox reaction
  - Oxidation: $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$
  - Reduction: $MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq)$
  - $5Fe^{2+}(aq) + MnO_4^-(aq) \cancel{+ 5e^-} \rightarrow 5Fe^{3+}(aq) \cancel{+ 5e^-} + Mn^{2+}(aq)$
  - Overall: $5Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq)$

- Step 6: Check the total charge on the reactant and product sides
  - Total charge on reactant side: 9+
  - Total charge on product side: 17+

Main

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

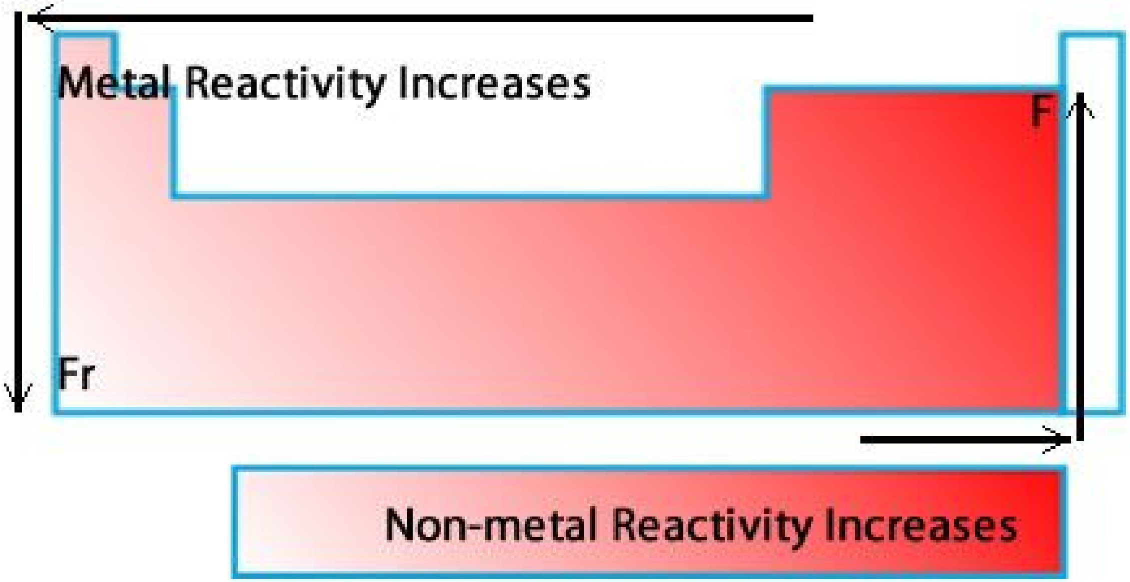
- Step 7: Balance the charge by adding H^+ and H_2O to the appropriate sides
  - $5Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq)$
  - To balance, $8H^+$ must be added on the reactant side
  - $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+ \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq)$
  - Balance the hydrogens by adding water on whichever side of the equation it is needed.
  - $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+ \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

- The oxidizing agent is $MnO_4^-(aq)$ and the reducing agent is $Fe^{2+}(aq)$

Main

Redox and Reactivity

- Redox behavior is closely linked to reactivity
- The most reactive metals are the best reducing agents
- The most reactive non-metals are the best oxidizing agents



The Activity Series

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

- Zinc is above copper in the series, therefore it is more reactive and can displace Cu^{2+} ions

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

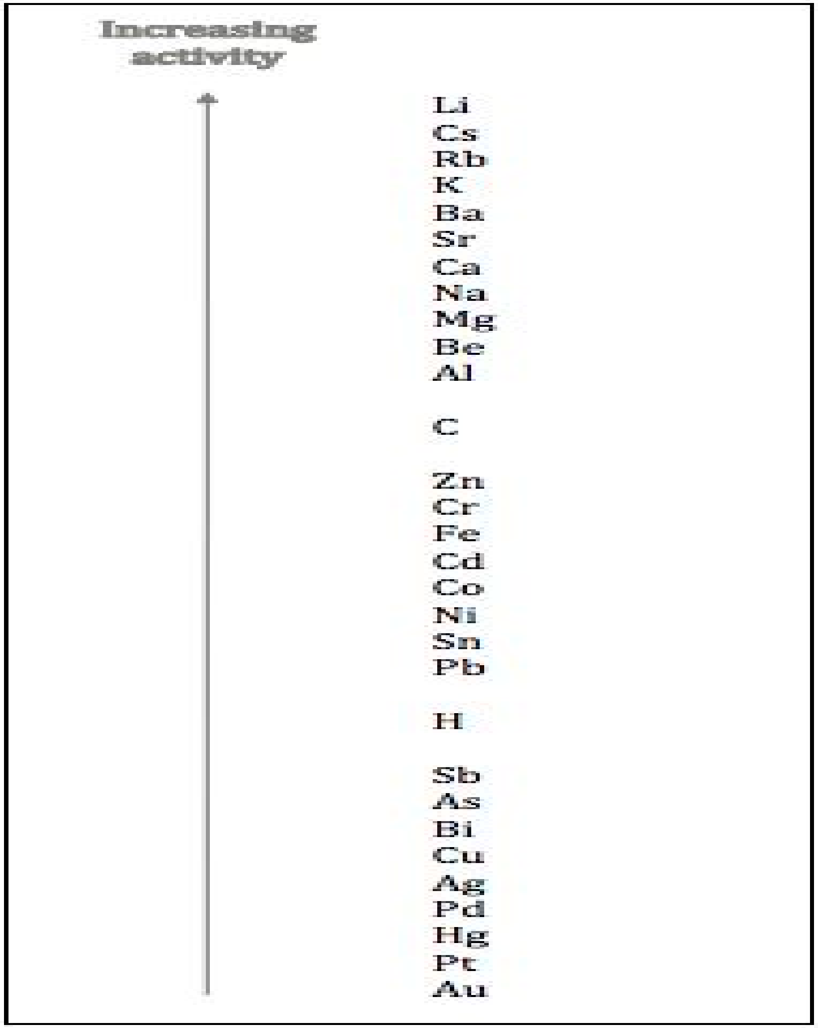
- Zinc is above hydrogen in the series so it can displace hydrogen ions in hydrochloric acid to form hydrogen gas

$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(l) + Al_2O_3(s)$

- Aluminum is above iron, forming molten iron

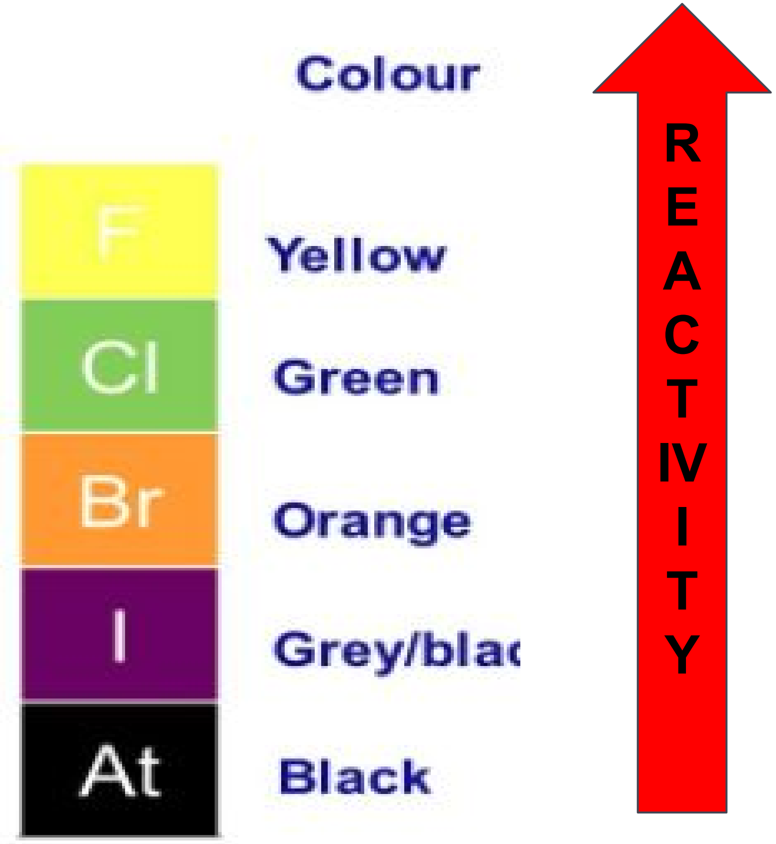
$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

- Hydrogen is displaced from water by sodium



Redox and Reactivity

- $2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$
- The more reactive element is found higher in the series and will displace the other
- Cl changes from 0 to -1 indicative of a reduction process
- Br changes from -1 to 0 indicative of an oxidation process



	Colour
F	Yellow
Cl	Green
Br	Orange
I	Grey/blac
At	Black

Main

Complete the following equations by writing in the products formed or "no rxn"

Ex 1: $Zn + PbCl_2$

Ex 2: $Zn + BaO$

Ex 3: $Ca + CrF_2$

Ex 4: $Mn + NiS$

Ex 5: $Fe + MgI_2$

Ex 6: $Co + PbCl_2$

Lesson 3

9.1 Oxidation and Reduction

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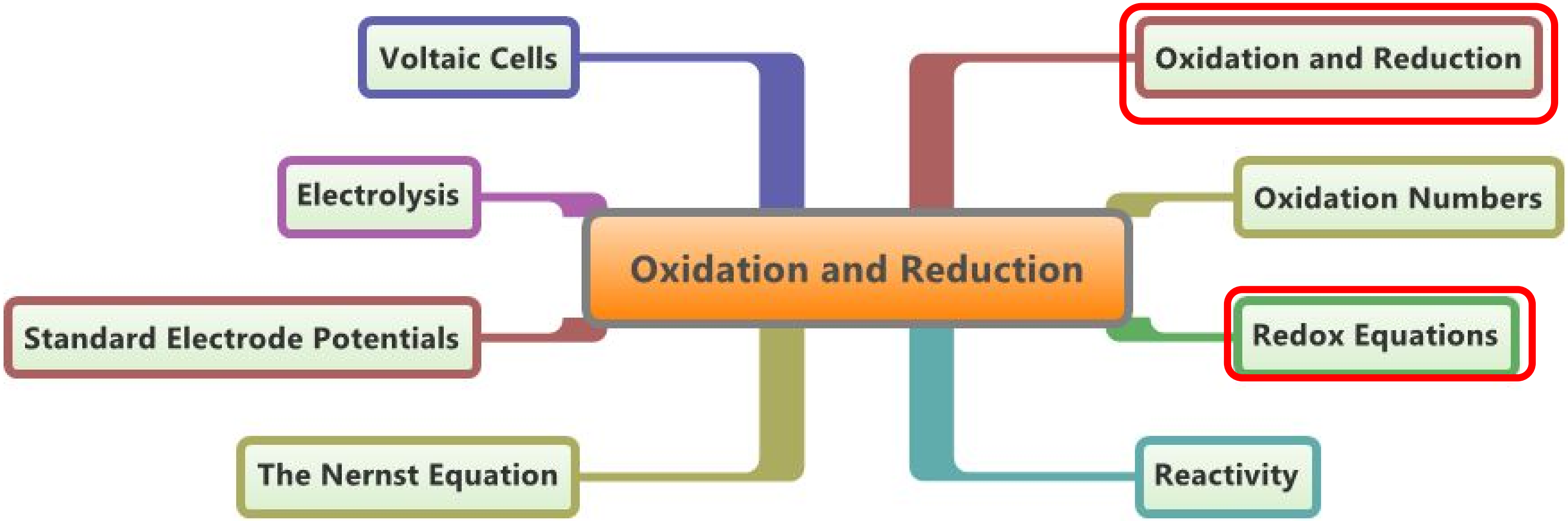
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Redox Titration Reactions

- Step 1: Deduce the balanced redox equation, using oxidation states

- Step 2: From the information given, state which three pieces of data are given and identify the fourth variable that needs to be determined. Identify the coefficients from the balanced equation.

Main

Redox Titration Reactions

- Step 3: Set up the following expression and fill in the known data
  - $1/\mathcal{V}_A (V_A \times C_A) = 1/\mathcal{V}_B (V_B \times C_B)$
  - V_A = volume of reactant A in dm^3
  - C_A = concentration of reactant A in mol dm^{-3}
  - V_B = volume of reactant B in dm^3
  - C_B = concentration of reactant B in mol dm^{-3}
  - $\mathcal{V}_A$ and $\mathcal{V}_B$ are the stoichiometric coefficients

- Step 4: Solve for the unknown variable

- Step 5: Change units if necessary

Main

Example

- Consider the following balanced equation for the reaction of potassium manganate (VII) with ammonium iron sulfate

$5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

In a titration to determine the concentration of a potassium manganate (VII) solution, $28.0cm^3$ of the potassium manganate (VII) solution reacted completely with $25.0cm^3$ of a 0.0100 mol dm^{-3} solution of ammonium iron (II) sulfate. Determine the concentration in g dm^{-3}, of the potassium manganate (VII) solution.

Main

Example

- Step 1: Deduce the balanced redox equation, using oxidation states
  - $5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$ given from question

Example

- Step 2: From the information given, state which three pieces of data are given and identify the fourth variable that needs to be determined. Identify the coefficients from the balanced equation.
  - A represents Fe^{2+} and B represents MnO_4
  - V_A = volume of Fe^{2+} = 0.0250dm^3
  - C_A = concentration of Fe^{2+} = 0.0100 mol dm^{-3}
  - V_B = volume of MnO_4^- = 0.0280dm^3
  - C_B = concentration of MnO_4^- = **must be calculated**
  - $\mathcal{V}_A = 5$
  - $\mathcal{V}_B = 1$

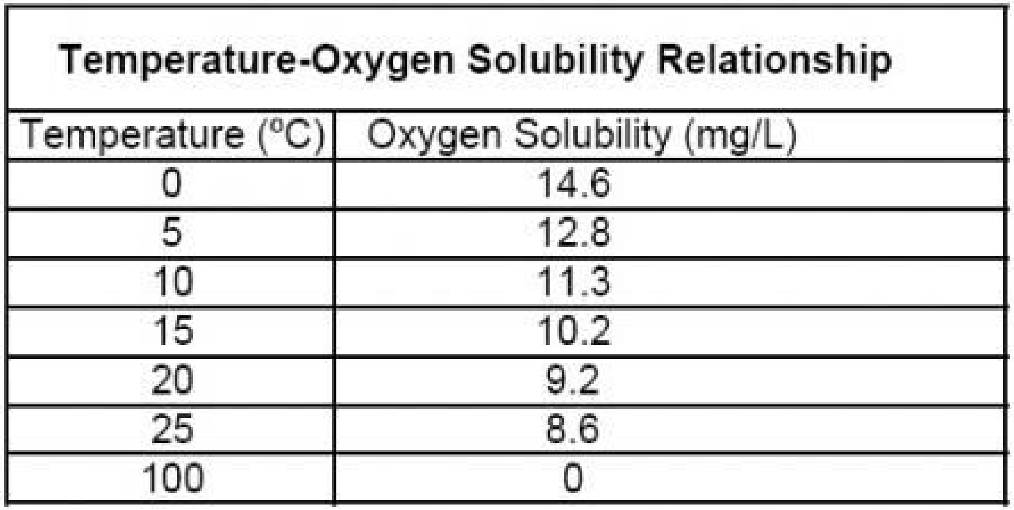
Example

- Step 3: Set up the following expression and fill in the known data
  - $(1/5)\ (0.0250 \times 0.0100) = (1/1)\ (0.0280 \times C_{B,})$
- Step 4: Solve for the unknown variable
  - $C_{B,} = 0.00179\ \text{mol dm}^{-3}$
- Step 5: Change units if necessary
  - $$\frac{0.00179\ \text{mol}}{1\ \text{dm}^3} \times \frac{158.04\text{g KMnO}_4}{1\ \text{mol}} = 0.283\ \text{g dm}^{-3}$$

Main

The Winkler Method

- Aquatic life depends on gases such as carbon dioxide and oxygen dissolved in the water to survive.
- Oxygen, O_2, is a non-polar molecule, but water, H_2O, is polar
- The solubility of oxygen in water will be very low
- The solubility of oxygen in water is temperature dependent.



Temperature-Oxygen Solubility Relationship

Temperature (°C)	Oxygen Solubility (mg/L)
0	14.6
5	12.8
10	11.3
15	10.2
20	9.2
25	8.6
100	0

Main

The Winkler Method

- As the temperature increases, the solubility of the gas decreases
- The Winkler method is based on redox reactions is one technique that can be used to measure the amount of dissolved oxygen in water
- A high concentration of dissolved oxygen indicates a low level of pollution

Main

The Winkler Method

- The degree of organic pollution in a sample of water can be measured by the biochemical oxygen demand, BOD.
- BOD: the amount of oxygen required to oxidize organic matter in a sample of water at a definite temperature over a period of 5 days.
- BOD is measured in ppm

$$\text{ppm} = \frac{\text{grams of solute}}{\text{grams of solution}} \times 10^{6}$$

Main

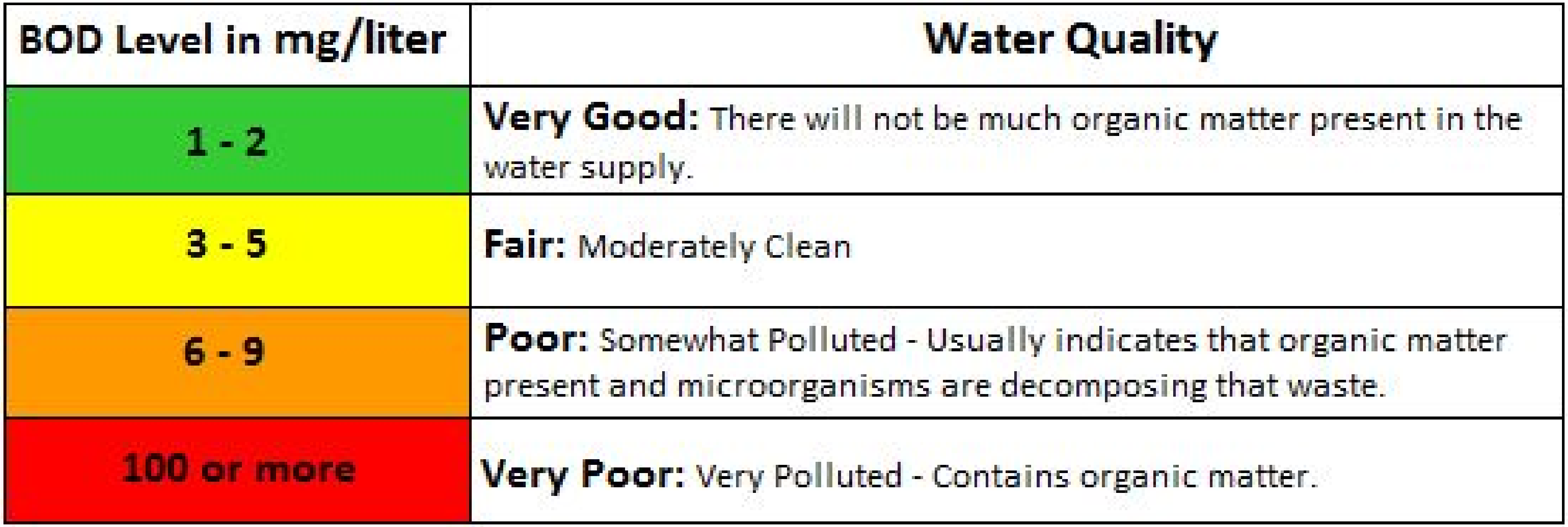
The Winkler Method

- ppm is often used as the standard unit of concentration to indicate the maximum allowable upper limit of a potentially toxic or carcinogenic substance
- The World Health Organization, WHO, states the maximum allowed concentration of lead (II) cation, $Pb^{2+}(aq)$, in drinking water is 0.001mg dm^{-3} or 0.001ppm

World Health Organization

Main

The Winkler Method



BOD Level in mg/liter	Water Quality
1 - 2	**Very Good:** There will not be much organic matter present in the water supply.
3 - 5	**Fair:** Moderately Clean
6 - 9	**Poor:** Somewhat Polluted - Usually indicates that organic matter present and microorganisms are decomposing that waste.
100 or more	**Very Poor:** Very Polluted - Contains organic matter.

The Winkler Method

A 50.0cm^3 sample of water was taken from a location where treated effluent is discharged into a marina in Dubai, UAE, was first saturated with oxygen and then left for a period of 5 days at 293K in the dark. The Winkler method was carried out to measure the dissolved oxygen content in the water sample before and after the 5-day incubation period.

Main

The Winkler Method

The following is the series of reactions related to the method:

$$Mn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mn(OH)_2(s)$$

$$2Mn(OH)_2(s) + O_2(g) \rightarrow 2MNO(OH)_2(s)$$

$$MnO(OH)_2(s) + 4H^{+}(aq) + 2I^{-}(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 3H_2O(l)$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

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The Winkler Method

It was found that 5.25cm^3 of a 0.00500 mol dm^{-3} solution of sodium thiosulfate, $Na_2S_2O_3(aq)$ was required to react with the iodine produced

a. Determine the concentration of dissolved oxygen, in ppm, in the sample of water
b. Deduce the BOD, in ppm, of the water sample, assuming that the maximum solubility of oxygen in the water is 9.0ppm at 293K
c. Comment on the BOD value obtained

Main

The Winkler Method

- Step 1: Deduce the balanced redox equation, using oxidation states
  - 1 mol $O_2(g)$ → 2 mol $MnO(OH)_2(s)$ → 4 mol $S_2O_3^{2-}(aq)$

The Winkler Method

- Step 2: From the information given, state which three pieces of data are given and identify the fourth variable that needs to be determined. Identify the coefficients from the balanced equation
- A represents $S_2O_3^{2-}$ and B represents O_2
- V_A = volume of $S_2O_3^{2-}$ = 0.00525dm^3
- C_A = concentration of $S_2O_3^{2-}$ = 0.00500mol dm^{-3}
- V_B = volume of O_2 = 0.0500dm^3
- C_B = concentration of O_2= **must be calculated**
- $\mathcal{V}_A = 4$
- $\mathcal{V}_B = 1$

Main

The Winkler Method

- Step 3: Set up the following expression and fill in the known data
  - $(1/4)\ (0.00525 \times 0.00500) = (1/1)\ (0.0500 \times C_{B,})$
- Step 4: Solve for the unknown variable
  - $C_{B,} = 1.31 \times 10^{-4}$ mol dm^{-3}
- Step 5: Change units if necessary
  - $$\frac{1.31 \times 10^{-4}\ \text{mol}}{1\ \text{dm}^3} \times \frac{32\text{g}\ O_2}{1\ \text{mol}} = 4.19 \times 10^{-3}\ \text{g dm}^{-3}$$
    $$= 4.19\ \text{mg dm}^{-3} = 4.19\text{ppm}$$

The Winkler Method

- This BOD value shows reasonable water quality for the sample taken at the effluent discharge point in Dubai, suggesting that an effective sewage treatment plan must be in place

- Typically untreated domestic sewage has a BOD in the range of 100-400 ppm

Main

Lesson 4

9.2 Electrochemical Cells

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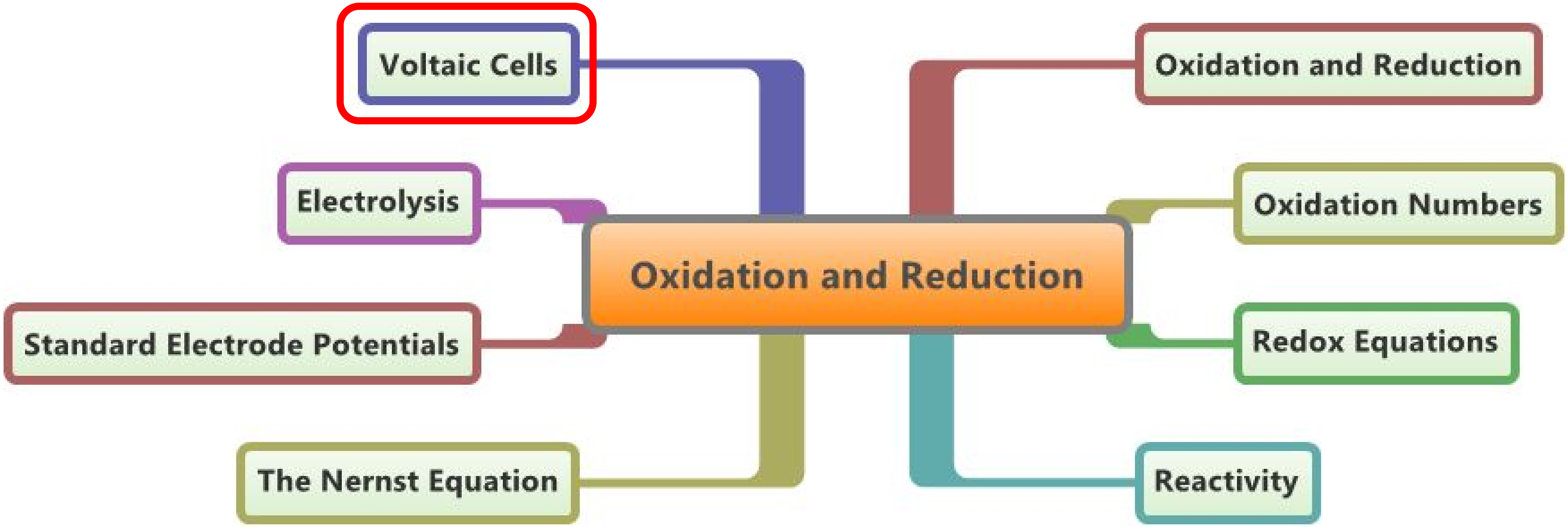

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Electrochemical Cells

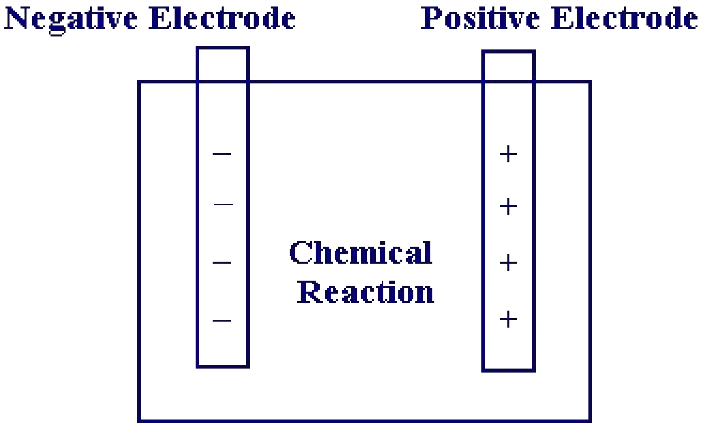
- In an electrochemical cell chemical energy-electrical energy conversions take place, which can go either direction.
  - Voltaic Cells (or galvanic cells) - these convert chemical energy to electrical energy.
    - Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy

  - Electrolytic cells - these convert electrical energy to chemical energy, bringing about a non-spontaneous process

Main

Electrodes

- Electrodes are carries of electric charge in metals
- Electrode - conductor of electricity used to make contact with a non-metallic part of a circuit, such as the solution in the cell (electrolyte)
- An electrochemical cell contains two electrodes:
  - Anode: Oxidation always takes place
  - Cathode: Reduction always takes place



Main

Electrodes

- In a voltaic cell:
  - The cathode is the positive electrode
    - The mass of the anode increases because it is gaining electrons
  - The anode is the negative electrode
    - The mass of the anode decreases because it is losing electrons
  - The metal that is higher in the activity series is oxidized and the metal lower in the activity series is reduced

- In an electrolytic cell:
  - The cathode is the negative electrode
  - The anode is the positive electrode

Main

Voltaic Cell

- A voltaic cell consists of two half-cells

- Oxidation occurs at the anode and reduction occurs at the cathode

- Types of electrodes used in voltaic cells:
  - **Metal/metal electrodes- metal ions in two different oxidation states**
  - Gas ion electrode

Key Parts of a Voltaic Cell

- Anode
  - Electrode or ‘half-cell’ where oxidation happens
  - Contains the more reactive metal
  - The negative electrode: produces electrons
- Cathode
  - Electrode or ‘half-cell’ where reduction happens
  - Contains the less reactive metal
  - The positive electrode: accepts electrons
- Salt Bridge
  - Contains a neutral salt such as potassium nitrate
  - Made of a tube of jelly or a filter paper soaked in salt solution
  - Ions diffuse in and out to balance charge and complete circuit
- Voltmeter
  - Measures the difference in potential between half-cells
  - Could be replaced with other circuitry to do useful work

REMEMBER

- **AnOx**
  - **An**ode-**Ox**idation
- **CaRe**
  - **Ca**thode-**Re**duction

Metal/Metal Ion Electrode

- A metal/metal ion electrode consists of a bar of metal dipped into a solution containing cations of the same metal
- Examples:
  - $Fe(s) \mid Fe^{2+}(aq)$
  - $Zn(s) \mid Zn^{2+}(aq)$
  - $Cu(s) \mid Cu^{2+}(aq)$
- The vertical line represents a phase boundary or junction
- In a voltaic cell the two half-cells are separated-if the solutions were allowed to mix in a single container, a spontaneous reaction would occur but there would be no movement of electrons through the circuit

Main

Metal/Metal Ion Electrode

- The two electrodes are in electrical contact via a liquid junction called a salt bridge
- Functions of a salt bridge
    - Allows physical separation of the cathode and anode, preventing mixing of the two solutions
    - Provides electrical continuity - a path for the migration of the positive ions and the negative ions in the cell
    - Reduces the liquid-junction potential - voltage generated when two different solutions come in contact with each other, which occurs due to unequal cation and anion migration across the junction

Main

Salt Bridge

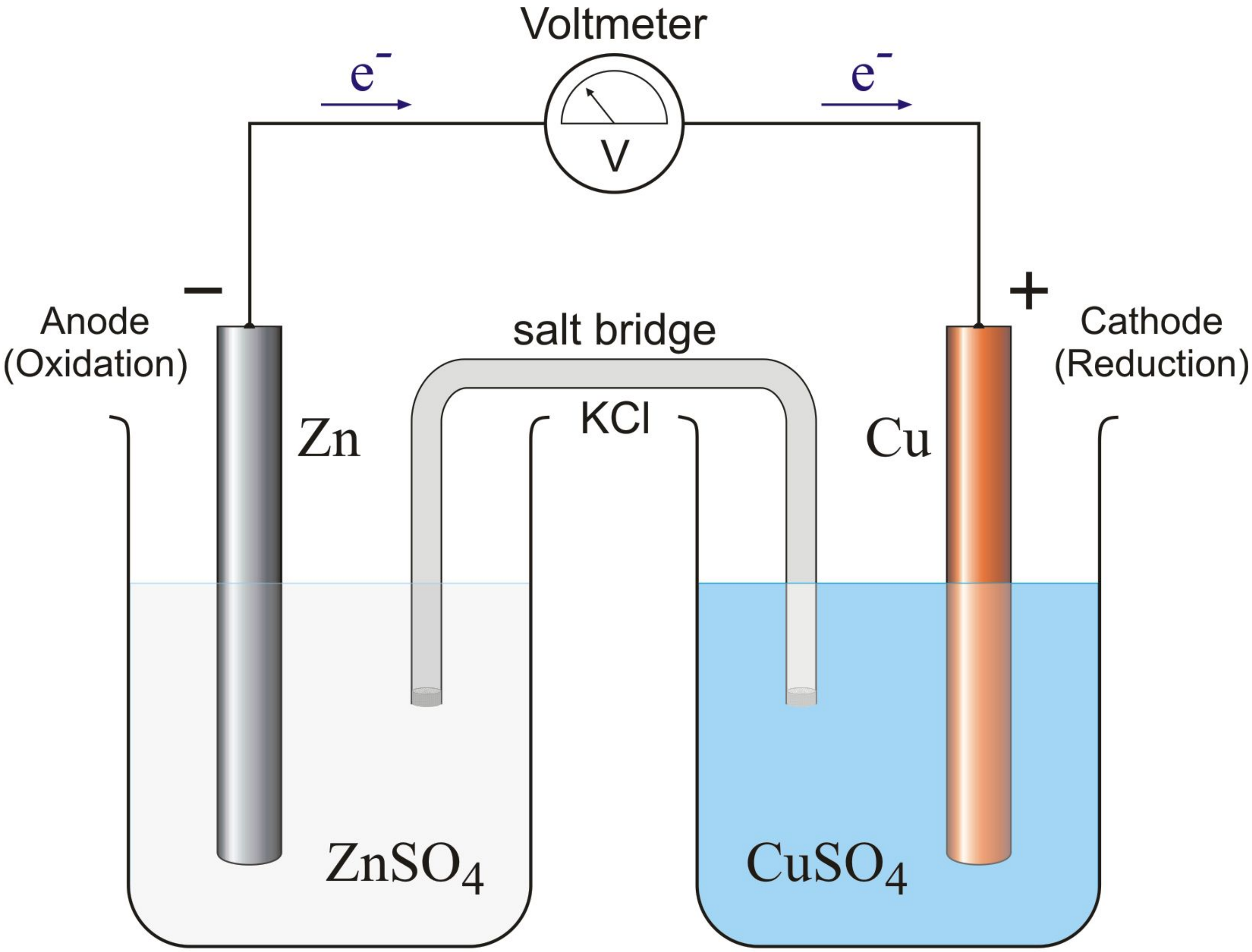
- Completes the circuit and keeps the half-cells electrically neutral
- Typical compounds used in the salt bridge
  - $Na_2SO_4(aq)$
  - KCl
  - NaCl
  - KNO_3
- The ions used for the salt bridge must be inert - they should not react with the other ions in the solution
- Cations migrate towards the cathode and anions migrate towards the anode

Main

Example

- Anode (negative electrode) : oxidation
  - $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- Cathode (positive electrode) : reduction
  - $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- Overall reaction:
  - $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

Main



$Zn(s) + 2e^- \longrightarrow Zn^{2+}$ $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$

Voltaic Cells

- When drawing voltaic cells, the cathode is drawn on the right hand side

- Electrons flow from negative electrode (anode) to positive electrode (cathode)

- You determine which metal is being oxidized and which metal is being reduced by using the activity series, Table 24 in the Data Booklet

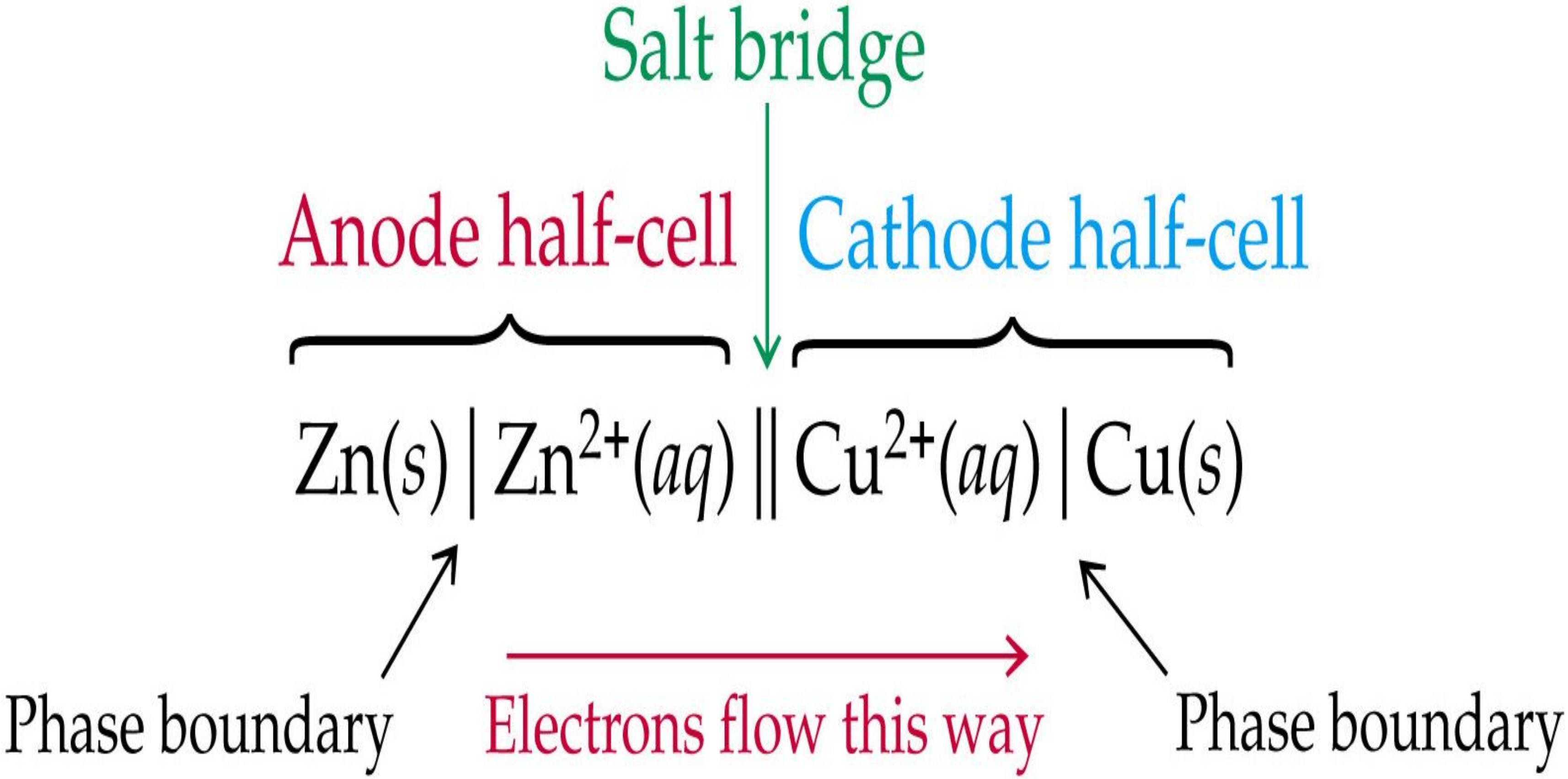
Main

Cell Diagrams

- Cell diagrams are used as a convenient shorthand to represent a voltaic cell
- By convention the anode is always written on the left and the cathode on the right
- The salt bridge is represented by two parallel vertical lines

Main

Cell Diagram Convention



Salt bridge

Anode half-cell

Cathode half-cell

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq)\,||\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s)$$

Phase boundary

Electrons flow this way

Phase boundary

Main

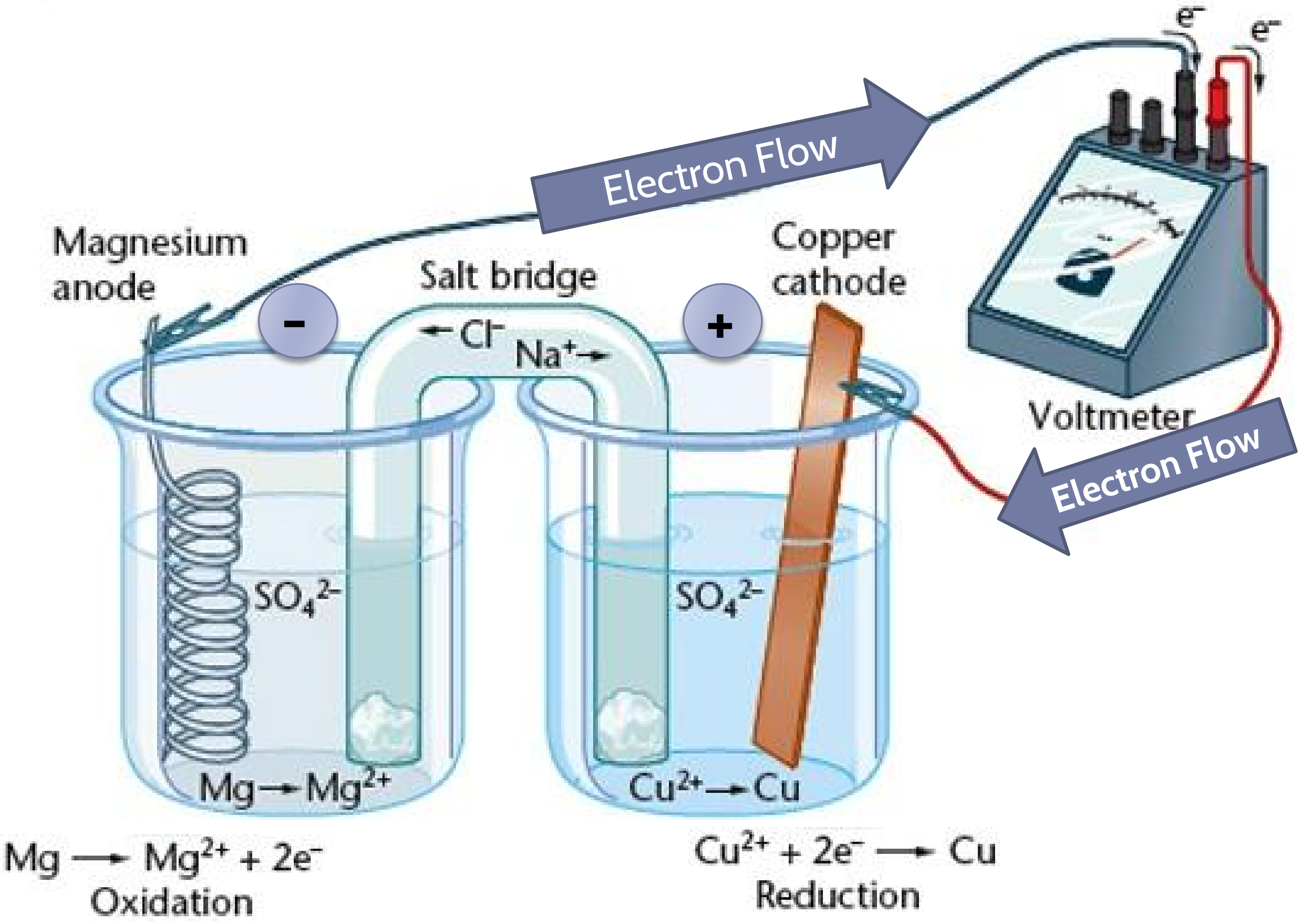
Drawing a cell

- Draw and fully label a magnesium/copper cell in a sulfate solution. Include:
  - Labels for cathode and anode
  - Labels for positive and negative
  - Each half-equation
  - Arrow showing direction of electron flow
  - NaCl salt bridge
  - Cell diagram

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

Main

Voltaic Cells



Main

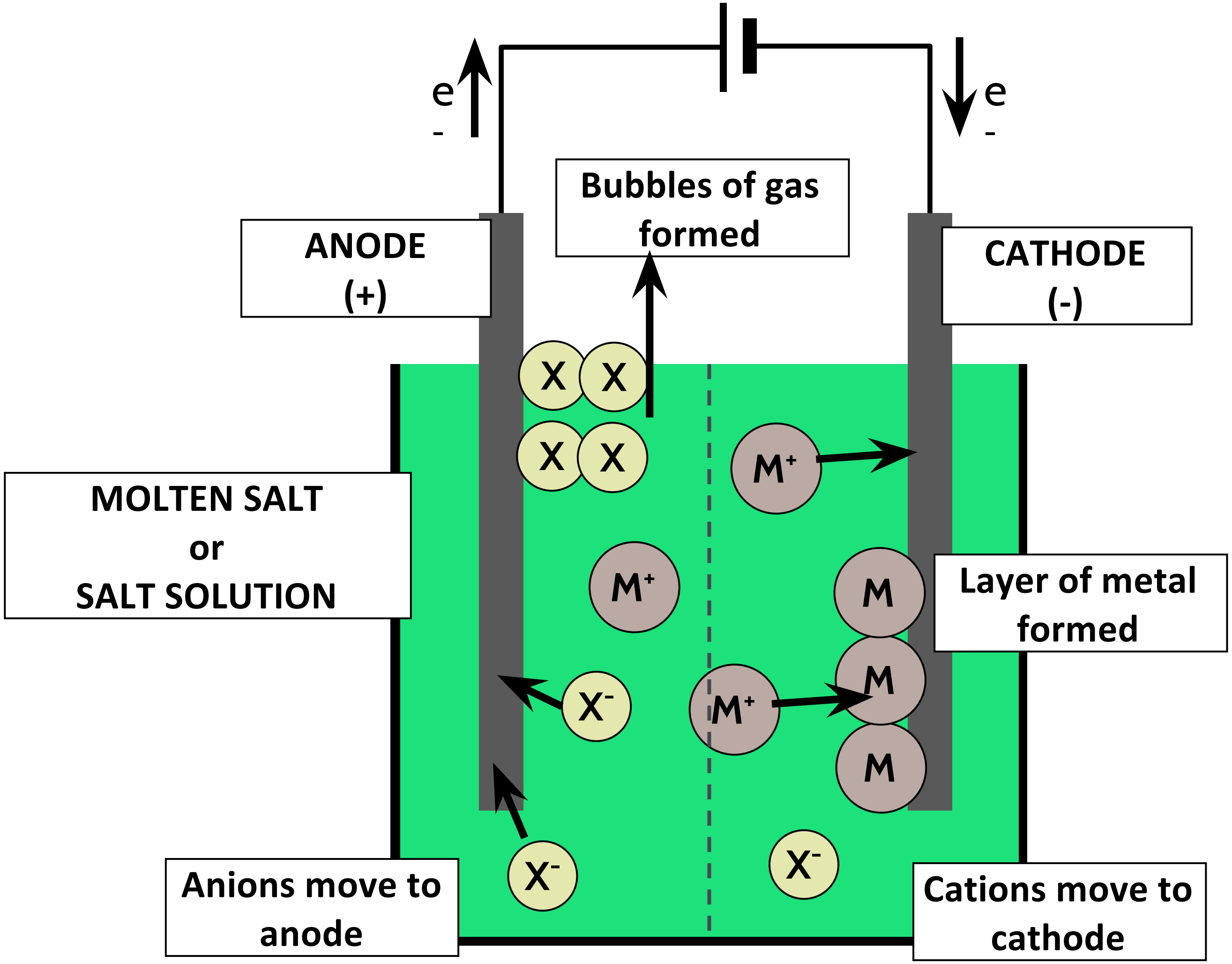
Electrolytic Cells

- Electrolysis is the process by which electrical energy is used to drive a non-spontaneous chemical reaction; utilize electrolytic cells
- Electrolytic cells consist of a single container, two electrodes, a solution, and a battery which can be considered an electron pump
- There are many types of electrolytic cells but you will only be assessed on the electrolysis of a molten salt (electrolyte)
  - Molten salt - ionic compound that is heated until it melts
  - When a compound is molten, the ions are free to move around

Electrolytic Cells

- Electrolysis is the breaking down of a substance by the passage of electricity through it
- Current is carried by moving ions
  - Cations (+) move to the cathode (negative electrode)
  - Anions (-) move to the anode (positive electrode)
- Electrons move in the wire
- Ions move in the electrolyte
- The negative cathode reduces positive metal ions
- The positive anode oxidises negative non-metal ions

An Electrolytic Cell:



ANODE
(+)

Bubbles of gas formed

CATHODE
(-)

MOLTEN SALT
or
SALT SOLUTION

Layer of metal formed

Anions move to anode

Cations move to cathode

Main

Products of Electrolysis

- Assuming a molten simple metal salt involving only monatomic ions
  - **Cathode – metal**
    - Deposited on the surface of the electrode
  - **Anode – non-metal**
    - Typically as bubbles of gas

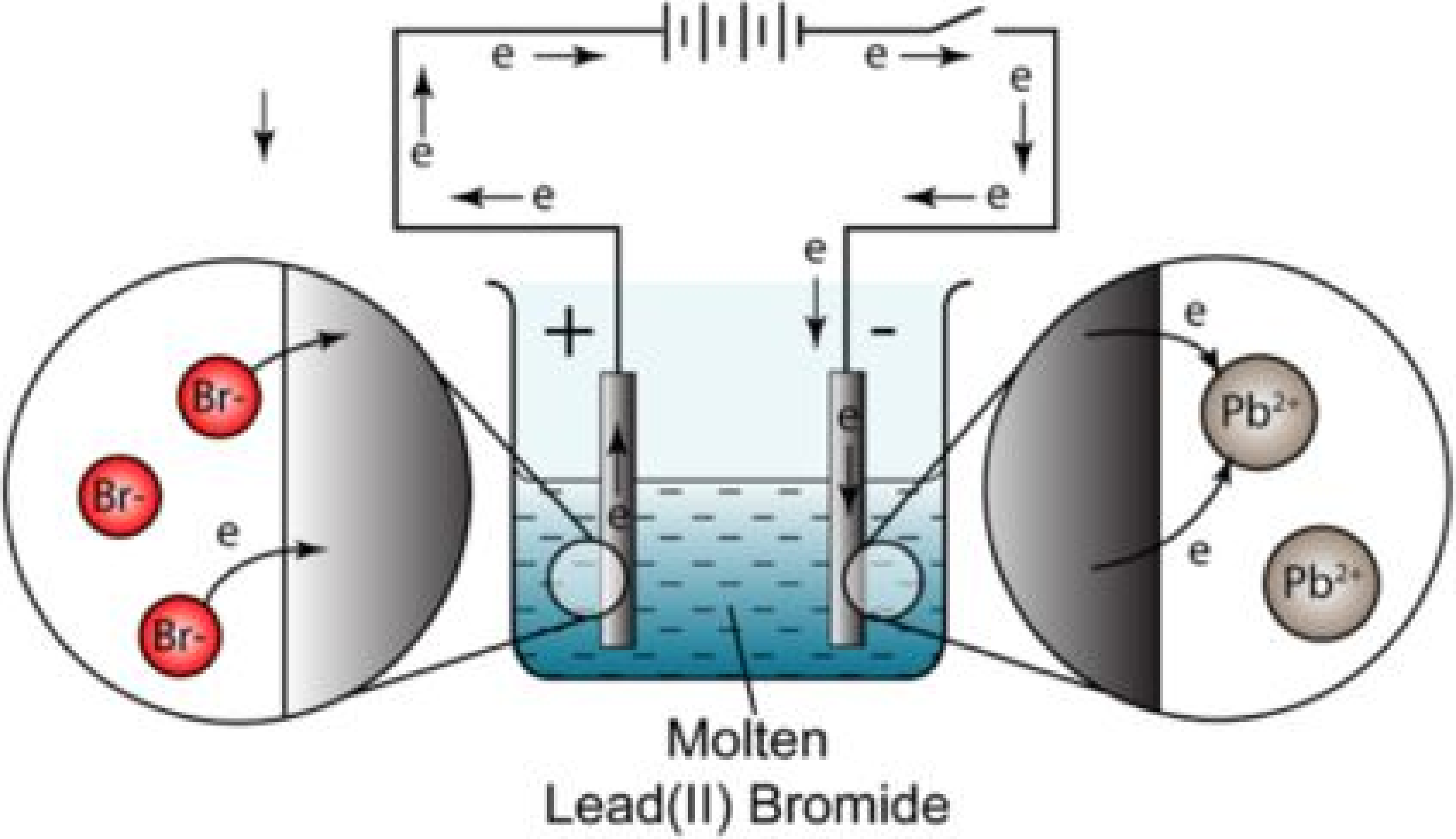
- For example, electrolysis of molten magnesium bromide:
  - **Cathode:** a layer of magnesium metal ($Mg^{2+} + 2e^- \rightarrow Mg$)
  - **Anode:** bubbles of bromine gas ($2Br^- \rightarrow Br_2 + 2e^-$)

- At the anode oxidation occurs

- At the cathode reduction occurs

Electrolysis of Molten Salt

- In the electrolysis of molten lead (II) bromide, $PbBr_2(l)$, inert graphite electrodes are dipped into the $PbBr_2(l)$ electrolyte
- The following half-equations show the processes that take place at the electrodes:
  - Anode (positive electrode) : oxidation
    - $2Br^- \rightarrow Br_2(g) + 2e^-$
  - Cathode (negative electrode) : reduction
    - $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$
  - Overall cell reaction:
    - $PbBr_2(l) \rightarrow Pb(l) + Br_2(g)$


e
e
e
e
e
e
e
+
-
Br-
Br-
Br-
e
e
e
Pb2+
Pb2+
Molten
Lead(II) Bromide

Steps for Electrolysis of a Molten Salt

- **Step 1:** Identify all species present
- **Step 2:** Identify which species are attracted to the cathode (negative electrode) and which species are attracted to the anode (positive electrode)
- **Step 3:** Deduce the half-equations taking place at the cathode and anode and the overall cell reaction
- **Step 4:** Draw and annotate the electrolytic cell and show the direction of the movement of electrons and the direction of ion flow
- **Step 5:** State what would be observed at each electrode

Main

Describe the electrolysis of molten sodium chloride

- **Step 1:** Identify all species present
  - $NaCl \rightarrow Na^+ + Cl^-$
  - $Na^+(l)$ and $Cl^-(l)$ ions are present

- **Step 2:** Identify which species are attracted to the cathode (negative electrode) and which species are attracted to the anode (positive electrode)
  - Cathode (negative electrode): Na^+
  - Anode (positive electrode): Cl^-

Main

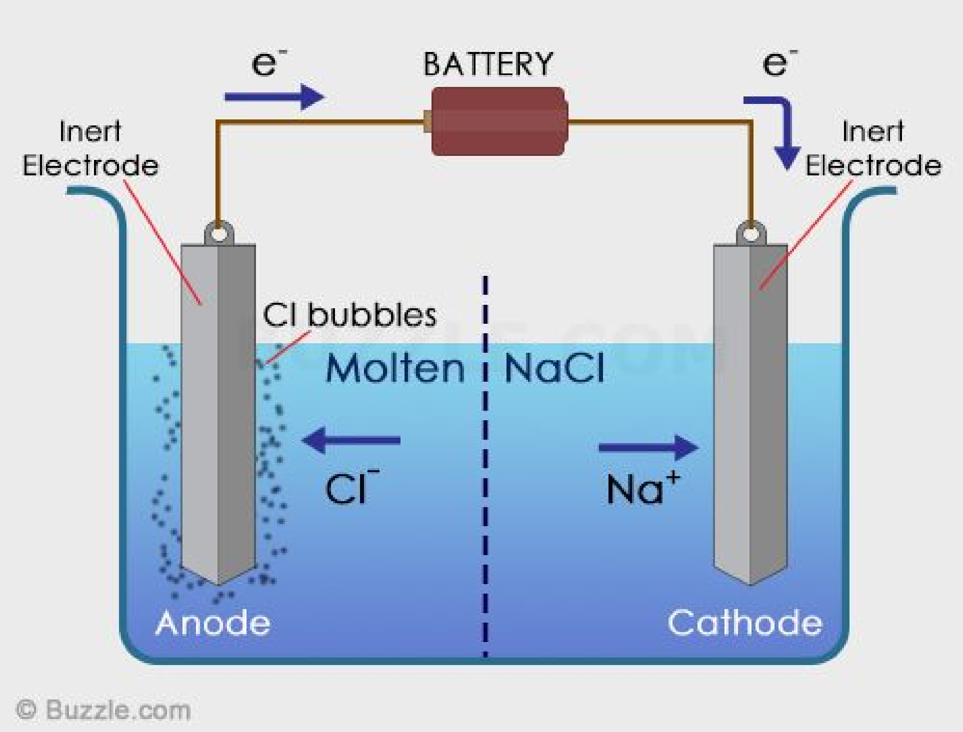
Describe the electrolysis of molten sodium chloride

- **Step 3:** Deduce the half-equations taking place at the cathode and anode and the overall cell reaction
  - Anode (positive electrode) : oxidation
    - $2Cl^- \rightarrow Cl_2(g) + 2e^-$
  - Cathode (negative electrode) : reduction
    - $Na(l)^+ + e^- \rightarrow Na(l)$
    - This needs to be multiplied by 2 to balance the number of electrons from the anode equation: $2Na(l)^+ + 2e^- \rightarrow 2Na(l)$
  - Overall reaction
    - $2Cl^- + 2Na(l)^+ \rightarrow 2Na(l) + Cl_2(g)$

Main

Describe the electrolysis of molten sodium chloride

- **Step 4:** Draw and annotate the electrolytic cell and show the direction of the movement of electrons and the direction of ion flow



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Main

Describe the electrolysis of molten sodium chloride

- **Step 5:** State what would be observed at each electrode
  - At the anode (positive electrode) : bubbles of chlorine gas are observed
  - At the cathode (negative electrode) : a pool of liquid sodium forms

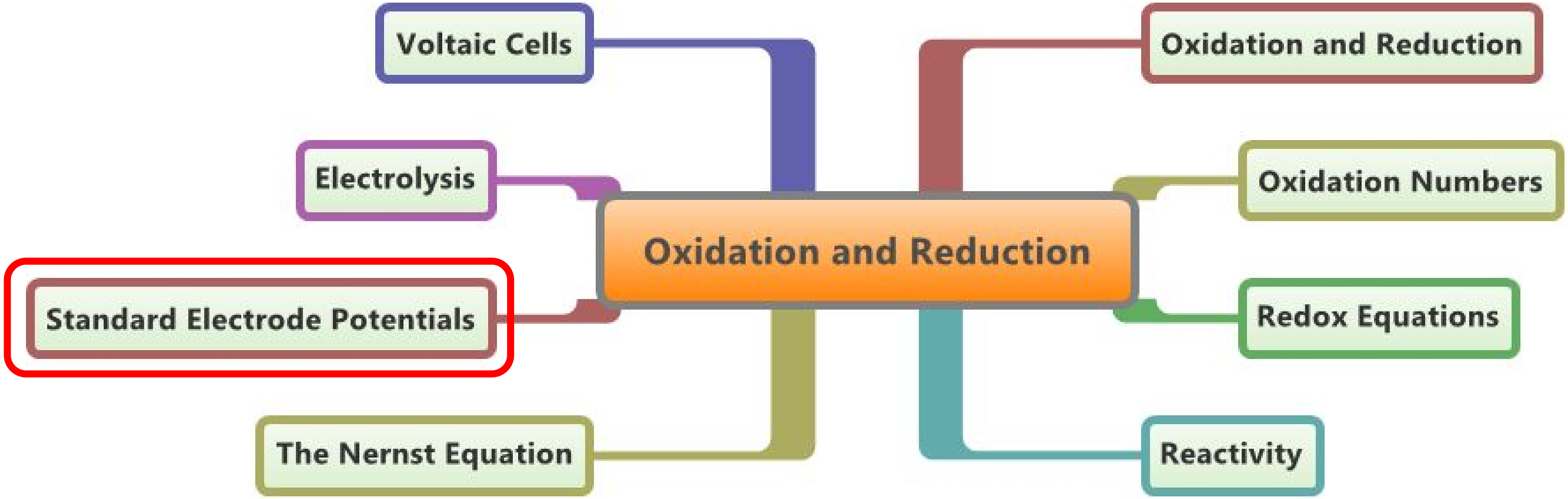
Voltaic Cell	**Electrolytic Cell**
A spontaneous reaction produces an electric current	An electric current drives a non-spontaneous reaction
Current is conducted by electron flow in wires and movement of ions in salt bridge	Current is conducted by electron flow in wires and movement of ions in electrolyte
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Chemical energy is converted to electrical energy	Electrical energy is converted to chemical energy
Reaction is exothermic	Reaction is endothermic
Oxidation occurs at the anode and reduction occurs at the cathode **(AN OX and RED CAT)**	Oxidation occurs at the anode and reduction occurs at the cathode **(AN OX and RED CAT)**

Lesson 5

19.1 Electrochemical Cells

Main Menu

We Are Here



Oxidation and Reduction

Voltaic Cells

Electrolysis

Standard Electrode Potentials

The Nernst Equation

Oxidation and Reduction

Oxidation Numbers

Redox Equations

Reactivity

Main

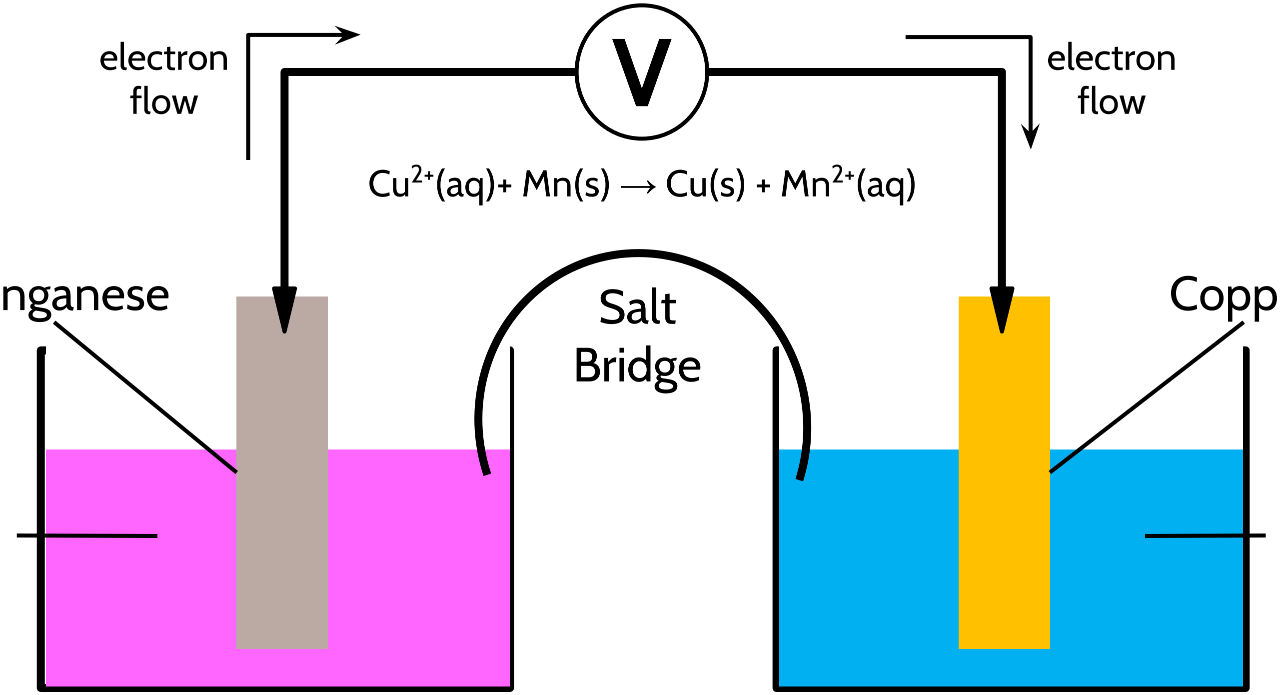
Lesson 7: Standard Electrode Potentials

- Objectives:
  - Describe the standard hydrogen electrode
  - Define the term standard electrode potential
  - Use standard electrode potentials to calculate the potential of a cell
  - Use standard electrode potentials to determine the feasibility of a reaction

Main

Drawing and Labeling a Cell

- **Example:** The manganese-copper cell



electron flow

electron flow

V

$Cu^{2+}(aq) + Mn(s) \rightarrow Cu(s) + Mn^{2+}(aq)$

Manganese

Salt Bridge

Copper

1.00 mol dm^{-3} $Mn^{2+}(aq)$

1.00 mol dm^{-3} $Cu^{2+}(aq)$

ANODE, (-)
oxidation occurs:

$Mn(s) \rightarrow Mn^{2+}(aq) + e^-$

CATHODE, (+)
reduction occurs

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Main

Drawing a cell

- Draw and fully label a zinc/iron cell. Include:
  - Labels for cathode and anode
  - Labels for positive and negative
  - Each half-equation
  - Arrow showing direction of electron flow

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

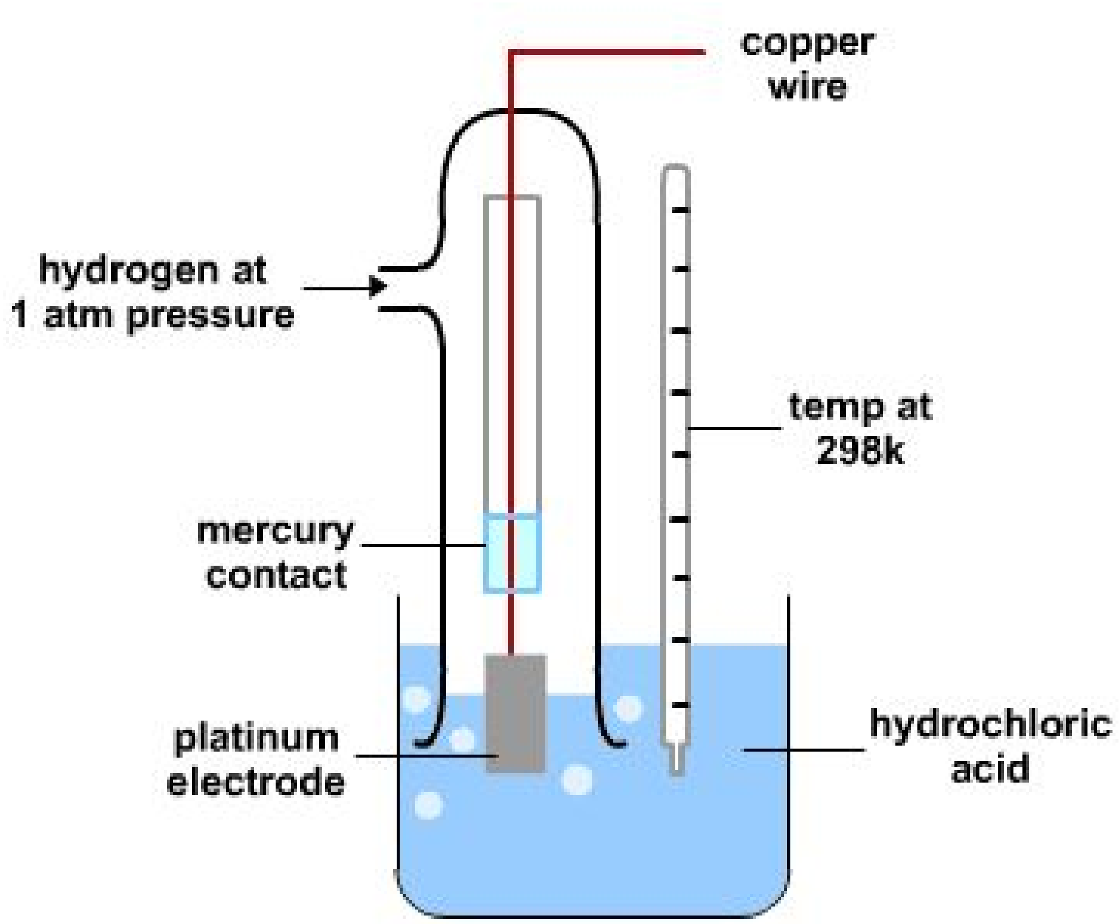
Half-cell potential

- When you set up a half-cell, it has a certain ‘POTENTIAL’.
- When two half-cells are joined, electrons flow away from the half-cell with more negative potential towards the half-cell with more positive potential
- You can think of this a little like enthalpy
  - There is no absolute measure of potential, only relative
  - You can only measure potential differences (voltage) between two half-cells
- The potential of a half-cell is always measured relative to the standard hydrogen electrode.

Main

The Standard Hydrogen Electrode

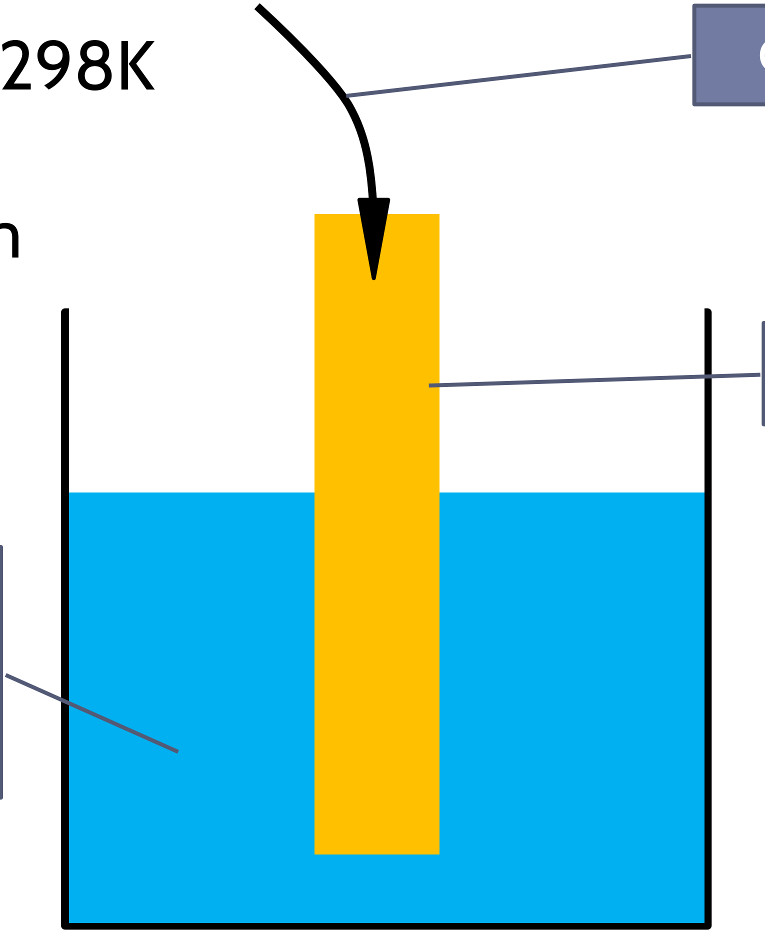
- Standard electrode potential defined as 0.00 V



Main

Standard Electrode

- Temperature = 298K
- Pressure = 1 atm



Connecting wire

Metal Electrode

Aqueous solution of metal ions:

[M$^+$] = 1.0 mol dm^{-3}

Main

Standard Electrode Potential, $E^\ominus$

- This is the potential of a standard electrode relative to the standard hydrogen electrode.
- Always measure the potential of the reduction
- Measured in Volts, V
- Full table in the data booklet

Half Cell	Standard Electrode Potential, $E^\ominus$ / V
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$	0.00
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.19
$Cu^{2+}(aq) + 2e- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2} Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.07

- Look at the table in the data booklet:
  - What trends do you notice?
  - How do the values relate to your ideas of reactivity?
  - How do the values compare to the reactivity series you constructed earlier?

Main

The Potential of a Cell, $E^{\ominus}_{cell}$

- To make a cell, two half-cells are connected by a salt-bridge and a volt-meter
- The potential of a cell is easy to calculate:
  - Subtract the potential of the more negative ½-cell from the potential of the more positive
  - This gives the potential difference:

Half Cell	Standard Electrode Potential, $E^{\ominus}$ / V
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$	0.00
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.19
$Cu^{2+}(aq) + 2e- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2} Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.07

- What is the potential of a Lithium-Manganese cell?
  - Lithium: -3.04 V, Manganese: -1.19V
  - $E^{\ominus}_{cell} = -1.19 - -3.04 = 1.85$ V
- What is the potential of a Manganese-Bromine cell?
  - Manganese: -1.19 V, Bromine: 1.07 V
  - $E^{\ominus}_{cell} = 1.07 - -1.19 = 2.26$ V

Main

Determining the Reaction in a Cell:

- A little more tricky, but still OK
- **The more negative half-cell moves to the left (gets oxidised)**
- **The more positive half-cell moves to the right (gets reduced)**
- Determine the reaction for each half cell and then combine them (making sure they balance)

Main

Determining the Reaction in a Cell: Example 1

Half Cell	**Standard Electrode Potential, E° / V**
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$	0.00
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.19
$Cu^{2+}(aq) + 2e- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2} Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.07

- The Lithium-Manganese cell?
  - Lithium: -3.04 V, Manganese: -1.19V
    - Lithium: $Li(s) \rightarrow Li^+(aq) + e^-$ ....more negative so goes left
    - $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ ...more positive so goes right
  - $2 Li(s) + Mn^{2+}(aq) \rightarrow 2 Li^+(aq) + Mn(s)$

Determining the Reaction in a Cell: Example 2

Half Cell	Standard Electrode Potential, E° / V
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$	0.00
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.19
$Cu^{2+}(aq) + 2e- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2} Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.07

- The Manganese-Copper cell?
  - Copper: +0.34 V, Manganese: -1.19 V
    - Manganese: $Mn(s) \rightarrow Mn^{2+}(aq) + e^-$ ....more negative so goes left
    - Copper: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ ...more positive so goes right
  - $Mn(s) + Cu^{2+}(aq) \rightarrow Mn^{2+}(aq) + Cu(s)$

Predicting The Feasibility of a Reaction

- Will iron (II) react with copper?
  - The only possible reaction between Cu and Fe^{2+} is:

$$Cu(s) + Fe^{2+}(aq) \rightarrow Cu^{2+}(aq) + Fe(s)$$

  - Select relevant ½-cells:
    - $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$ **+0.34 V**
    - $Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$ **-0.45 V**
  - Compare the ½-cell potentials:
    - The more negative ½-cell, ($Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$), always gets oxidised (moves to the left)
    - This reaction shows it being reduced (moving to the right)
    - Therefore this reaction can't happen

Main

Predicting The Feasibility of a Reaction

- Will zinc ions react with magnesium?
  - The only possible reaction between Zn^{2+} and Mg is:

$$Mg_{(s)} + Zn^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Zn_{(s)}$$

  - Select relevant ½-cells:
    - $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ **-0.76 V**
    - $Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$ **-2.37 V**
  - Compare the ½-cell potentials:
    - The more negative ½-cell, ($Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$), always gets oxidised (moves to the left)
    - This reaction shows it being oxidised (moving to the left)
    - Therefore this reaction will happen

Determine whether each of the following reactions is feasible, stating why/why not in each case.

- Pb^{2+} ions reacting with calcium
- Zn^{2+} ions reacting with iron
- Cl^- ions reacting with fluorine
- Silver reacting with chlorine
- Silver reacting with iodine

Main

Key Points:

- $E^{\ominus}_{cell}$ is the difference between the two $E^{\ominus}$ values
- The negative in front of the cell potenital value means it is harder to reduce
- The more negative half-cell gets oxidised
- The more positive half-cell gets reduced
- A reaction will only be feasible if it results in the more negative species being oxidised and the more positive

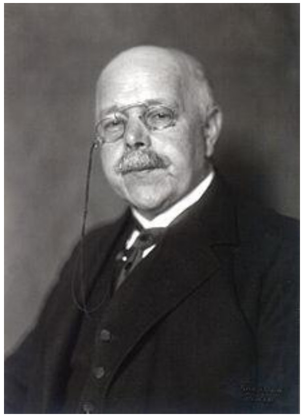
Main

The Nernst Equation

- You have learnt to calculate the potential of a cell in standard conditions
- Cells are rarely under standard conditions
- We can still calculate the cell potential using the **Nernst Equation**

$$E = E^{o} - \frac{RT}{nF} \ln Q$$

- Where:
  - E is the non-standard cell potential
  - E^o is the standard cell potential
  - R is the gas constant, 8.31
  - T is the temperature in Kelvins
  - N is the number of electrons transferred in the reaction
  - F is the Faraday constant, 96,500
  - Q is the reaction quotient: concentration of products divided by concentration of reactants



Walther Nernst

Main

What does the Nernst Equation mean?

$$E = E^{o} - \frac{RT}{nF} \ln Q$$

- From the maths of the Nernst equation we can draw three important conclusions

1. Increasing the temperature will decrease the cell potential
2. Increasing the concentration of the anode (the oxidised species, our 'product') will reduce cell potential
3. Increasing the concentration of the cathode (the reduced species, our reactant) will increase cell potential

- **Note:** effects two and three will be relatively small as they are logarithmic

Main

Key Points

- The Nernst Equation describes how E_{cell} changes under non-standard conditions
- Temperature reduces E_{cell}
- Increasing the anode concentration reduces E_{cell}
- Increasing the cathode concentration increases E_{cell}

Main

Electroplating

- Electroplating uses electrolysis to coat metal objects in a fine layer of another metal, by setting it as the cathode.

- Examples include:
  - Coating things in nice shiny chrome
  - Coating with gold to improve conductivity
  - Coating with sacrificial metal for protection

Lesson 9
HL Only

Advanced Electrolysis

Main
Menu

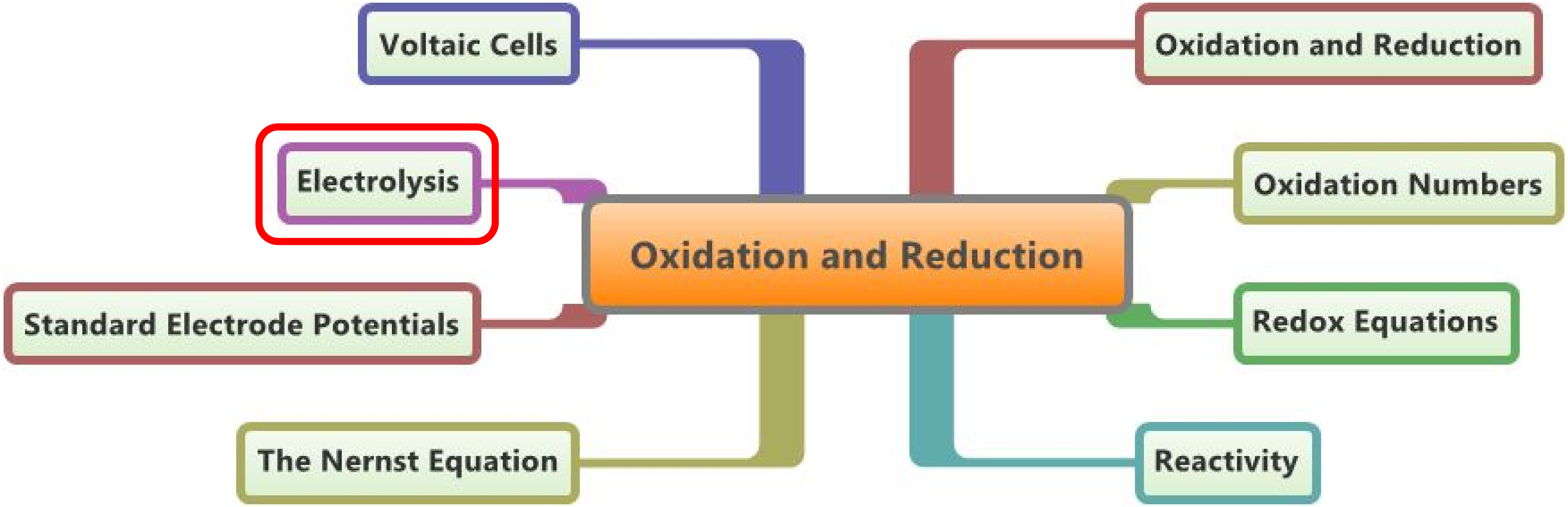
Refresh

- Consider the following cell:

$$Pb(s) + 2\ Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2\ Ag(s)$$

- Describe and explain what happens to cell potential upon:
  - Increasing the temperature
  - Reducing the concentration of Pb^{2+} ions
  - Increasing the concentration of Ag^{+} ions

We Are Here



Main

Lesson 9: Advanced Electrolysis

- Objectives:
  - Describe the products of electrolysis in aqueous solution
  - Explain the uses of electrolysis for electroplating
  - Complete an experiment to investigate electroplating

Main

Electrolysis of Water

- Water itself can be readily electrolysed
  - Since K_w of water is very low, H^+ is added to help carry current
- Anode (oxidation, moves to left):
  - $\frac{1}{2} O_2(g) + 2 H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$ $E^\ominus = +1.23V$
- Cathode (reduction, moves to right):
  - $2 H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2 OH^-(aq)E^\ominus = -0.83$ V
- Overall*:
  - $2 H_2O(l) \rightarrow 2 H_2(g) + O_2(g)$

***Note:** the reverse of this is the reaction that takes place in a hydrogen fuel cell and has an $E^\ominus_{cell}$ of 2.06 V.

Electrolysis of Aqueous Solutions

- Electrolysis of molten salts is simple:
  - Cathode → Metal
  - Anode → Non Metal

- Electrolysis of aqueous solutions is less straightforward due to the fact that the water can compete with the salts to undergo electrolysis.

- At the Anode:
  - If an anion has an $E^\ominus$ more positive than +1.23 V, water will be oxidised instead of the anion
  - Bubbles of O_2 gas will be formed and H^+ ions will enter solution
  - This happens for anions including (but not only): fluoride and sulphate
    - **Note:** Although chlorine has a potential of +1.36 V, it WILL be discharged in aqueous solution., contrary to what you might expect. The reasons for this are complex and are to do with changes in Cl^- concentrations at the anode once current starts to flow.

- At the Cathode:
  - If a cation has an $E^\ominus$ more negative than -0.83 V, water will be reduced instead of the cation
  - Bubbles of H_2 gas will be formed and OH^- ions will enter solution
  - This happens for cations including (but not only): lithium, potassium, sodium and magnesium

Main

Example 1: What are the products of the electrolysis of aqueous copper sulphate?

- Consider the standard electrode potentials:

- At the cathode:
  - $2\ H_2O(l) + e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$ -0.83 V
  - $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34 V

  - Copper less negative than water so Cu^{2+} is reduced, cathode gains coating of metallic copper

- At the anode:
  - $\frac{1}{2}\ O_2(g) + 2\ H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$ +1.23 V
  - $S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2\ SO_4^{2-}$ +2.01 V

  - Sulphate is more positive than water so water is oxidised, bubbles of O_2 gas produced and solution becomes acidic

- Overall reaction:

  - $Cu^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) \rightarrow Cu(s) + SO_4^{2-}(aq) + 2H^+(aq) + O_2(g)$

Example 2: Electrolysis of Sodium Chloride

- Consider the standard electrode potentials:
- At the cathode:
    - $2\ H_2O(l) + e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$ -0.83 V
    - $Na^+(aq) + e^- \rightleftharpoons Na(s)$ -2.71 V
    - Sodium more negative than water so water is reduced, cathode produces bubbles of H_2 gas and solution becomes more alkaline
- At the anode:
    - $½\ O_2(g) + 2\ H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$ +1.23 V
    - $½\ Cl_2(g) + e^- \rightleftharpoons Cl^-$ +1.36 V
    - Chlorine is more positive than water, so you expect it water to be oxidised, but chloride is due to reasons stated earlier.
- Overall reaction:
    - $2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Cl_2(g)$

Main

Predict the products at the anode and cathode for electrolysis of the following aqueous solutions. For each one, write the overall equation for the reaction.

- KCl
- $NiSO_4$
- PbI_2
- $ZnCl_2$
- LiOH

Investigating Electroplating

- In this short experiment, you will electroplate some small metal objects with a variety of different metals
- Follow the instructions here

Key Points

- In electrolysis of aqueous solutions, it is possible for water to be oxidised and reduced.

- At the cathode:
  - If a metal has a more negative $E^\ominus$ than water:
    - Water will be reduced
    - Hydrogen gas and OH^- ions will be produced

- At the anode:
  - If a species has a more positive $E^\ominus$ than water:
    - Water will be oxidised
    - O_2 gas and H^+ ions will be produced

Main