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Tutorials for IB Chemistry

Topic 9 Redox SL

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**Definitions of oxidation
and reduction**

Oxidation and reduction

Oxidation and reduction can be defined in terms of:

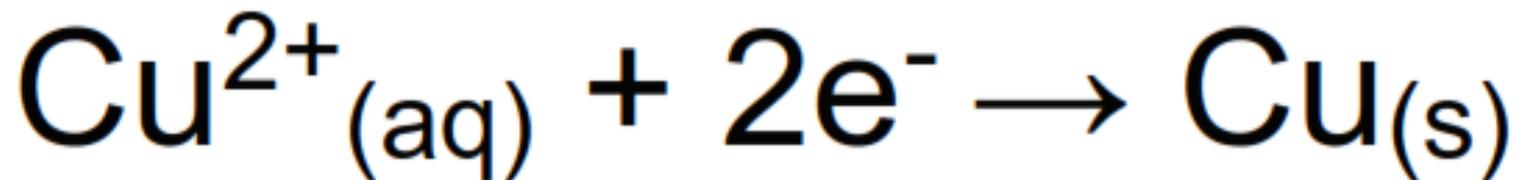
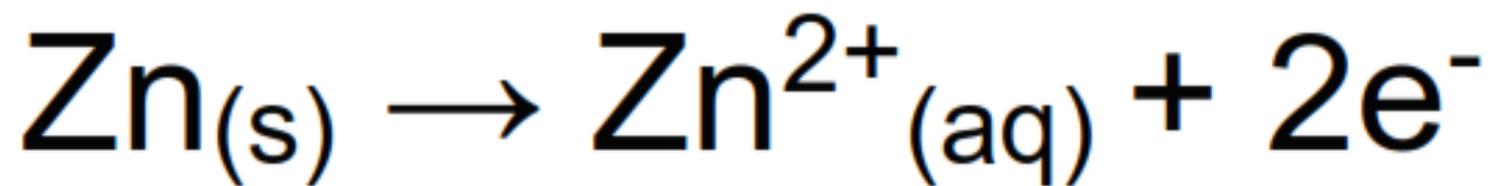
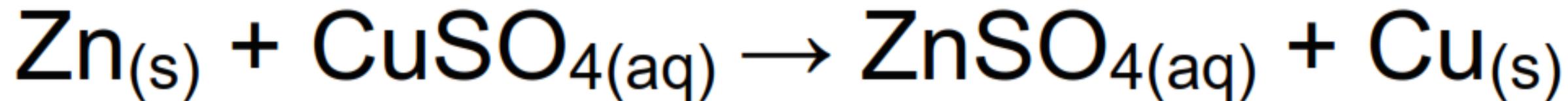
- Loss or gain of electrons (electron transfer)
- Loss or gain of oxygen
- Loss or gain of hydrogen

Electron transfer

Oxidation is the loss of electrons.

Reduction is the gain of electrons.

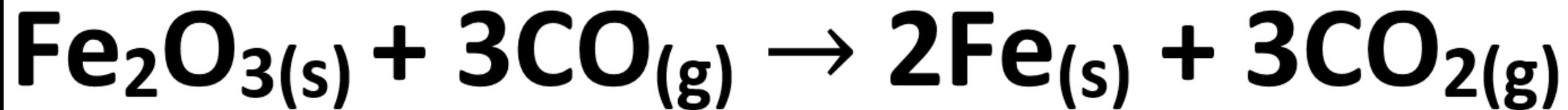
OILRIG



Loss or gain of oxygen

Oxidation is the gain of oxygen.

Reduction is the loss of oxygen.



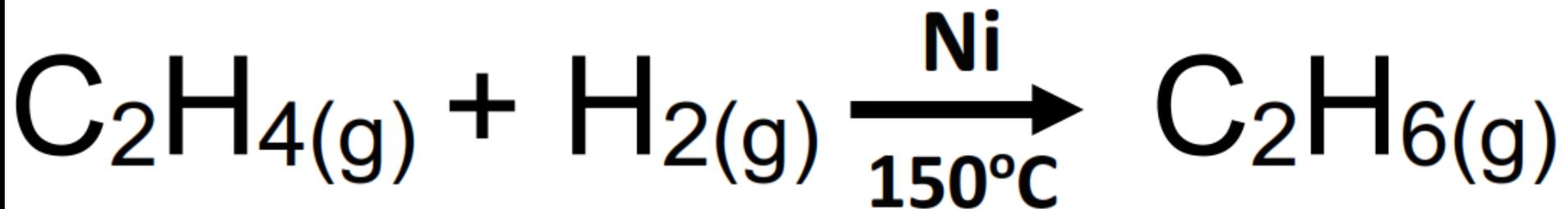
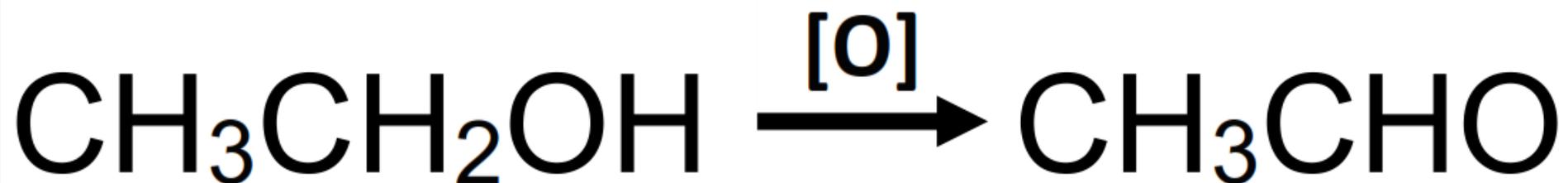
CO has gained oxygen – oxidation.

Fe₂O₃ has lost oxygen – reduction.

Loss or gain of hydrogen

Oxidation is the loss of hydrogen.

Reduction is the gain of hydrogen.



Oxidation and reduction

Electron transfer	Loss or gain of oxygen	Loss or gain of hydrogen
oxidation is loss of electrons	oxidation is gain of oxygen	oxidation is loss of hydrogen
reduction is gain of electrons	reduction is loss of oxygen	reduction is gain of hydrogen

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Oxidation states

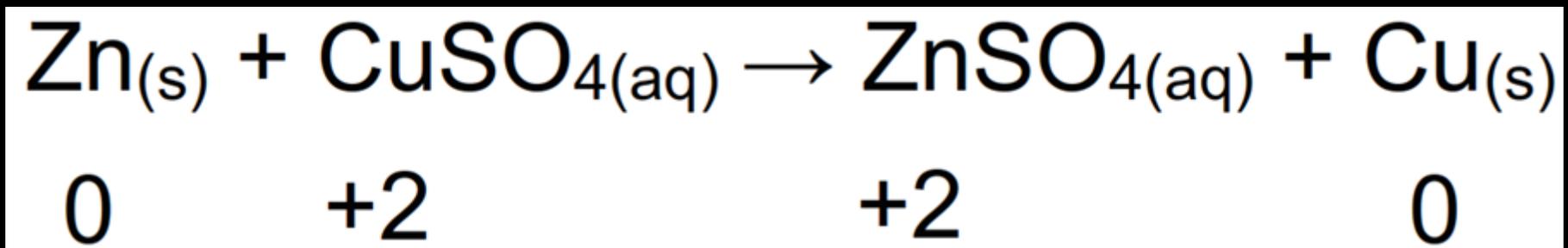
Oxidation states

The oxidation state is the hypothetical charge an atom would have if the bonds are assumed to be 100% ionic with no covalent character.

Oxidation states are written with the + or – first followed by the number (+2, not 2+).

Oxidation is an increase in oxidation state.

Reduction is a decrease in oxidation state.

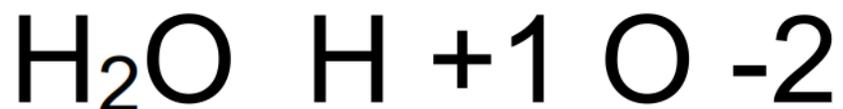


Oxidation states

Elements have an oxidation state of zero.



Oxygen in a compound has an oxidation state of -2, except in peroxides when it is -1.



Oxidation states

Hydrogen in a compound has an oxidation state of +1, except in metal hydrides when it is -1.



Group 1 and 2 elements in compounds have oxidation states of +1 and +2 respectively.

Fluorine in compounds always has an oxidation state of -1.

Oxidation states

The remaining group 17 elements can have variable oxidation states.

Halogen	Oxidation state in compounds
Chlorine	-1, +1, +2, +3, +5, +6, +7
Bromine	-1, +1, +3, +5, +7
Iodine	-1, +1, +3, +5, +6, +7
Astatine	-1, +1, +3, +5, +7

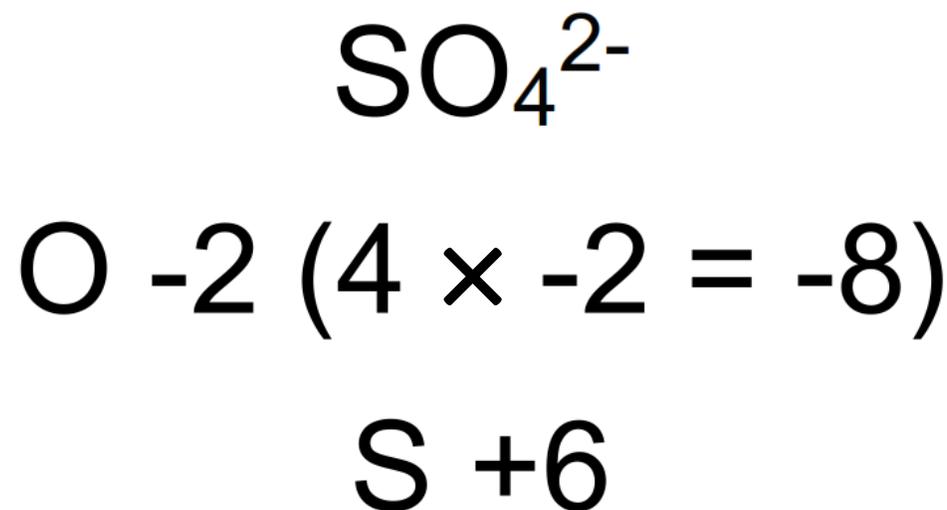
Oxidation states

Oxidation states of the first row d-block elements.

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

Oxidation states

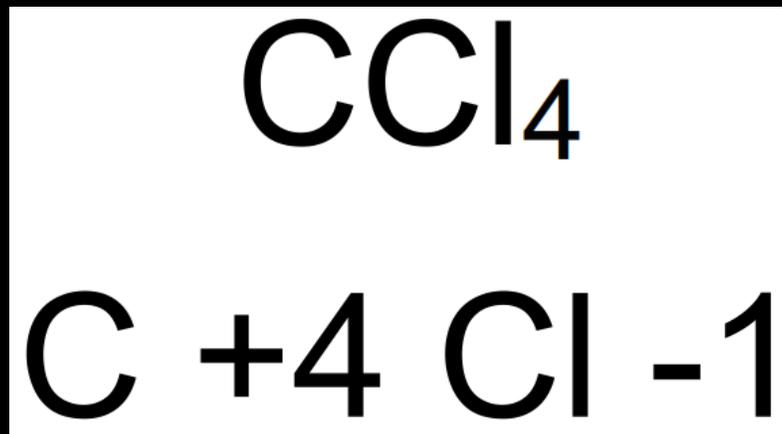
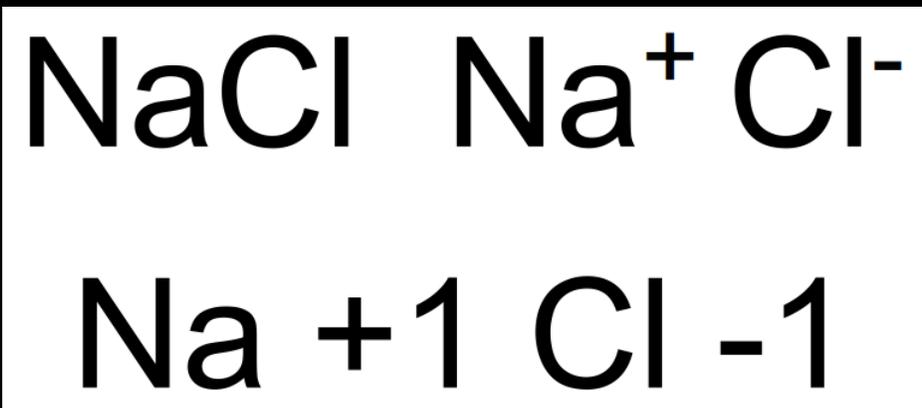
The sum of the oxidation states in a neutral compound is equal to zero.



The sum of the oxidation states in a polyatomic ion is equal to the charge on the ion.

Oxidation states

In ionic compounds, the oxidation state of each species is the same as the charge on the ion.



For covalent compounds, assume that the more electronegative atom has a negative oxidation state and the less electronegative atom has a positive oxidation state.

Oxidation numbers

Oxidation numbers are represented by a Roman numeral.



copper(I) oxide



copper(II) oxide



Iron(II) chloride



Iron(III) chloride

Oxidation states

Deduce the oxidation state of S in H_2SO_4

$$\text{H} = +1 \quad (2 \times +1 = +2)$$

$$\text{O} = -2 \quad (4 \times -2 = -8)$$

No charge on compound therefore $\text{S} = +6$

Oxidation states

Deduce the oxidation state of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$

$$\text{K } +1 \quad (2 \times +1 = +2)$$

$$\text{O } -2 \quad (7 \times -2 = -14)$$

No charge on compound therefore $\text{Cr} = +6$

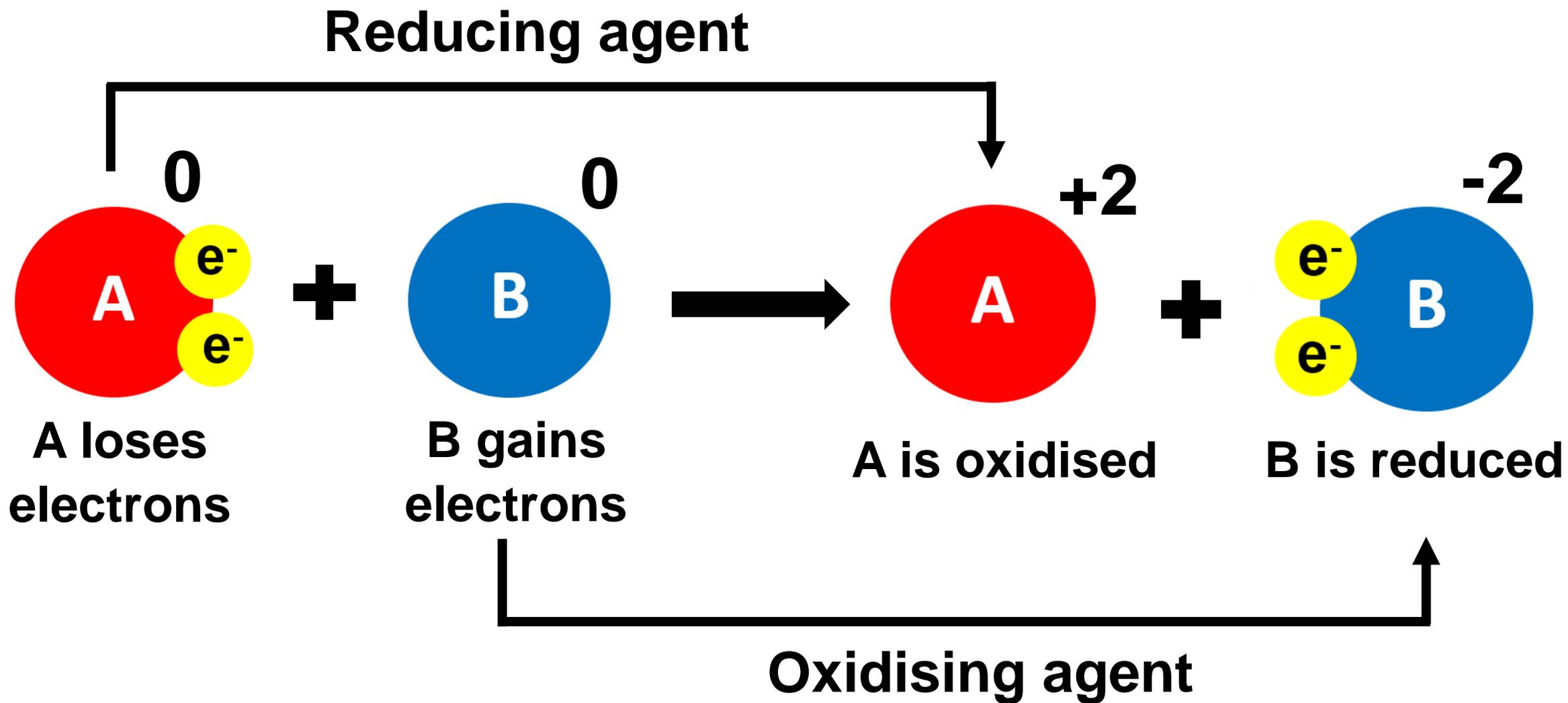
potassium dichromate(VI)

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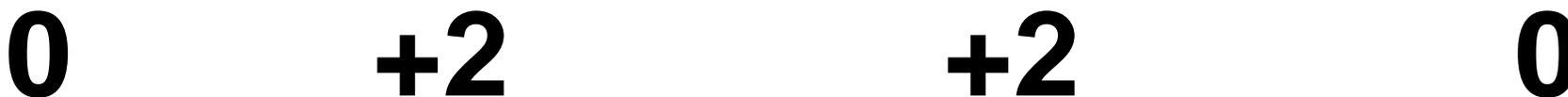
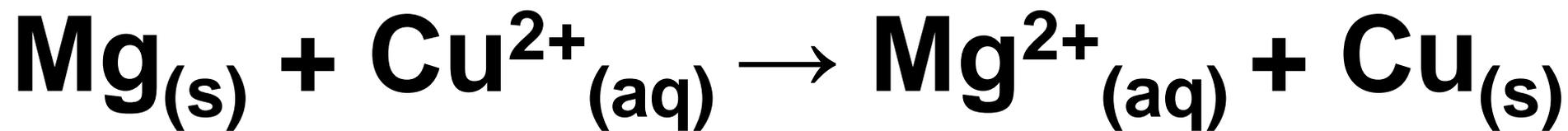
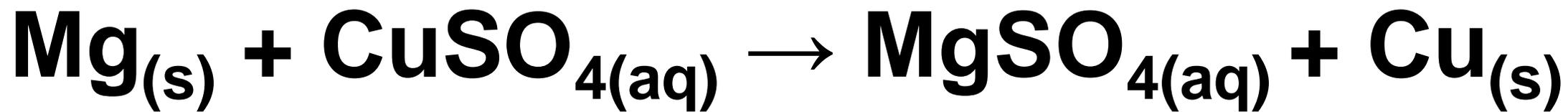
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**Oxidising and
reducing agents**

Oxidising and reducing agents



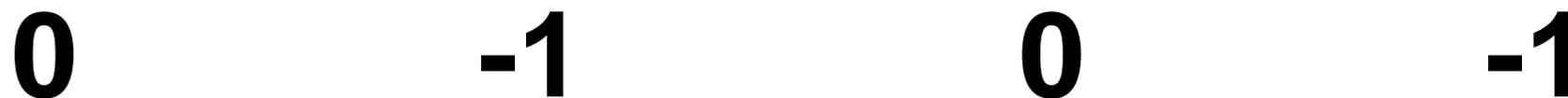
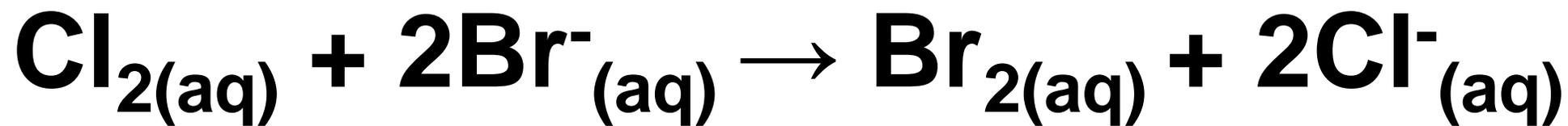
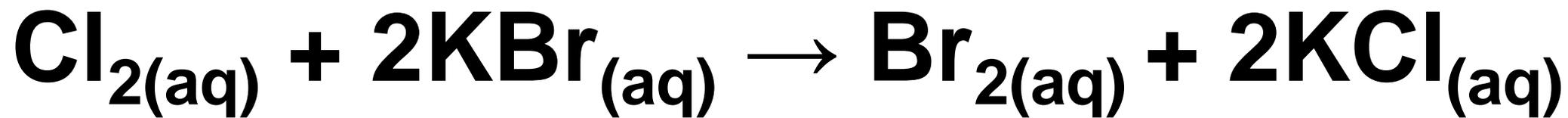
Oxidising and reducing agents



Mg_(s) is the reducing agent

Cu²⁺_(aq) is the oxidising agent

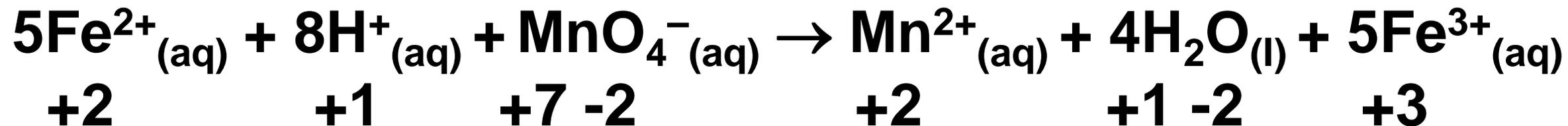
Oxidising and reducing agents



$\text{Cl}_{2(\text{aq})}$ is the oxidising agent

$\text{Br}^{-}_{(\text{aq})}$ is the reducing agent

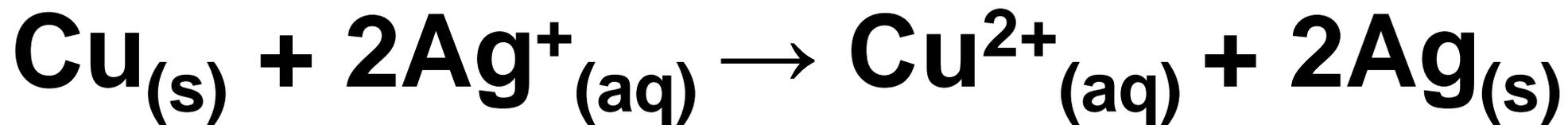
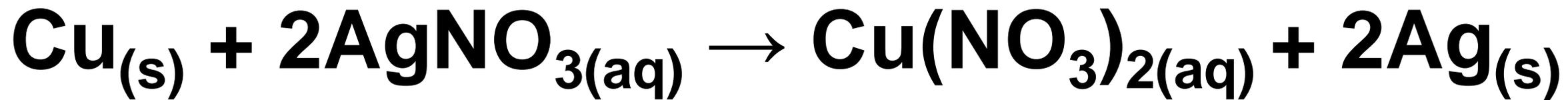
Oxidising and reducing agents



$\text{Fe}^{2+}_{(\text{aq})}$ is the reducing agent

$\text{MnO}_4^{-}_{(\text{aq})}$ is the oxidising agent

Oxidising and reducing agents



$\text{Cu}_{(s)}$ is the reducing agent

$\text{Ag}^+_{(aq)}$ is the oxidising agent

Oxidising and reducing agents

Reducing agent	Oxidising agent
Is oxidised in a redox reaction (undergoes oxidation)	Is reduced in a redox reaction (undergoes reduction)
Oxidation state increases	Oxidation state decreases
Loses electrons	Gains electrons
Causes the reduction of another species	Causes the oxidation of another species

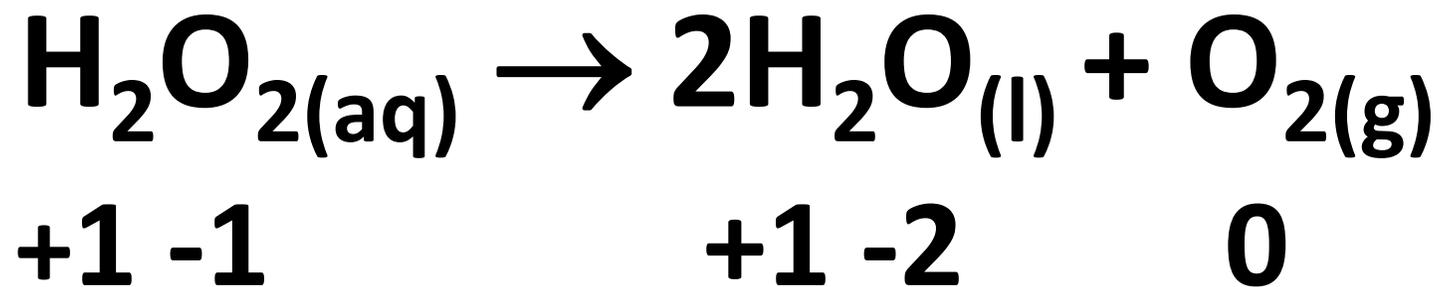
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**Disproportionation
reactions**

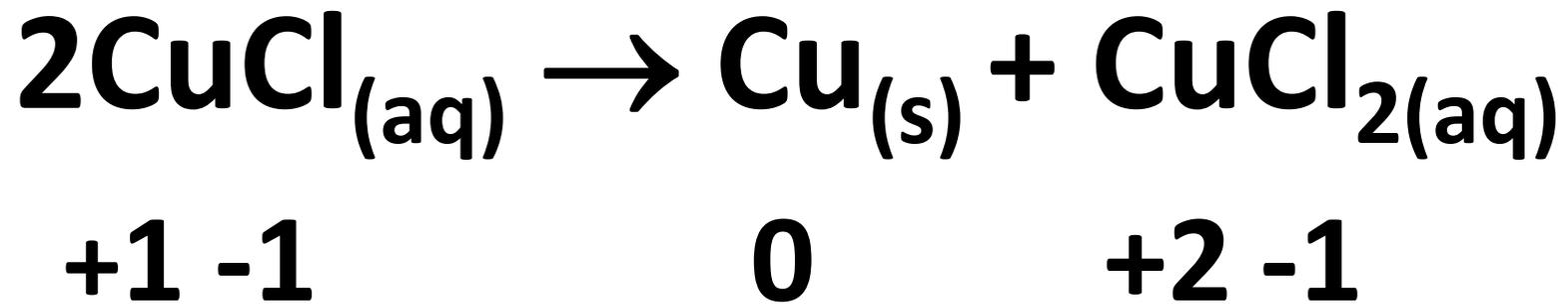
Disproportionation reactions

A disproportionation reaction is a redox reaction in which one species is simultaneously oxidised and reduced.

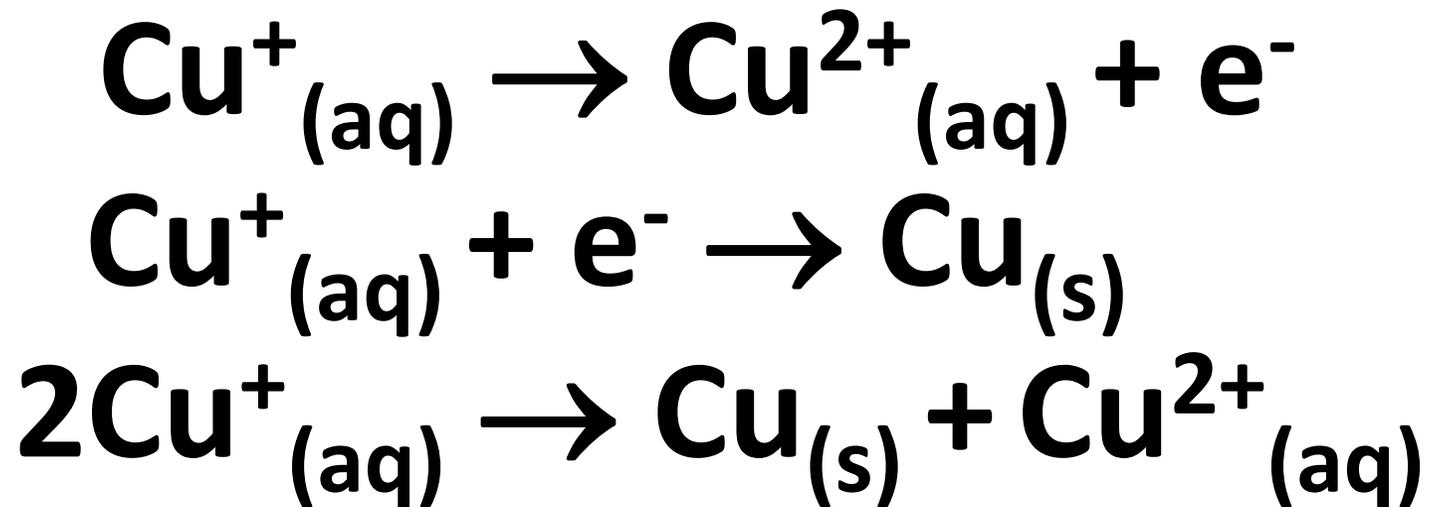


The oxygen has been both oxidised (increase in oxidation state) and reduced (decrease in oxidation state).

Disproportionation reactions



The Cu^+ has been both oxidised and reduced.



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**The activity series and
displacement reactions**

The activity series

The activity series lists metals in order of their strength as reducing agents.

Increasing activity

Li
Cs
Rb
K
Ba
Sr
Ca
Na
Mg
Be
Al
C
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H
Sb
As
Bi
Cu
Ag
Pd
Hg
Pt
Au

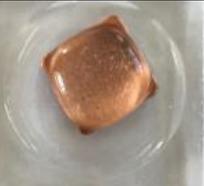
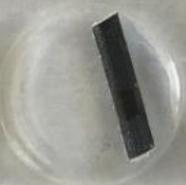
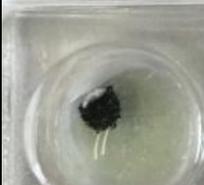
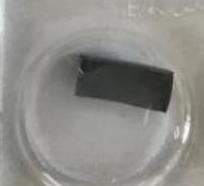
Metals at the top of the activity series are stronger reducing agents (more readily oxidised).

Metals at the bottom of the activity series are weaker reducing agents (less readily oxidised).

The activity series can be used to predict if a displacement reaction will occur.

Displacement reactions

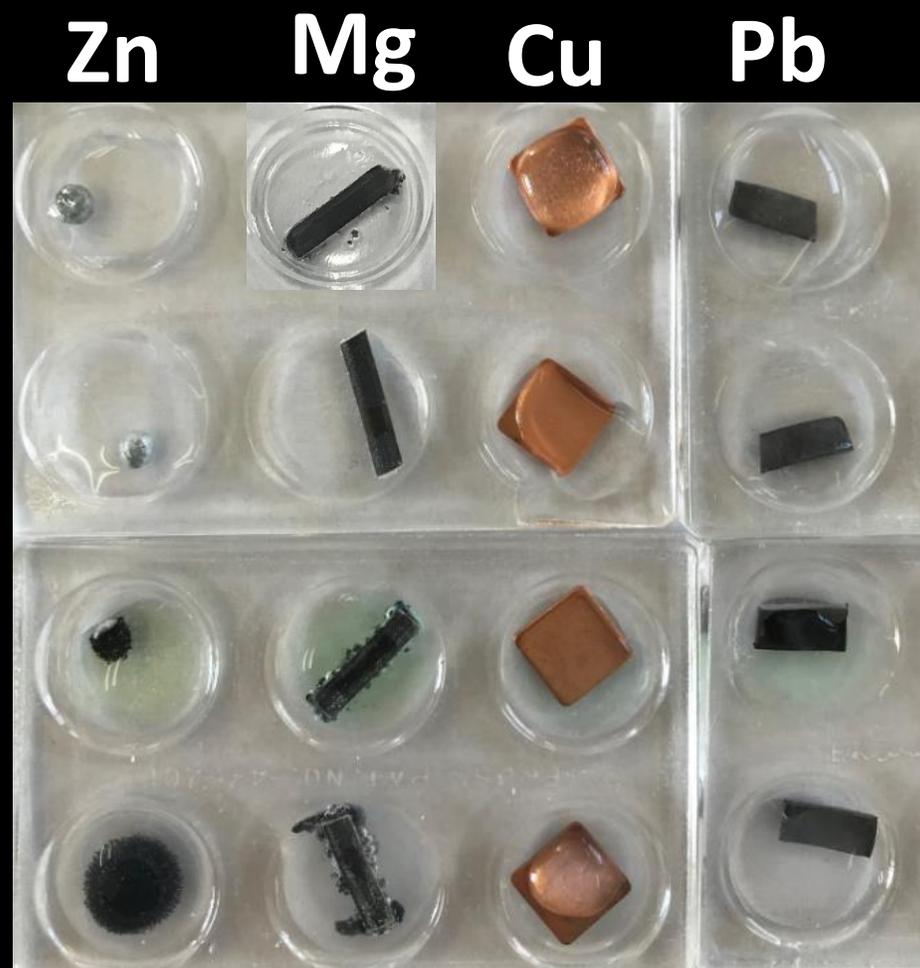
In a displacement reaction, a more reactive metal displaces the ions of a less reactive metal from solution.

	Zn	Mg	Cu	Pb
Zn ²⁺				
Mg ²⁺				
Cu ²⁺				
Pb ²⁺				

Mg can displace Zn²⁺, Cu²⁺ and Pb²⁺ ions from solution.
Zn can displace Pb²⁺ and Cu²⁺ ions from solution.
Pb can displace Cu²⁺ ions from solution.

Displacement reactions

In a displacement reaction, a more reactive metal displaces the ions of a less reactive metal from solution.



Mg > Zn > Pb > Cu

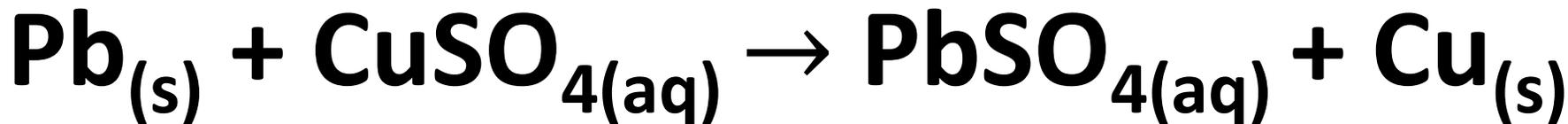
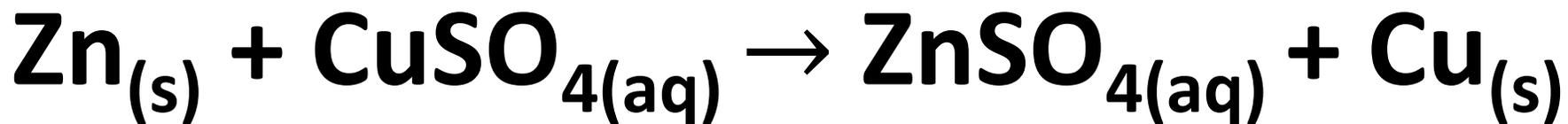
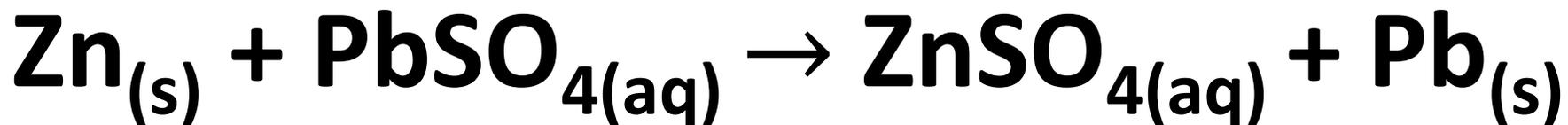
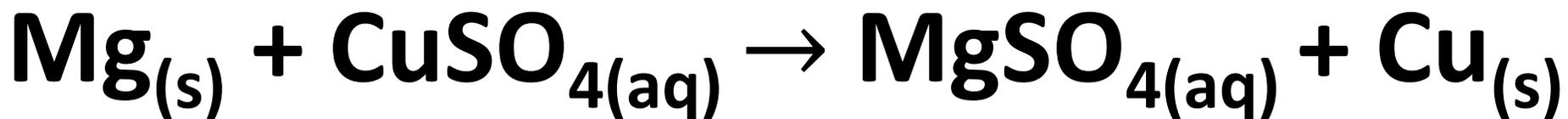
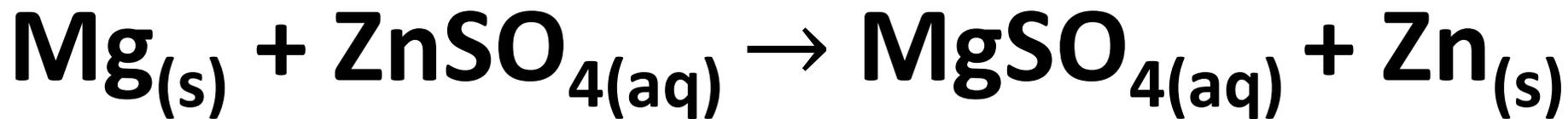
Mg Highest in activity series

Zn

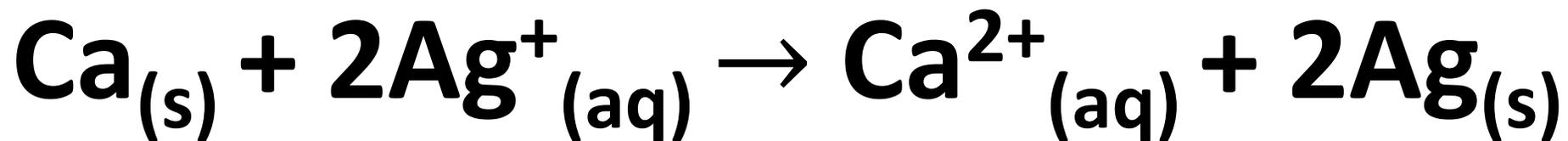
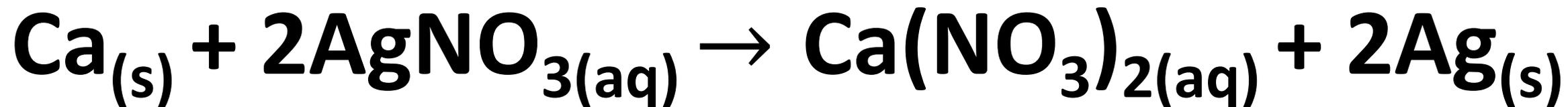
Pb

Cu Lowest in activity series

Displacement reactions



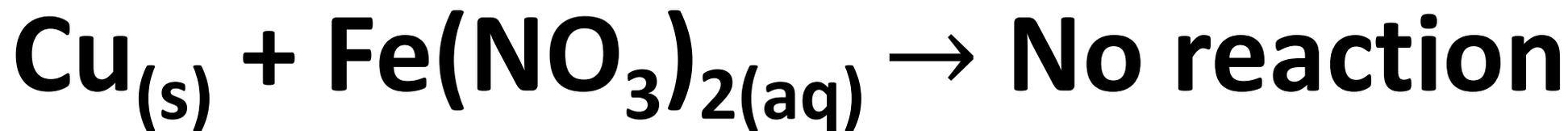
Displacement reactions



A displacement reaction will occur because Ca is higher in the activity series than Ag.

Ca is a stronger reducing agent than Ag (Ca is more reactive than Ag).

Displacement reactions

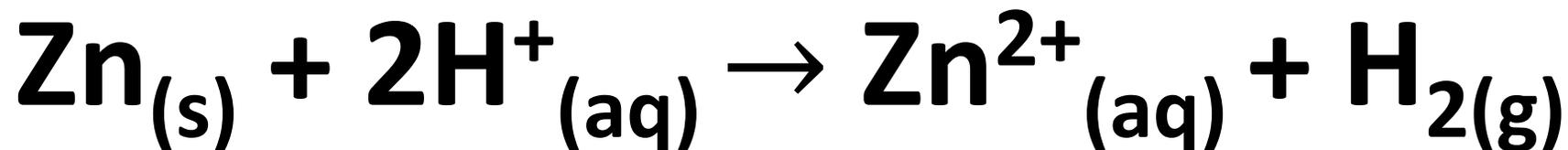
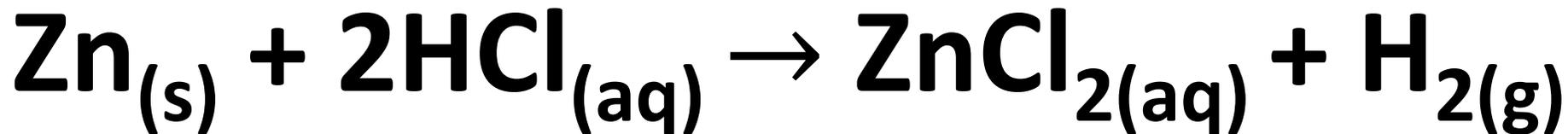
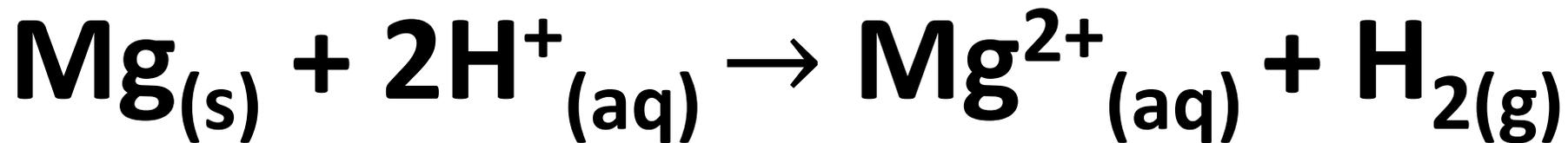
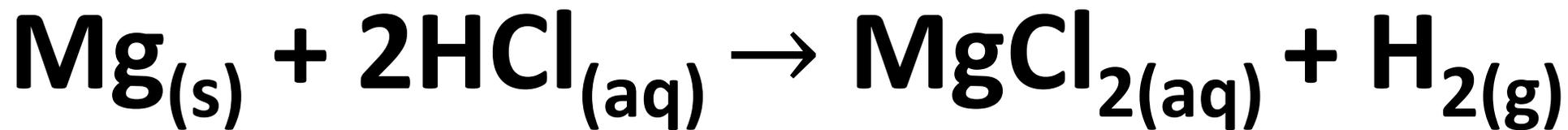


No reaction occurs because Cu is below Fe in the activity series.

Cu is a weaker reducing agent than Fe (Cu is less reactive than Fe).

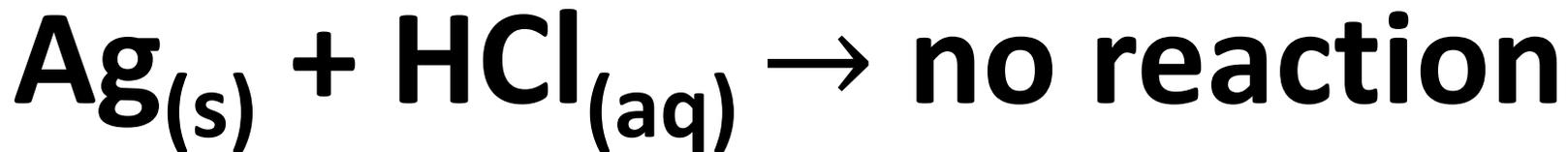
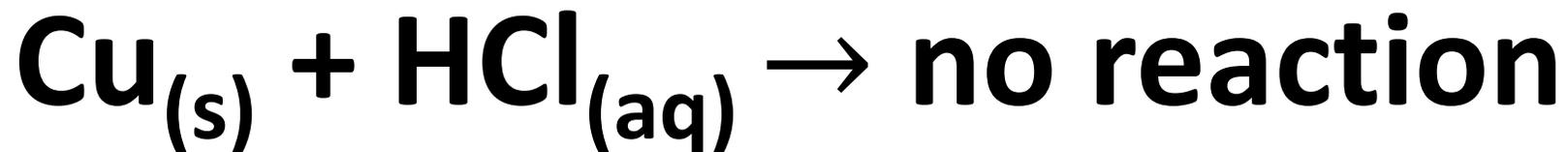
Displacement reactions

Metals above hydrogen on the activity series can displace $\text{H}^+_{(\text{aq})}$ ions from solution to form $\text{H}_{2(\text{g})}$.



Displacement reactions

Metals below hydrogen on the activity series cannot displace $\text{H}^+_{(\text{aq})}$ ions from solution to form $\text{H}_{2(\text{g})}$.



The activity series

Metals at the top of the activity series are stronger reducing agents (more reactive).

Metals at the bottom of the activity series are weaker reducing agents (less reactive).

Metals higher up in the activity series can displace the ions of a metal lower in the activity series.

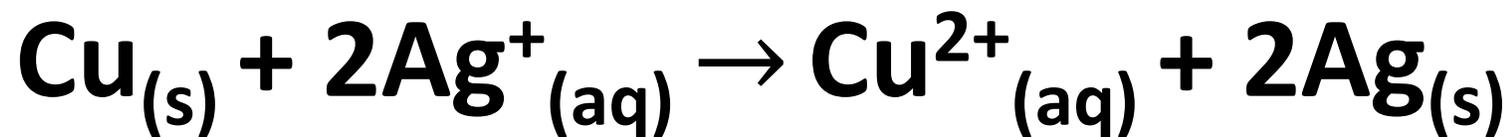
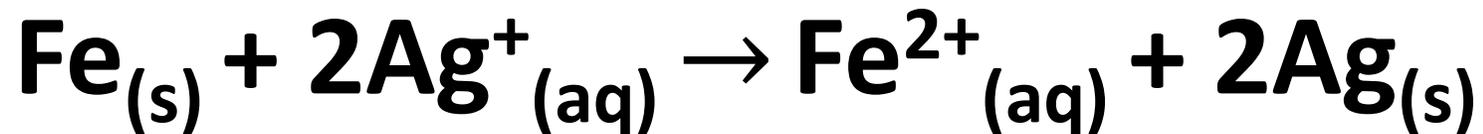
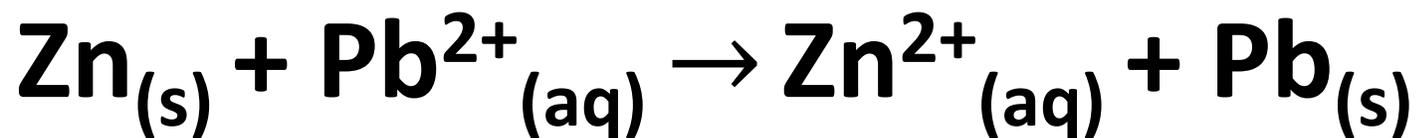
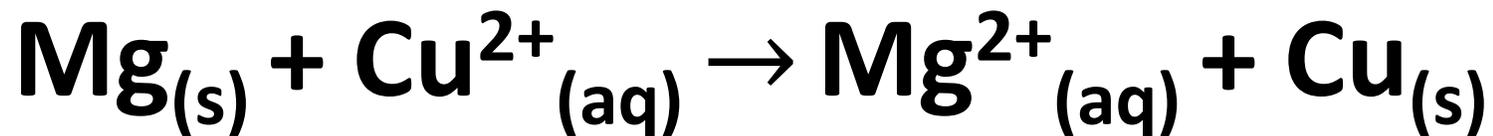
Metals above hydrogen can displace hydrogen ions from solution to form hydrogen gas.

25 Mn Manganese 54.938045	16 S Sulfur 32.065	J	6 C Carbon 12.0107	2 He Helium 4.002602	25 Mn Manganese 54.938045
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**Writing net ionic
equations**

Writing net ionic equations

A net ionic equation is an equation for a redox reaction that includes only those species that participate in the reaction.

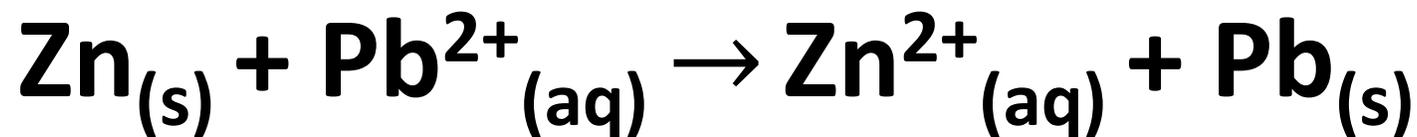
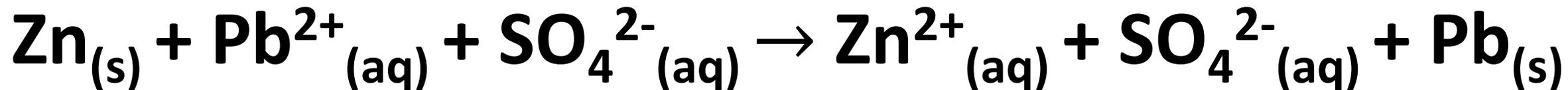
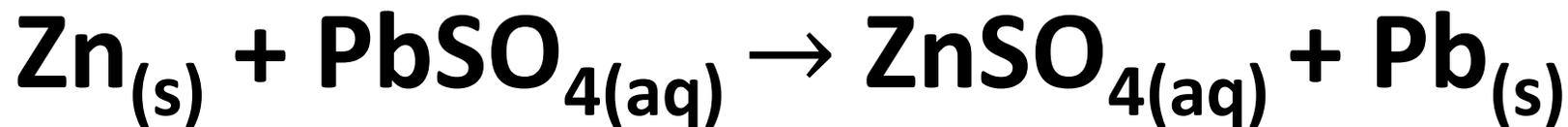
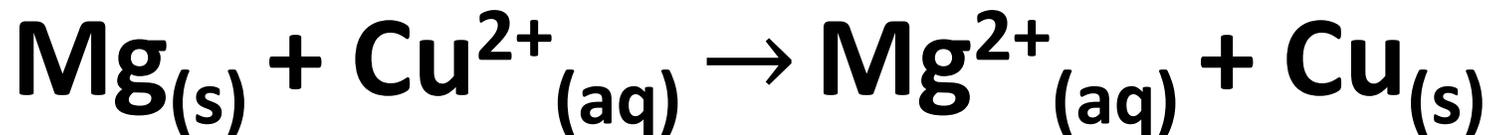
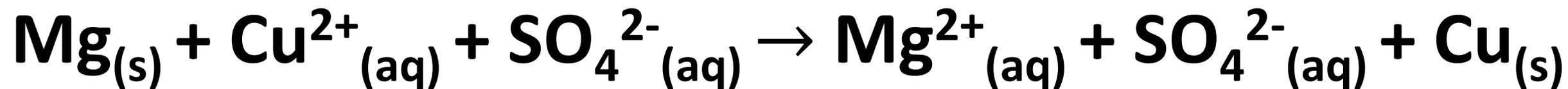


Writing net ionic equations

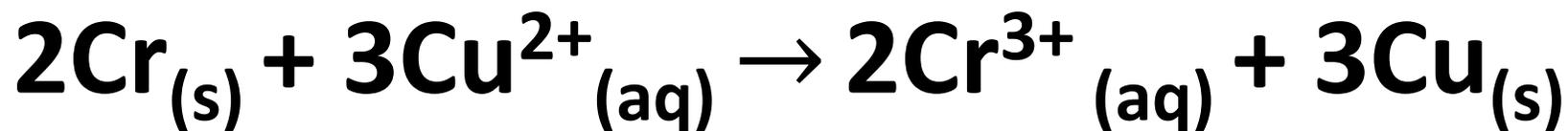
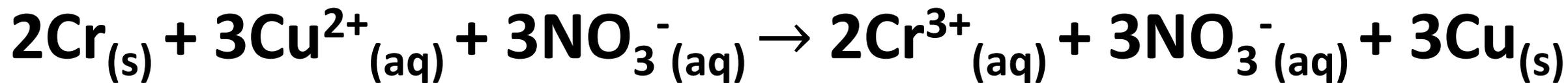
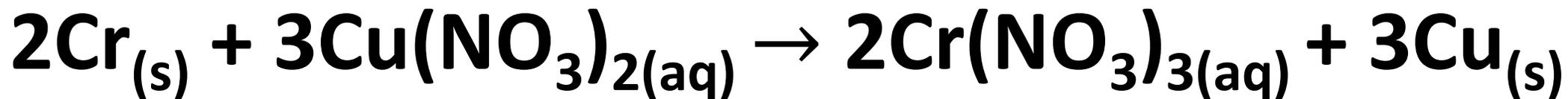
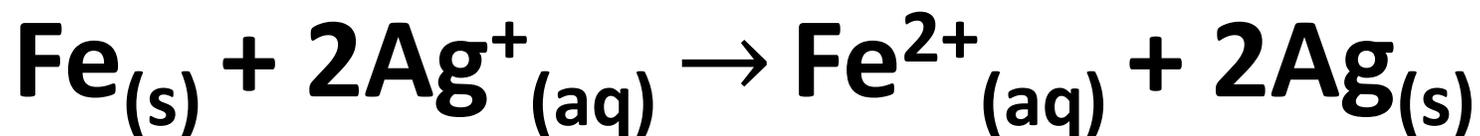
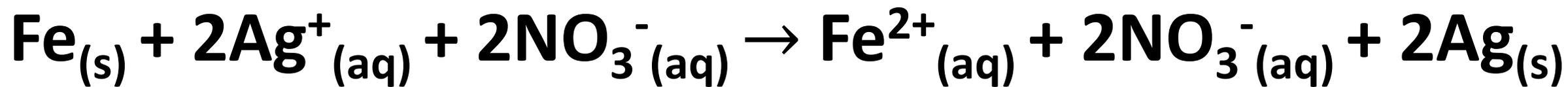
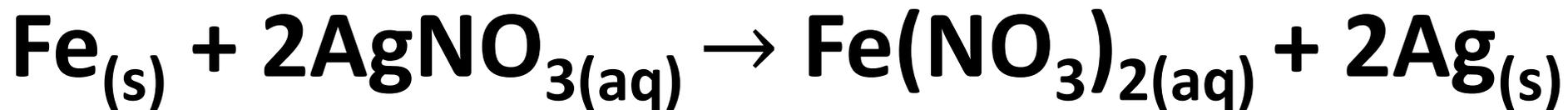
A net ionic equation is an equation for a redox reaction that includes only those species that participate in the reaction.

1. Write the molecular equation for the reaction.
2. Write the complete ionic equation that shows all aqueous species broken down into their constituent ions.
3. Cancel out the spectator ions (ions that appear unchanged on both sides of the equation).
4. Write the net ionic equation.

Writing net ionic equations



Writing net ionic equations



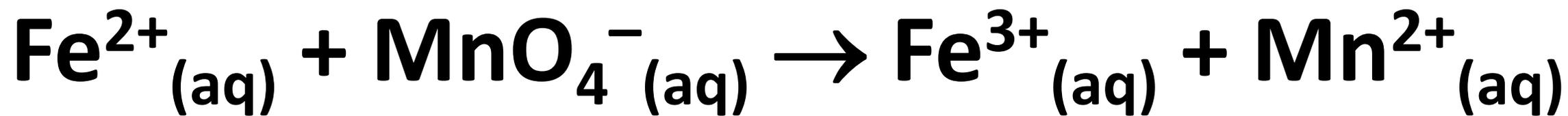
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**Balancing redox
equations in acidic
solutions**

Balancing redox equations

Balance the following redox equation in acidic solution.

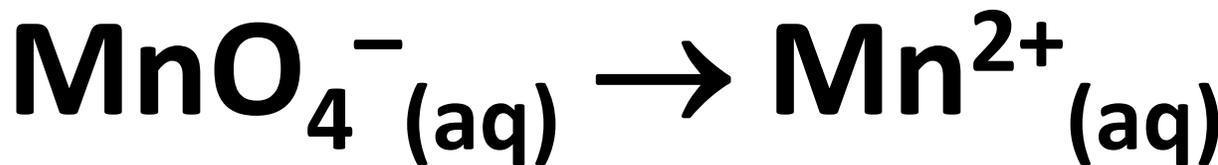


+2

+7 -2

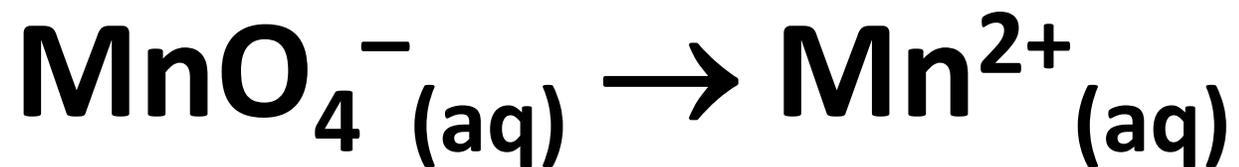
+3

+2



Balancing redox equations

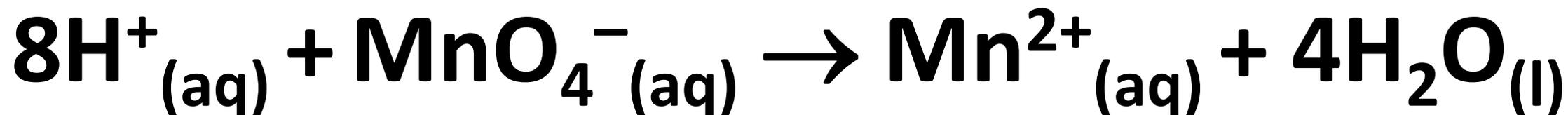
1) Balance for atoms other than H or O.



2) Balance for O by adding H₂O

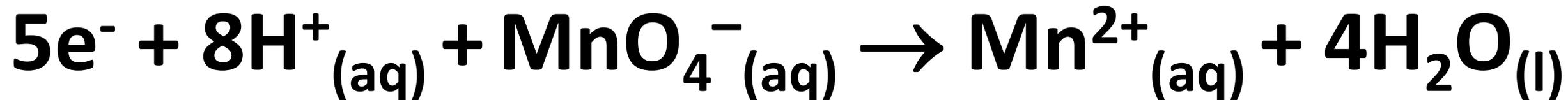


3) Balance for H by adding H⁺

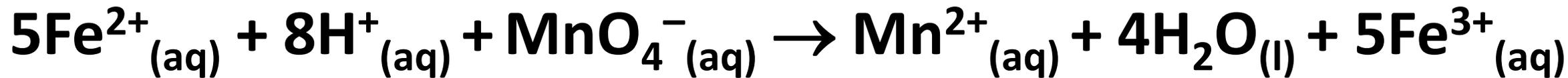
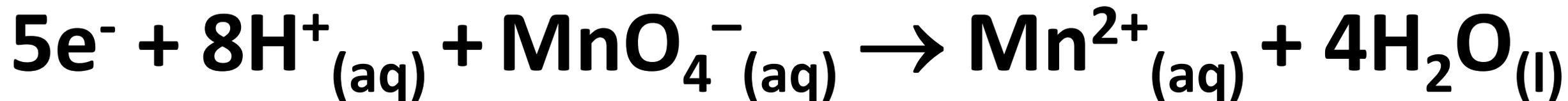


Balancing redox equations

4) Balance for charge by adding e^-



5) Balance for e^- and combine the two half-equations.



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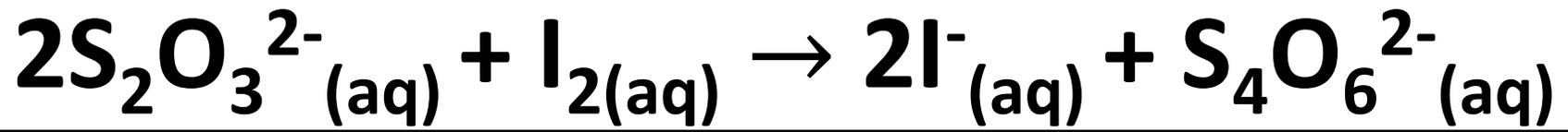
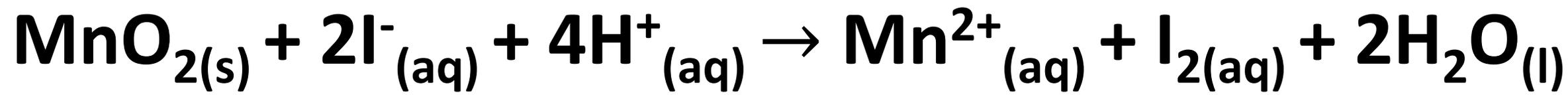
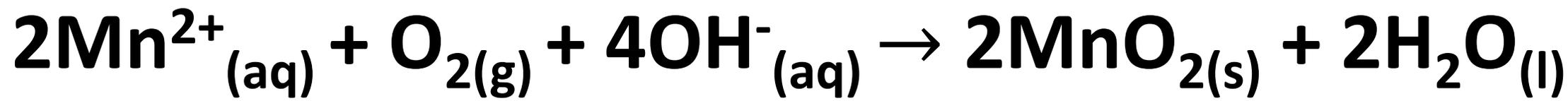
Tutorials for IB Chemistry

The Winkler method

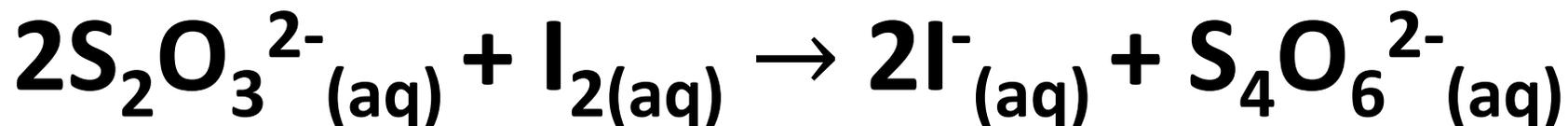
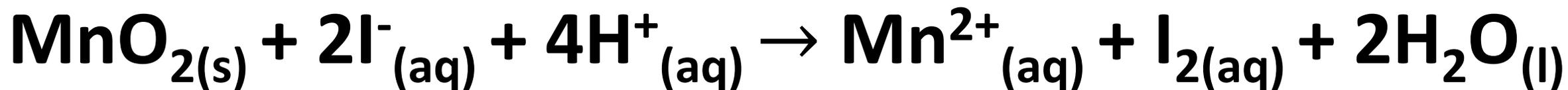
The Winkler method

The Winkler method determines the concentration of dissolved oxygen in a water sample.

It is used to measure the biochemical oxygen demand (BOD).



The Winkler method

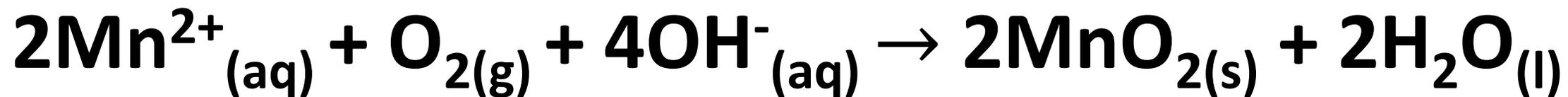


Ratio of O_2 to $\text{S}_2\text{O}_3^{2-}$ is 1:4

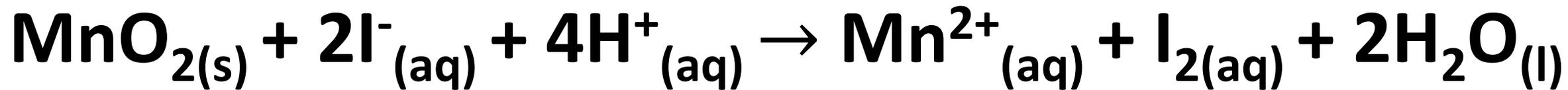
One mol of O_2 reacts
with 4 mol of $\text{S}_2\text{O}_3^{2-}$

The Winkler method

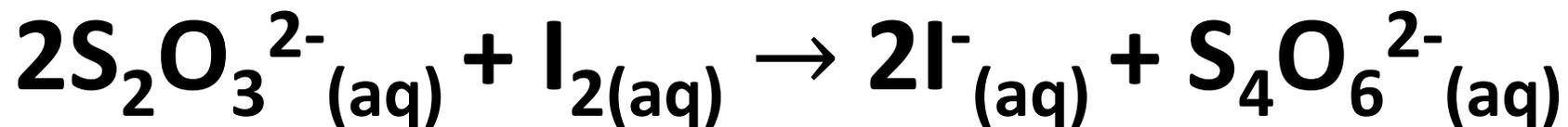
An excess of $\text{MnSO}_4(\text{aq})$ is added to the water sample.



Iodide ions, $\text{I}^-(\text{aq})$, are oxidised to form I_2



The I_2 is titrated with $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$



The Winkler method

Two samples of water are collected.

One sample is immediately tested for $[O_2]$.

The second sample is stored in the dark for 5 days at a constant temperature.

After 5 days the $[O_2]$ is determined.

To calculate the BOD, subtract the final $[O_2]$ from initial $[O_2]$.

The BOD is usually given in mg dm^{-3} or ppm.

The Winkler method

Two 300.0 cm³ samples of river water were collected. One sample was tested for the concentration of dissolved O₂ immediately and the other was stored in a dark place to be tested after 5 days.

At day 0, 15.20 cm³ of 0.0200 mol dm⁻³ Na₂S₂O_{3(aq)} was required to react with the I₂ produced. Calculate the dissolved oxygen content of the water.

$$n(\text{S}_2\text{O}_3^{2-}) = 0.0200 \times (15.20 / 1000)$$

$$n(\text{S}_2\text{O}_3^{2-}) = 3.04 \times 10^{-4} \text{ mol}$$

The Winkler method

Ratio of O_2 to $S_2O_3^{2-} = 1:4$

$$n(O_2) = 3.04 \times 10^{-4} / 4 = 7.60 \times 10^{-5} \text{ mol}$$

$$m(O_2) = 7.60 \times 10^{-5} \text{ mol} \times 32.00 \text{ g mol}^{-1}$$

$$m(O_2) = 2.43 \times 10^{-3} \text{ g} = 2.43 \text{ mg}$$

$$[O_2] = 2.43 / (300.0 / 1000)$$

$$[O_2] = 8.11 \text{ mg dm}^{-3} \text{ or } 8.11 \text{ ppm}$$

The Winkler method

After 5 days, the concentration of dissolved oxygen was determined. The second sample required 8.75 cm^3 of $0.0200 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ to react with the I_2 produced.

The Winkler method

$$n(\text{S}_2\text{O}_3^{2-}) = 0.0200 \times (8.75 / 1000)$$

$$n(\text{S}_2\text{O}_3^{2-}) = 1.75 \times 10^{-4} \text{ mol}$$

$$n(\text{O}_2) = 1.75 \times 10^{-4} / 4 = 4.38 \times 10^{-5} \text{ mol}$$

$$m(\text{O}_2) = 4.38 \times 10^{-5} \text{ mol} \times 32.00 \text{ g mol}^{-1}$$

$$m(\text{O}_2) = 1.40 \times 10^{-3} \text{ g} = 1.40 \text{ mg}$$

$$[\text{O}_2] = 1.40 / (300.0 / 1000)$$

$$[\text{O}_2] = 4.67 \text{ mg dm}^{-3} \text{ or } 4.67 \text{ ppm}$$

The Winkler method

BOD = initial $[O_2]$ – final $[O_2]$

BOD = 8.11 mg dm^{-3} – 4.67 mg dm^{-3}

BOD = 3.44 mg dm^{-3} or 3.44 ppm

BOD (ppm)	Water quality
1-2	Very good
3-5	Moderately clean
6-9	Somewhat polluted
>10	Polluted

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Tutorials for IB Chemistry

Redox titration

Redox titration

A redox titration is used to determine the concentration of an analyte containing either an oxidizing or a reducing agent.

This analytical technique can be used to find the amount of iron in a sample.

In these titrations Fe^{2+} is oxidised to Fe^{3+} by an oxidising agent:



Redox titration

The sample is dissolved in acid and all of the iron is converted to Fe^{2+} .

The resulting solution is titrated with a standard solution of potassium manganate(VII), KMnO_4 .

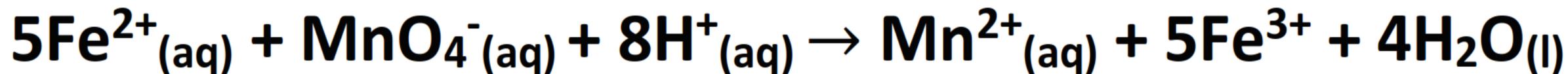
In acidic solution, MnO_4^- reacts with Fe^{2+} ions to form Mn^{2+} and Fe^{3+} and the end point is indicated by a slight pink colour.

Redox titration

The oxidising agent is usually acidified potassium manganate(VII) or potassium dichromate(VI).



Balanced redox equation in acidic solution:



Redox titration

The data below is from an experiment used to determine the percentage of iron present in a sample of iron ore.

Mass of iron ore / g	3.682×10^{-1}
concentration of KMnO_4 solution / mol dm^{-3}	2.152×10^{-2}

Titre	1	2	3
Initial burette reading / cm^3	1.00	23.60	10.00
Final burette reading / cm^3	24.60	46.10	32.50
Volume used / cm^3	23.60	22.50	22.50

Redox titration

Calculate the amount, in moles, of MnO_4^- used in the titration.

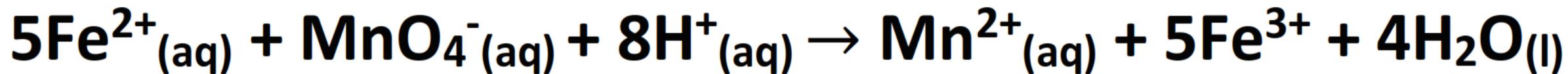
$$n = CV$$

$$n(\text{MnO}_4^-) = 2.152 \times 10^{-2} \times (22.50 \div 1000)$$

$$n(\text{MnO}_4^-) = 4.842 \times 10^{-4} \text{ mol}$$

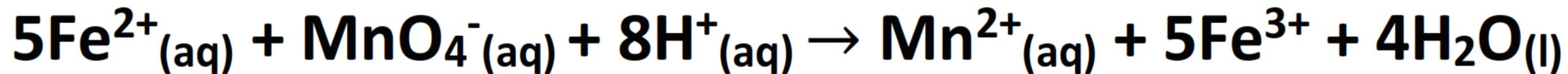
Redox titration

Deduce the balanced redox equation for the reaction in acidic solution.



Redox titration

Deduce the balanced redox equation for the reaction in acidic solution.



Calculate the amount, in moles, of MnO_4^{-} used in the titration.

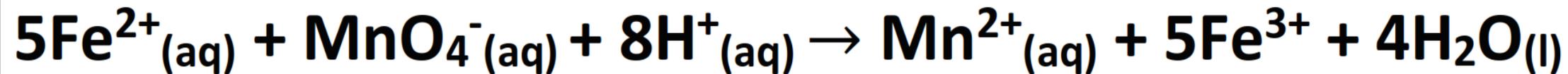
$$n = CV$$

$$n(\text{MnO}_4^{-}) = 2.152 \times 10^{-2} \times (22.50 \div 1000)$$

$$n(\text{MnO}_4^{-}) = 4.842 \times 10^{-4} \text{ mol}$$

Redox titration

Calculate the amount, in moles, of Fe present in the 3.682×10^{-1} g sample of iron ore.



$$n(\text{Fe}) = 4.842 \times 10^{-4} \times 5$$

$$n(\text{Fe}) = 2.421 \times 10^{-3} \text{ mol}$$

$$\text{mass of Fe} = 2.421 \times 10^{-3} \times 55.85$$

$$\text{mass of Fe} = 0.1352 \text{ g}$$

Redox titration

Determine the percentage by mass of Fe present in the 3.682×10^{-1} g sample of iron ore.

$$\frac{\text{mass of iron}}{\text{mass of sample}} \times 100$$

$$\frac{0.1352}{0.3682} \times 100 = 36.72\%$$

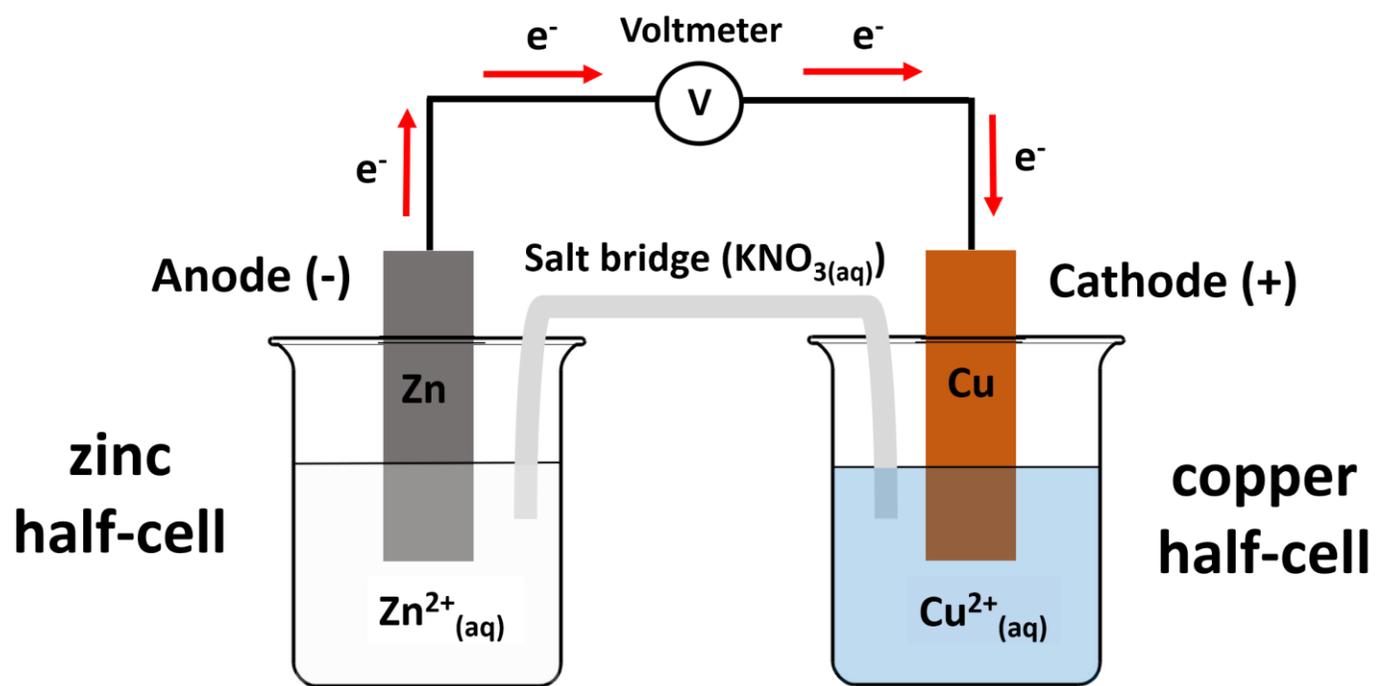
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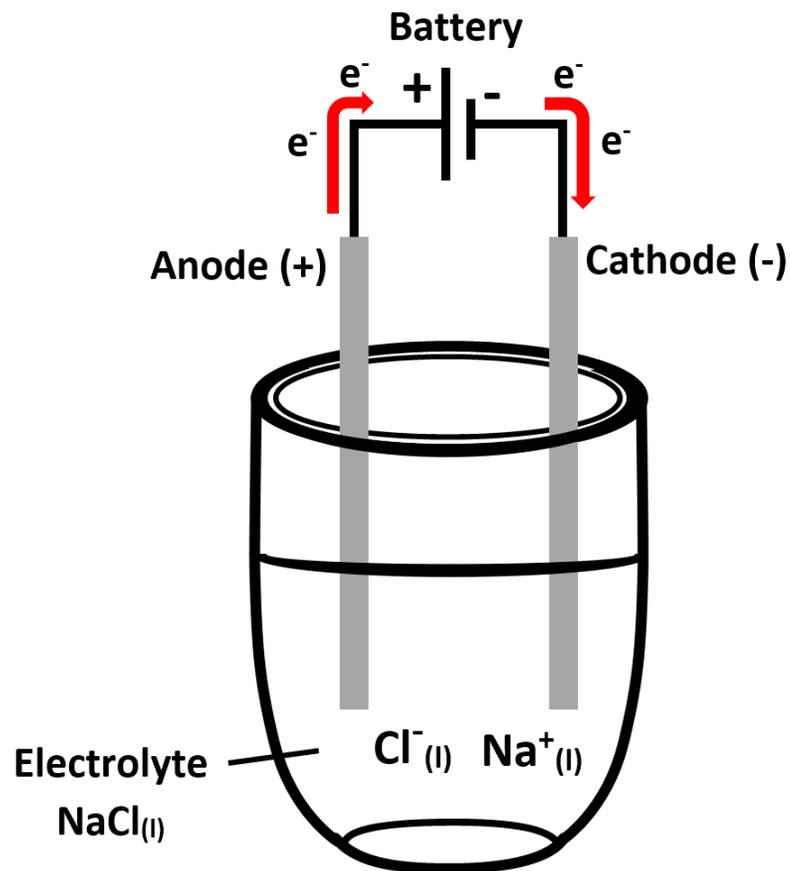
Electrochemical cells

Electrochemical cells

Voltaic (galvanic) cell



Electrolytic cell



Electrochemical cells

Voltaic cell	Electrolytic cell
A spontaneous reaction produces electrical energy	Electrical energy drives a non-spontaneous reaction
Chemical energy is converted to electrical energy	Electrical energy is converted to chemical energy
Reaction is exothermic	Reaction is endothermic

Electrochemical cells

Voltaic cell

Current is conducted by electron flow in wires and movement of ions in salt bridge

Anode is negative and cathode is positive

Electrolytic cell

Current is conducted by electron flow in wires and movement of ions in electrolyte

Anode is positive and cathode is negative

Electrochemical cells

Voltaic cell	Electrolytic cell
Oxidation occurs at the anode and reduction at the cathode	Oxidation occurs at the anode and reduction at the cathode

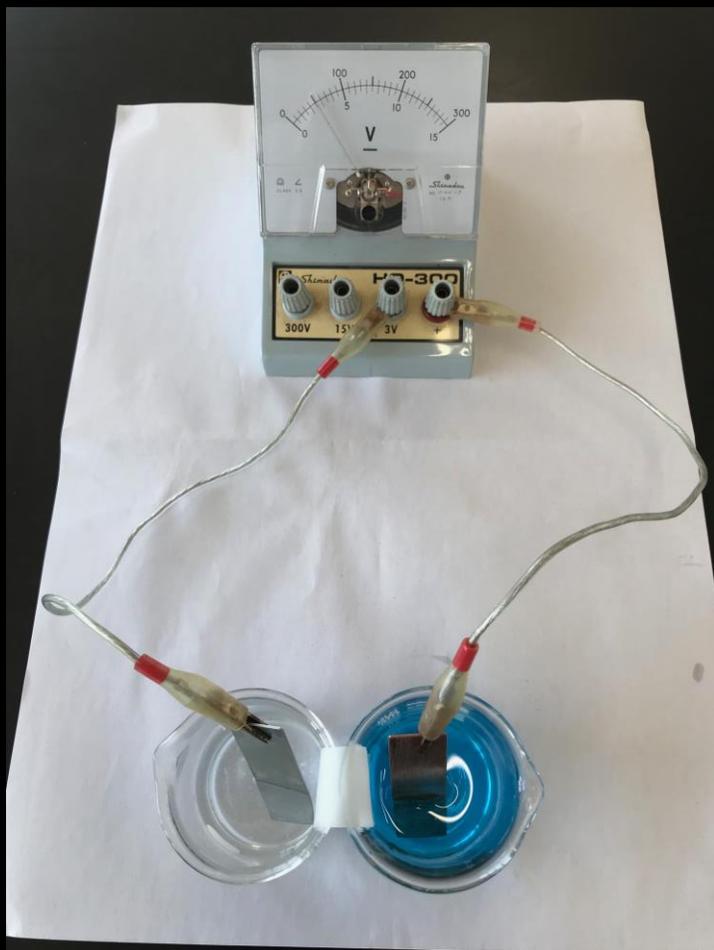
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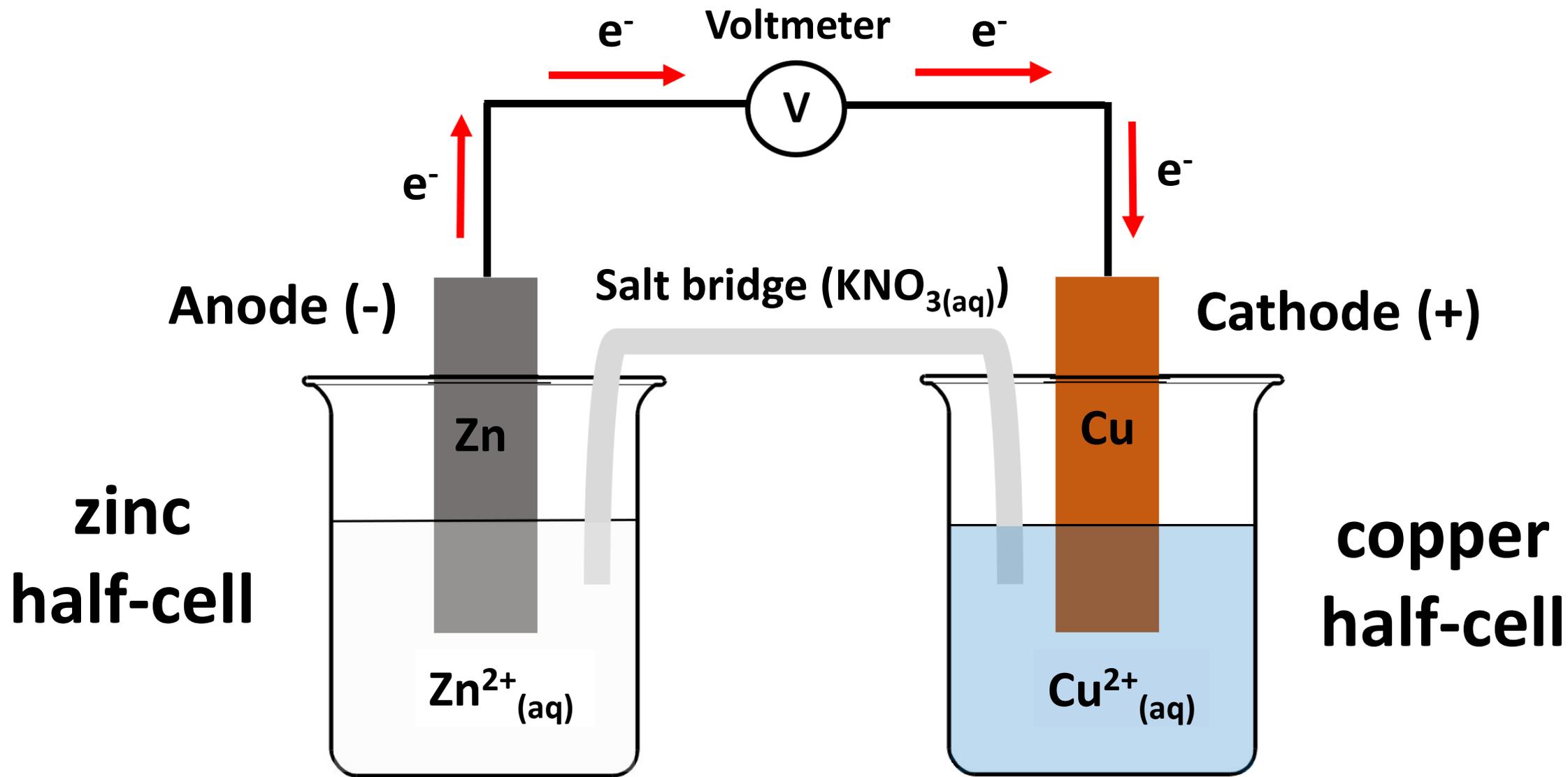
Voltaic cells

Voltaic cells

A voltaic cell (galvanic cell) uses a spontaneous redox reaction to generate electrical energy.



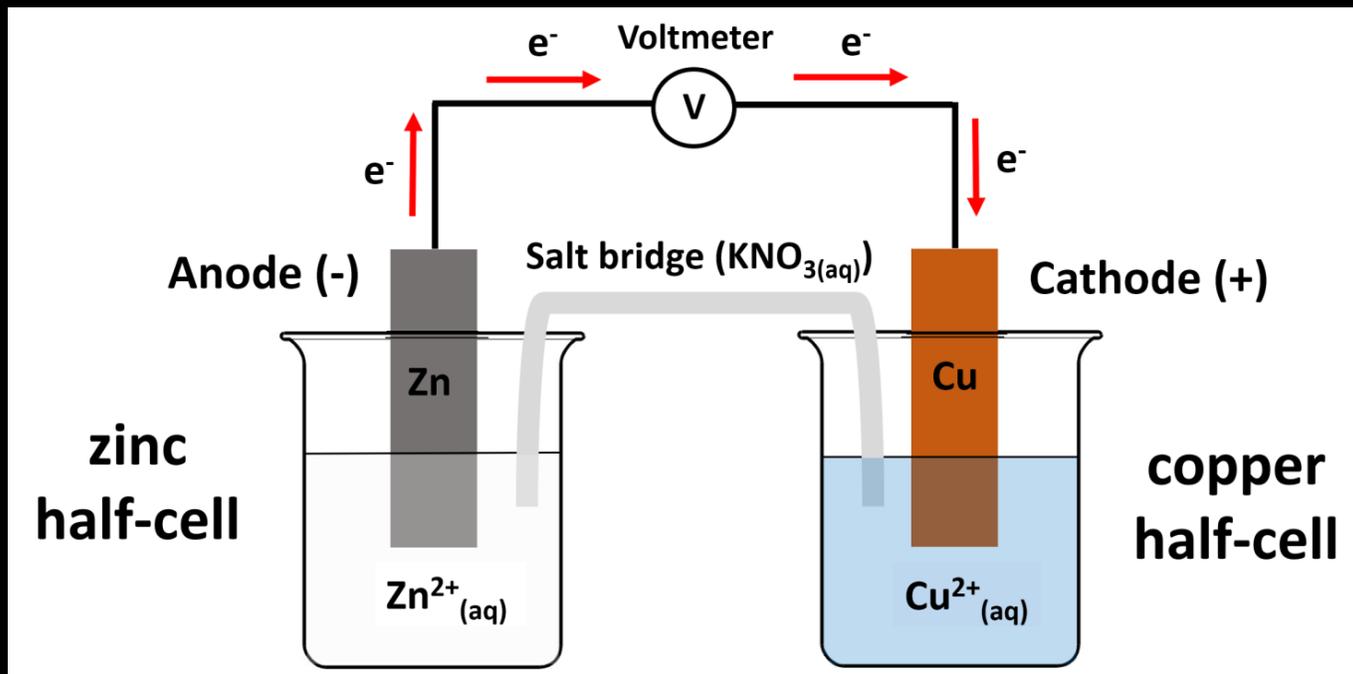
Voltaic cells



Voltaic cells

Increasing activity ↑

Li
Cs
Rb
K
Ba
Sr
Ca
Na
Mg
Be
Al
C
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H
Sb
As
Bi
Cu
Ag
Pd
Hg
Pt
Au

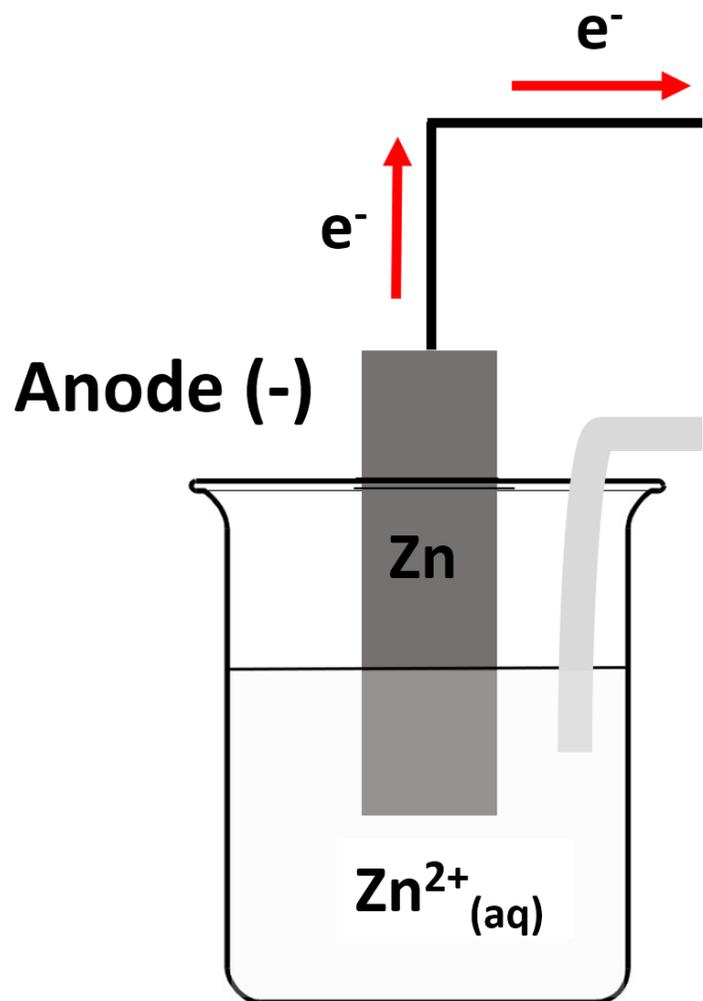


The metal higher up in the activity series will be the anode.

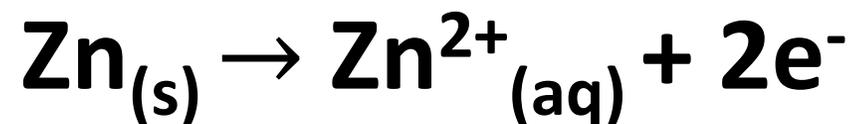
The metal lower down in the activity series will be the cathode.

Voltaic cells

At the anode (negative electrode)



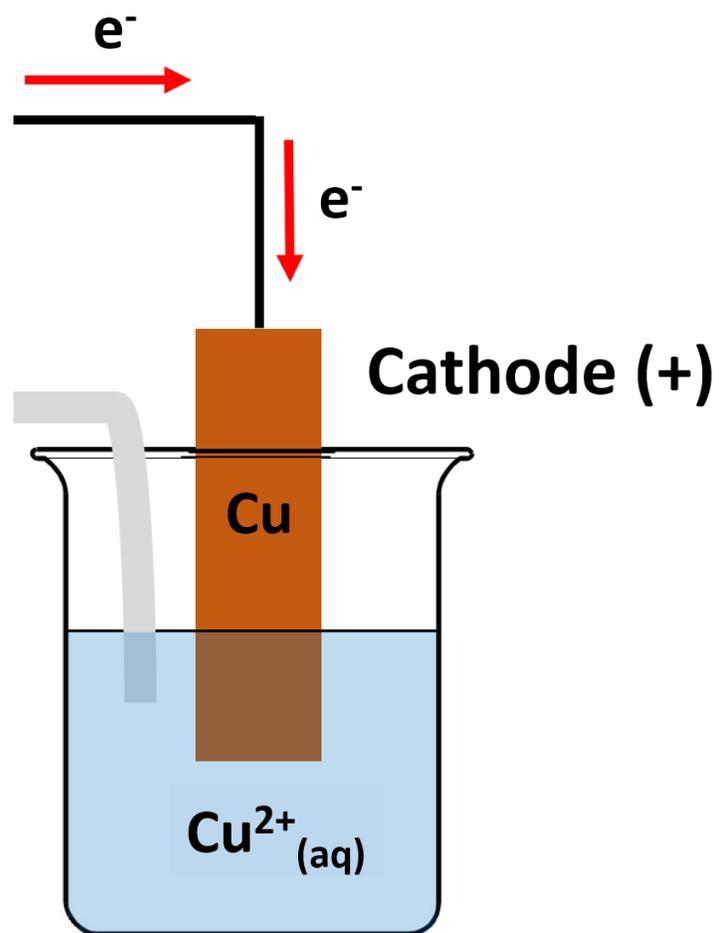
The $\text{Zn}_{(\text{s})}$ undergoes oxidation.



The electrons flow in the wire to the cathode (copper half-cell).
The mass of the zinc electrode decreases.

Voltaic cells

At the cathode (positive electrode)



Electrons flow to the cathode from the anode.

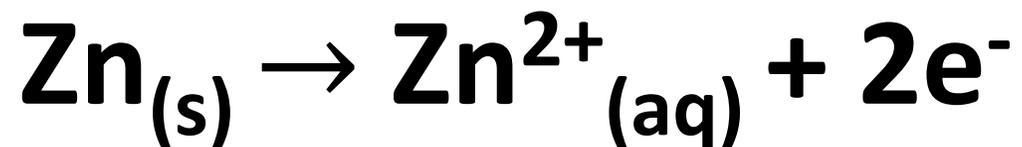
The $\text{Cu}^{2+}_{(\text{aq})}$ undergo reduction.



The mass of the copper electrode increases.

Voltaic cells

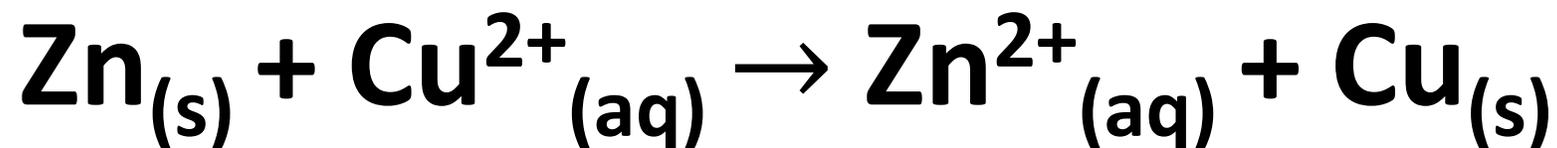
At the anode:



At the cathode:

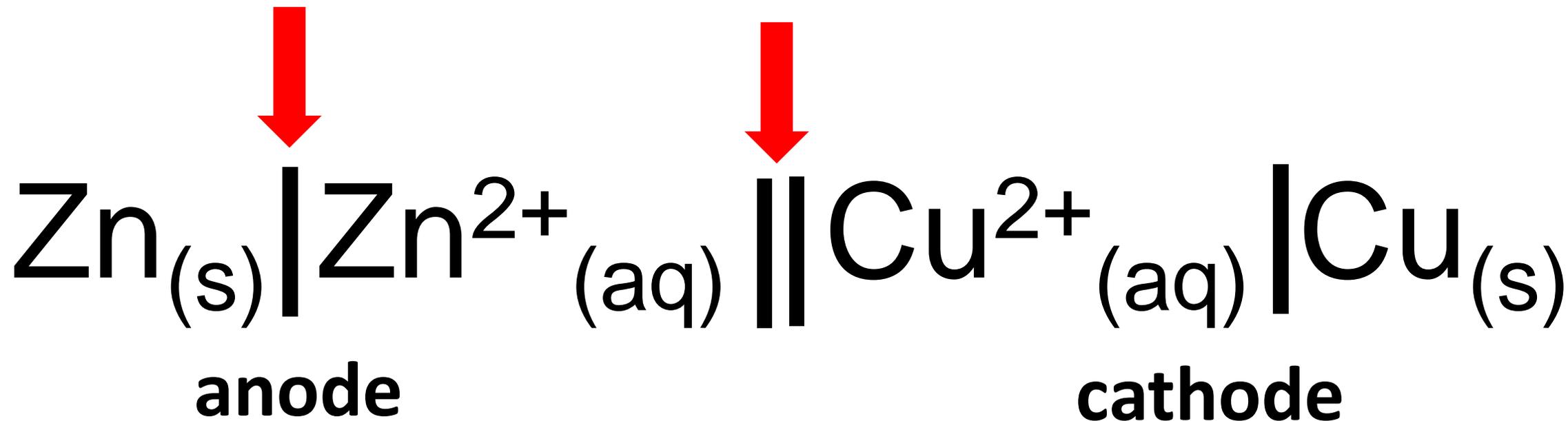


Overall equation:



Voltaic cells

phase boundary salt bridge



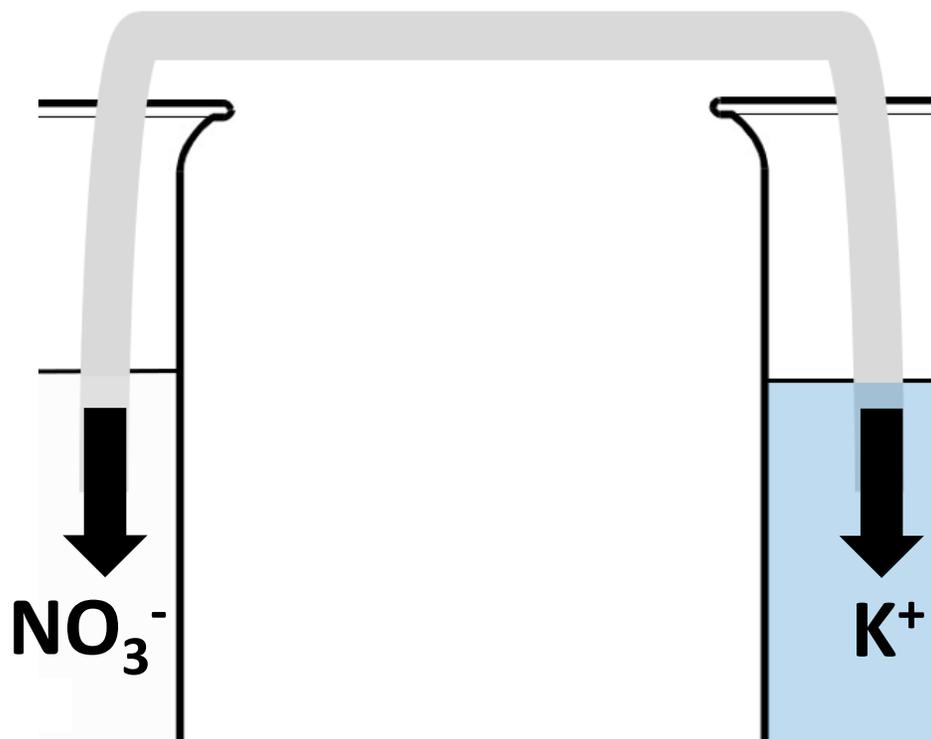
electron flow

Voltaic cells

The salt bridge allows movement of ions between half-cells which balances the charge and completes the circuit.

Salt bridge ($\text{KNO}_3(\text{aq})$)

Negative ions
(anions)
migrate to the
anode



Positive ions
(cations)
migrate to
the cathode

Summary

Oxidation occurs at the anode (negative electrode).
Reduction occurs at the cathode (positive electrode).
The metal higher up in the activity series is oxidised (it will be the anode).

Electric current is conducted in two ways:

- ion flow in the salt bridge
- electron flow in the wires

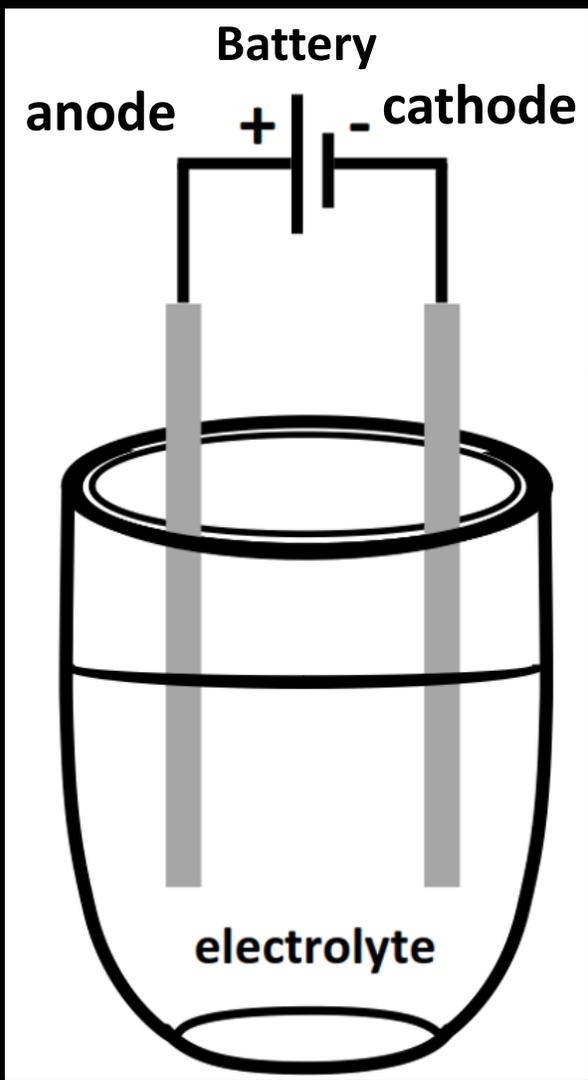
In the salt bridge, anions migrate to the anode and cations migrate to the cathode.

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Electrolytic cells

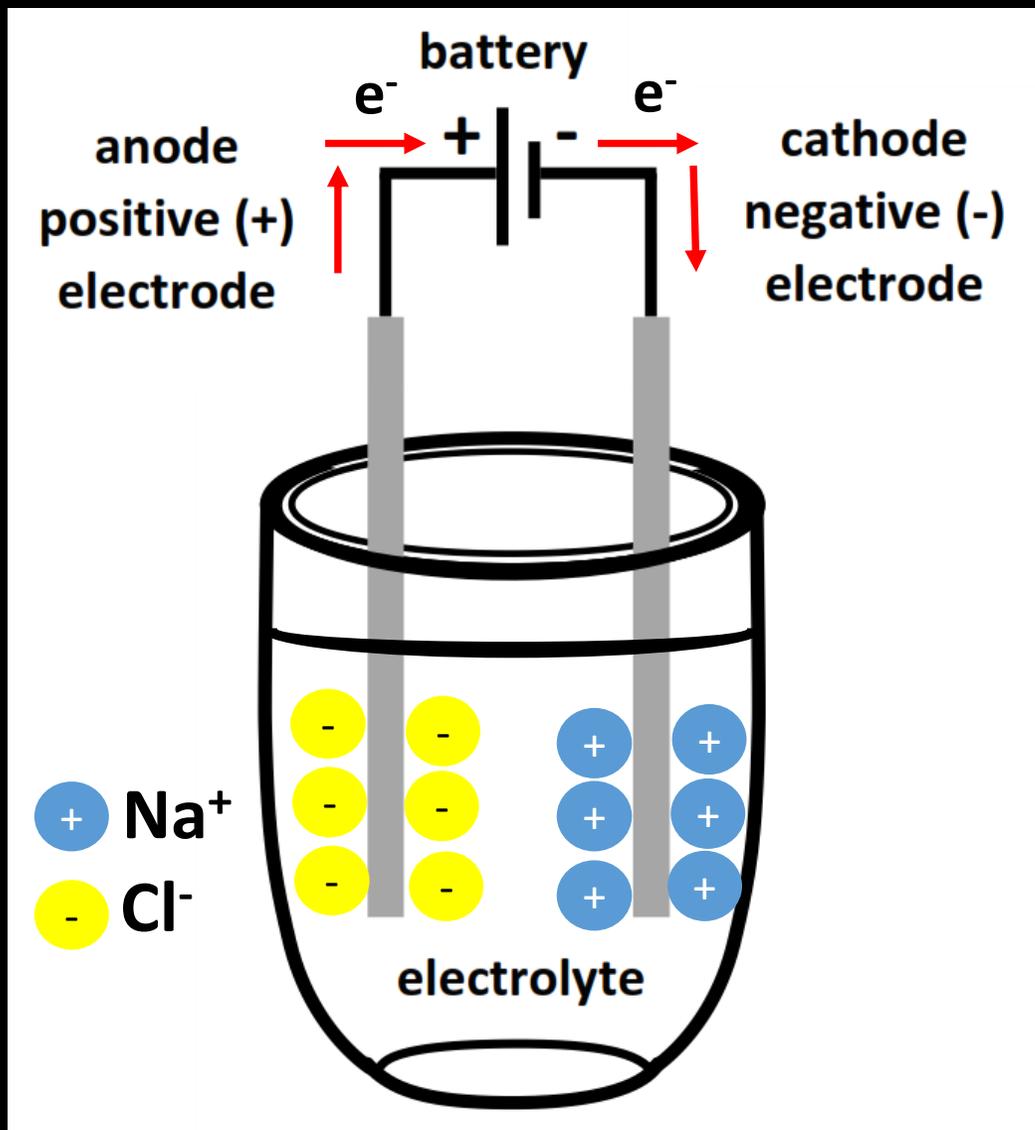
Electrolytic cells



heat ↑

Electrolytic cells are used to split ionic compounds into their constituent elements. An electrolytic cell uses a single container in which an ionic compound is heated until it melts (becomes molten). Once molten, the constituent ions are free to move around in the electrolyte. An electric current is supplied from a battery and the oppositely charged ions are attracted to the anode or cathode.

Electrolytic cells



At the anode (oxidation)



At the cathode (reduction)



The electrons move in the wires and ions move in the electrolyte.