

# Electrochemistry

## Chapter 9

- ### Terms for Electrochemistry
- **Oxidation** is the loss of electrons
  - **Reduction** is the gaining of electrons
  - OIL RIG
  - The substance that loses the electrons is the **reducing agents** (causes another substance to be reduced – gain electrons)
  - The substance that gains the electrons is the **oxidising agent** (causes another substance to be oxidised – lose electrons)

### Oxidation and Reduction

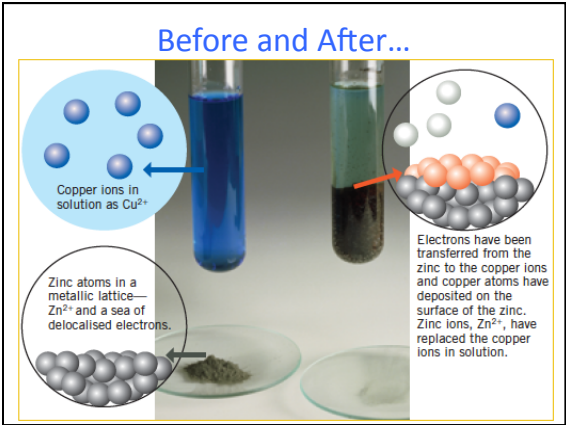
Oxidation

- $Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$
- Metallic zinc is oxidised to zinc ion. Metallic zinc is acting as reducing agent

Reduction

- $Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu(s)$
- Copper ion is reduced to copper metal. Copper ion is serving as an oxidising agent

Overall:  $2e^{-}$  transferred from  $Zn_{(s)}$  to  $Cu_{(s)}$

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


### Strength of reductant and oxidant...

- Zinc more reactive than copper.
- Therefore loses its electrons and is oxidised.
- Called a reducing agent or reductant.

Increasing reductant strength

Reductant

Mg  
Zn  
Fe  
Cu  
Ag

Increasing oxidant strength

Oxidant

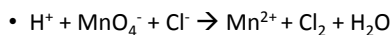
Mg<sup>2+</sup>  
Zn<sup>2+</sup>  
Fe<sup>2+</sup>  
Cu<sup>2+</sup>  
Ag<sup>+</sup>

- ### Old Transition Lenses
- Based on REDOX reaction involving Cu, Ag and UV light
  - $Cu + UV \rightarrow Cu^{2+} + e^{-}$
  - $Ag + e^{-} \rightarrow Ag$
  - Silver crystals caused glasses to go dark, reverse occurs when no UV light.

## Oxidation Numbers

- Oxidation numbers are used when it is difficult to identify which substance loses and gains electrons and how many...

Example:



- Here we need oxidation numbers!!

## Rules for assigning oxidation numbers

- Elements** have oxidation numbers of zero. Monatomic (noble gas), molecule or covalent network – example Ne, H<sub>2</sub>, O<sub>3</sub>, P<sub>4</sub> or C (diamond)
- The oxidation number of a **monatomic ion** is the charge on the ion. Example: Cu<sup>2+</sup> has o.n. of +2. In Cl<sup>-</sup> the o.n. = -1. **Elemental groups** e.g. group 1 = +1, group 2 = +2 etc...
- Oxidation number of **combined oxygen** is -2 except in peroxides (e.g. Na<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, o.n. = -1 and exception F<sub>2</sub>O o.n. = +2)

## Rules continued...

- Combined hydrogen** is always +1 except metal hydrides (e.g. NaH)
- The sum of all the oxidation numbers of the atoms in a molecule is **equal to its charge**. If no charge then equals zero example CO<sub>2</sub>
- In **polyatomic ion must equal to charge** on ion example SO<sub>4</sub><sup>2-</sup>
- Balance oxygen** by adding by adding water and **balance hydrogen** by adding hydrogen

## Summary

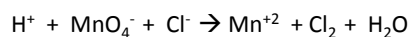
Species	Oxidation Number
Atoms in elemental state	0
Monatomic ions Group I metals in combined state Group II in combined state	Charge on the ion +1 +2
Oxygen in combined state Exception 1: Peroxide Na <sub>2</sub> O <sub>2</sub> or H <sub>2</sub> O <sub>2</sub> Exception 2: F <sub>2</sub> O	-2 -1 +2
Hydrogen in combined state Exception: Metal hydrides e.g. NaH	+1 -1
For polyatomic species the sum of the oxidation number	Charge on the ion

## Finding unknown oxidation numbers

- Problem:** What is the oxidation number of Mn in MnO<sub>4</sub><sup>-</sup>, the permanganate ion?
- Solution:** Mn is unknown  
Each O is -2 (rule 3)  
All of the oxidation numbers must add up to -1 (rule 5)  
Mn + 4(-2) = -1, **Mn = +7 in permanganate**
- Problem:** What is the oxidation number of Cr in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, potassium dichromate?
- Solution:** Cr is unknown  
Each K from Column I is +1  
Each O is -2 (rule 3)  
All the oxidation numbers add up to 0 (no charge on K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)  
2(+1) + 2 Cr + 7(-2) = 0, 2 Cr = 12, Cr = 12 / 2 = **+6**  
**Cr = +6 in potassium dichromate**

## Using oxidation numbers...

- Using oxidation numbers we will find the oxidising agent, the reducing agent, the number of electrons lost and gained, the oxidation half-reaction, the reduction half-reaction and the final balanced equation for:



## Using oxidation Numbers step by step..

- **Step I** – Find the oxidation number of each atom.
  - $\text{H}^+ + \text{MnO}_4^- + \text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + \text{H}_2\text{O}$   
 $+1 \quad (+7, -2) \quad -1 \quad +2 \quad 0 \quad (+1, -2)$
  - **Step II** – Which oxidation numbers change?  
 $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} \quad 2 \text{Cl}^- \rightarrow \text{Cl}_2$   
 $+7 \rightarrow +2 \quad 2(-1) \rightarrow 0$   
 5 electrons gained      2 electrons lost
- Identify oxidising and reducing agents.  
**(MnO<sub>4</sub><sup>-</sup> is the oxidising agent. It gained e<sup>-</sup> from Cl<sup>-</sup>)**  
**(Cl<sup>-</sup> is the reducing agent. It lost e<sup>-</sup> to MnO<sub>4</sub><sup>-</sup>)**

## continued....

- **Step III** - Electrons lost by a reducing agent must always equal electrons gained by the oxidising agent!  
**Balance electrons** in each half equ
- Therefore:  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   
 $5(2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-)$   
 $10 \text{Cl}^- \rightarrow 5\text{Cl}_2 + 10\text{e}^-$  (**oxidation half-eqn\***)
- And:  $\text{MnO}_4^- + 5\text{e}^- \rightarrow \text{Mn}^{2+}$   
 $2(\text{MnO}_4^- + 5\text{e}^- \rightarrow \text{Mn}^{2+})$   
 $2\text{MnO}_4^- + 10\text{e}^- \rightarrow 2\text{Mn}^{2+}$  (**reduction half-eqn**)

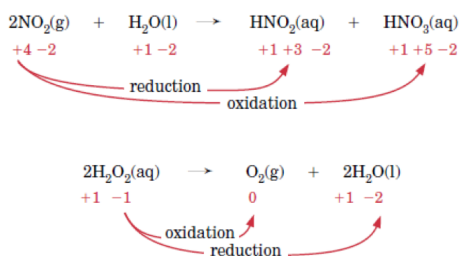
## continued...

- **Step IV** – Balance first half-reaction by adding H<sup>+</sup> ions and H<sub>2</sub>O molecules:  
 $16 \text{H}^+ + 2\text{MnO}_4^- + 10\text{e}^- \rightarrow 2\text{Mn}^{2+} + 8 \text{H}_2\text{O}$
  - **Step V** - Adding the oxidation half-reaction and reduction half-reaction the 10 electrons gained and lost cancel to give the overall reaction:  
 $16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$
- \* Half-equations refers to the reaction showing either the electron gain (reduction) or the electron loss (oxidation) step of the reaction.

## No change in oxidation numbers

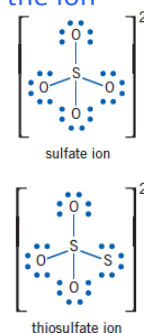
- Is no change in oxidation numbers then it is not a REDOX reaction...
- For example:  
 $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$   
 $+4 \quad -2 \quad +1 \quad +1 \quad -2 \quad +4 \quad -2$

## Disproportionation – single substance undergoes oxidation and reduction

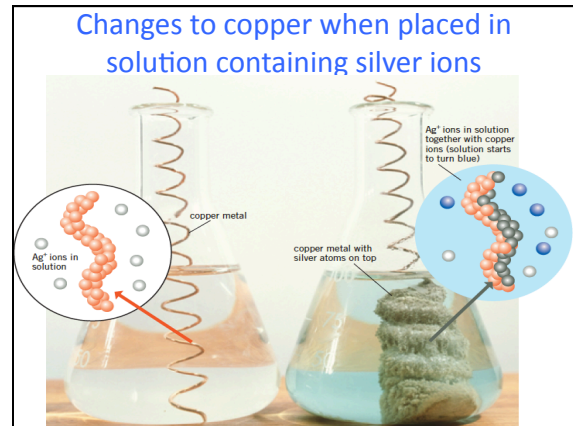


## Oxidation numbers does not always correlate to charge on the ion

- Example thiosulfate ion  $\text{S}_2\text{O}_3^{2-}$
- Here due to its shape one sulfur has oxidation number of +6 other has oxidation number of -2.
- This also occurs in some organic compounds and elements in group 15 to 17



Reactant	Product	Half-equation
<b>Oxidants</b>		
O <sub>2</sub>	H <sub>2</sub> O	O <sub>2</sub> (g) + 4H <sup>+</sup> (aq) + 4e <sup>-</sup> → 2H <sub>2</sub> O(l)
Cl <sub>2</sub>	Cl <sup>-</sup>	Cl <sub>2</sub> (g) + 2e <sup>-</sup> → 2Cl <sup>-</sup> (aq)
MnO <sub>4</sub> <sup>-</sup> purple	Mn <sup>2+</sup> pale pink	MnO <sub>4</sub> <sup>-</sup> (aq) + 8H <sup>+</sup> (aq) + 5e <sup>-</sup> → Mn <sup>2+</sup> (aq) + 4H <sub>2</sub> O(l)
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> orange	Cr <sup>3+</sup> green	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq) + 14H <sup>+</sup> (aq) + 6e <sup>-</sup> → 2Cr <sup>3+</sup> (aq) + 7H <sub>2</sub> O(l)
ClO <sup>-</sup>	Cl <sup>-</sup>	ClO <sup>-</sup> (aq) + 2H <sup>+</sup> (aq) + 2e <sup>-</sup> → Cl <sup>-</sup> (aq) + H <sub>2</sub> O(l)
H <sup>+</sup>	H <sub>2</sub>	2H <sup>+</sup> (aq) + 2e <sup>-</sup> → H <sub>2</sub> (g)
H <sub>2</sub> SO <sub>4</sub>	SO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> (l) + 2H <sup>+</sup> (aq) + 2e <sup>-</sup> → SO <sub>2</sub> (g) + 2H <sub>2</sub> O(l)
HNO <sub>3</sub>	NO <sub>2</sub> brown gas	NO <sub>3</sub> <sup>-</sup> (aq) + 2H <sup>+</sup> (aq) + e <sup>-</sup> → NO <sub>2</sub> (g) + H <sub>2</sub> O(l)
<b>Reductants</b>		
Zn	Zn <sup>2+</sup>	Zn(s) → Zn <sup>2+</sup> (aq) + 2e <sup>-</sup>
C	CO <sub>2</sub>	C(s) + 2O <sub>2</sub> (s) → CO <sub>2</sub> (g) + 4e <sup>-</sup>
H <sub>2</sub>	H <sup>+</sup>	H <sub>2</sub> (g) → 2H <sup>+</sup> (aq) + 2e <sup>-</sup>
Fe <sup>2+</sup> pale green	Fe <sup>3+</sup> orange	Fe <sup>2+</sup> (aq) → Fe <sup>3+</sup> (aq) + e <sup>-</sup>
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	CO <sub>2</sub>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (aq) → 2CO <sub>2</sub> (g) + 2e <sup>-</sup>



### REDOX - Producing electrical energy

- To do this an electrochemical cell must be built which transfers electrons from the reductant to the oxidant rather than allowing the reactants to come in direct contact.

### Electrolysis

To do this you have to separate the two half equations from one another and provide a path for the electrons to flow

But there is a problem.....

This problem can be solved

The solutions need to be linked so that ions can also flow to keep the net charge in each beaker equal.

This can be done by using a salt bridge

Or a porous disk in a tube linking the two solutions.

**Electrons are picked up by cations at the cathode (reduction occurs)**

Electrons move through the external circuit from anode to cathode. Copper is deposited at the cathode

$\text{Cu}^{+2} + 2e \rightarrow \text{Cu}$

**Electrons are lost at the anode (oxidation)**

Electrons move through the external circuit from anode to cathode. Zinc is dissolved at the anode.

$\text{Zn} \rightarrow \text{Zn}^{+2} + 2e$

**Electrochemical cell..**

- Two metals are called electrodes.
- Anode is where oxidation occurs (negative)
- Cathode is where reduction occurs (positive)
- Salt bridge contains electrolyte usually a saturated solution whose ions will not react. It's ions migrate from the salt bridge to neutralise increasing positive or negative solutions

**Summary**

- Oxidation takes place at the anode.
- Reduction takes place at the cathode.
- In an electrochemical cell the anode is negative—electrons are produced at this electrode.
- In an electrochemical cell the cathode is positive—electrons are consumed at this electrode.
- Electrons flow from the anode to the cathode through a wire in the external circuit.
- Anions are negative ions and migrate through the salt bridge towards the anode.
- Cations are positive ions and migrate through the salt bridge towards the cathode.
- Both the oxidant and its 'conjugate' reductant are normally present in a half-cell.

**Electrochemical cell using a gas**

- Electrochemical cell does not need to use metals – example reaction of Cl gas and potassium iodide to form Cl<sup>-</sup>(aq) and I<sub>2</sub>(aq)
- Inert electrodes (platinum or graphite) are needed to transfer electrons and not react.

Cathode (reduction)  
 $\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-(\text{aq})$

Anode (oxidation)  
 $2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2e^-$

**Four different types of half cells**

a metal / metal ion

b graphite or platinum / metal ion / metal ion

c graphite or platinum / non-metal / non-metal ion

d platinum electrode / non-metal gas / non-metal ion

### Electrochemical Cell Conventions

- Electrochemical cell that release energy spontaneously are call voltaic or galvanic cells. Those which require energy input in order to function are call electrolytic cells.
- Voltaic cells are often represented as follows for the reaction:  $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Solution concentration

Solution concentration

$$Zn / Zn^{2+} (1.0 M) // Cu^{2+} (1.0 M) / Cu$$

Anode  
Compartment  
components

Salt  
bridge

Cathode  
Compartment  
components

This is called an **electrochemical battery** or a **galvanic cell**

The electrons are forced to flow through a wire by separating the reducing agent from the oxidising agent.

Oxidation occurs at the **anode**

Reduction occurs at the **cathode**

$$+0.76 V = 0.00 V - E_{Zn^{2+}}^{\circ}$$

$$E_{Zn^{2+}}^{\circ} = -0.76 V$$

**Figure 22.10** This voltaic cell consists of zinc and hydrogen half-cells. What is the measured cell potential?

### Electric potential and standard reduction potentials

- Electric potential is the measure of the electron attracting power of an oxidising agent (electron gainer) in a half-cell.
- When two different oxidant – one with high electric potential and one with low electric potential → electrons are pulled towards half-cells with stronger oxidant
- Cell potential is the difference in electric potential of its two half cells

### Cell potential

- Also called emf, electromotive force or voltage of cell.
- Referred to as the potential difference and is measured in volts (V)
- Measured by a voltmeter
- E symbol for electric potential
- $E_{cell}$  is symbol for cell potential

### $E_{\text{cell}}$

- Depends on concentration of the electrolytes, the pressure of any gases and the temperature.
- $E^{\circ}_{\text{cell}}$  is standard cell potential – when conditions are 1 mol L<sup>-1</sup> conc of dissolved substances, 101.3kPa(1atm) pressure and 25°C

### Electrical Potential

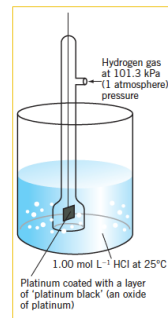
- Electrical potential is measured in volts and indicates the tendency of electrons to move from one substance to another.
- Potential depends on a variety of factors such as the concentration of reactant materials, temperature, gas pressures and the nature of the materials involved.

### Reduction Potentials

- Standard Reduction Potentials (measure the tendency of a substance to gain electrons) are determined at 25°C, 1M conc, 1 atm pressures
- They are compared to hydrogen ion's tendency to be reduced (gain electrons) to **hydrogen gas** ( $2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$ ) which is assigned a potential of 0.00 volts.
- Substances which **gain electrons better than  $\text{H}^+$**  ion are assigned positive potentials. Those which **gain electrons more poorly than  $\text{H}^+$**  ion are assigned negative potentials.

### Standard hydrogen half-cell

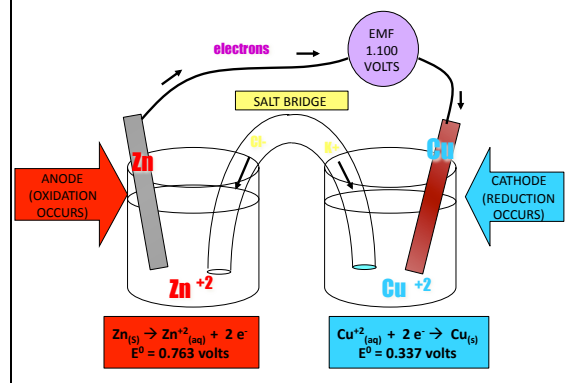
- $2\text{H}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) \quad E^{\circ} = 0 \text{ V}$
- This is used as a reference to compare other half-cells



### Standard Reduction Potential

$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54
$\text{NiO}_2(\text{s}) + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$	+0.49
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{SO}_4^{2-} + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}$	+0.17
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.36
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76

### An electrochemical cell



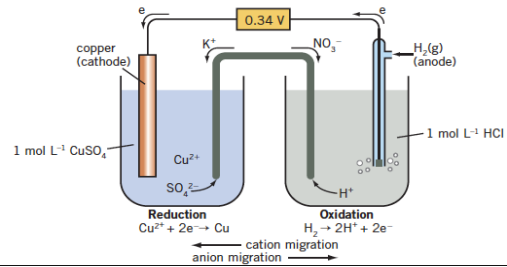
### Calculating $E^\circ_{\text{cell}}$

standard cell potential =  $\frac{\text{standard reduction potential of the half-cell containing the reacting oxidant}}{\text{standard reduction potential of the half-cell containing the reductant}}$

or  $E^\circ_{\text{cell}} = E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}}$

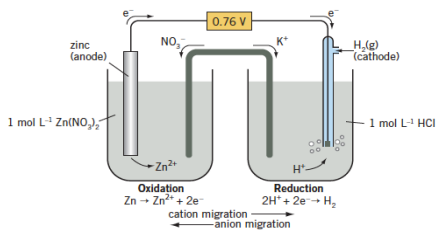
### Copper and hydrogen

- Copper gains electrons from hydrogen and has a positive reduction potential of + 0.34V



### Zinc and hydrogen

- Zinc is oxidised, therefore has a lower reduction potential than hydrogen. Given negative reduction potential -0.76volts



### Generalisation with Standard Reduction Potential table

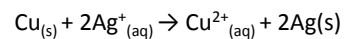
- Oxidants are on left reductants on right
- The more positive the reduction potential the stronger the oxidant
- The more negative the reduction potential the stronger the reductant
- Equilibrium arrows are used to represent the half-cell reactions because these reactions can proceed in both directions, depending what is present in the other half-cell.
- The cell potential of any combination of these half-cells is calculated from the half-cell reduction potentials using the expression:

$$E^\circ_{\text{cell}} = E^\circ_{\text{half-cell containing the oxidant}} - E^\circ_{\text{half-cell containing the reductant}}$$

### Generalisations continued...

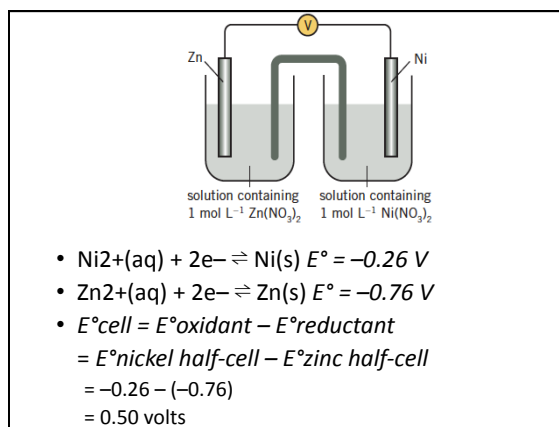
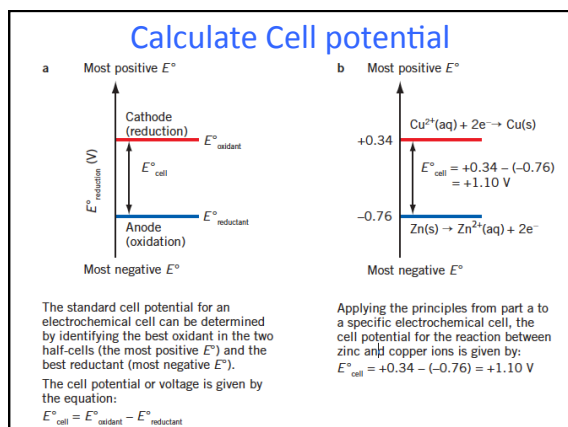
- Oxidants generally only react with reductants that have a more negative  $E^\circ$  (standard reduction potential) value.
- The greater the difference in  $E^\circ$  values the more likely the reaction is to proceed in the direction predicted. The greater the difference in  $E^\circ$  values, the larger the equilibrium constant for the reaction.
- Even when there may be a large difference in standard reduction potentials, the cell potential does not predict how fast the reaction will take place. It is possible that the rate of reaction at 25° is very slow.

### Calculate cell potential



- From standard potential table
- $\text{Ag}^+_{(aq)} + e^- \rightleftharpoons \text{Ag}_{(s)} E^\circ = +0.80 \text{ V}$
- $\text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}_{(s)} E^\circ = +0.34 \text{ V}$
- $E^\circ_{\text{cell}} = E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}}$
- $E^\circ_{\text{cell}} = +0.80 - (+0.34) = 0.46\text{V}$





### Predicting whether reactions will take place

- Redox reaction will occur when one reactant is an oxidant and other is a reductant
- Difference in  $E^\circ$  values
- Greater the  $E^\circ$  value the larger the equilibrium constant for the reaction (no effect on reaction rate)
- Must be under standard conditions of temperature and pressure

### Standard Reduction Potentials can be used to explain....

- Metal displacement reactions
- Halogen displacement reactions
- Reactions of metals with water—any metal with a reduction potential less than around  $-0.4 \text{ V}$  will react with water (even if it is very slow)
- Reactions of metals with acids—metals with a reduction potential ( $E^\circ$ ) less than  $0.0 \text{ V}$  will react with  $\text{HCl}$  and dilute  $\text{H}_2\text{SO}_4$  to form  $\text{H}_2$ . Metals with a reduction potential ( $E^\circ$ ) less than  $0.95 \text{ V}$  will react with reasonably concentrated nitric acid to form  $\text{NO}_{(\text{g})}$  (which will immediately oxidise to brown  $\text{NO}_{2(\text{g})}$  in the presence of air).

### Standard Reduction Potentials can be used to explain....

- Many substances will only react if acid is present, for example  $\text{MnO}_4^-_{(\text{aq})}$  and  $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$
- In an aqueous solution the very weak oxidant metal ions will not participate in a redox reaction. Cations of group 1 and 2 metals together with  $\text{Al}_{3(\text{aq})}$  can be ignored when predicting redox reactions involving aqueous solutions.

### Standard Reduction Potentials can be used to explain....

- Nitrate ions and sulfate ions will not participate in redox reactions unless they are present as reasonably concentrated nitric acid or sulfuric acid:
- Nitric acid—when a metal reacts with the concentrated acid, nitrogen dioxide is formed:
  - $\text{NO}_3^-_{(\text{aq})} + 2\text{H}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{NO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$
- When a metal reacts with less concentrated acid ( $4\text{--}6 \text{ mol L}^{-1}$ ), nitrogen monoxide forms:
  - $\text{NO}_3^-_{(\text{aq})} + 4\text{H}^+_{(\text{aq})} + 3\text{e}^- \rightarrow \text{NO}_{(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$
- Sulfuric acid—when a metal reacts with concentrated sulfuric acid, sulfur dioxide forms:
  - $\text{SO}_4^{2-}_{(\text{aq})} + 4\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightarrow \text{SO}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$

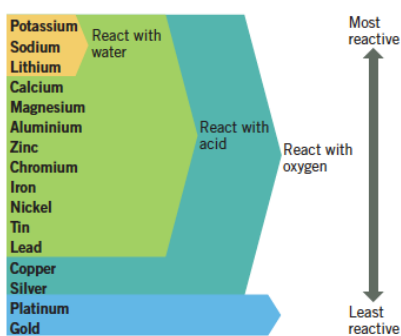
### Standard Reduction Potentials can be used to explain....

- Water can act as both an oxidant and a reductant. Standard reduction table only provides the  $E^\circ$  values for standard conditions.
- Water can also behave as an oxidant and a reductant in a neutral solution and in the absence of gases at 101.3 kPa pressure. While the reduction and oxidation half-equations remain the same, the values of the reduction potentials change.
- For example in an aqueous neutral solution ( $10^{-7} \text{ mol L}^{-1} \text{ H}^+$  and  $\text{OH}^-$ ) the relevant reduction potentials are:
  - $\text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}_{(\text{l})} \quad E = +0.82 \text{ V}$
  - $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})} \quad E = -0.41 \text{ V}$
- For this course of study the differences in these values from those in the table of standard reduction potentials will not be important

### Redox Reaction – volumetric analysis

- Reactions of acids and metals
- Metal displacement reactions
- Redox reactions in solution

### Reactions of Metals



### Redox reactions in solutions

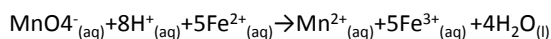
- Some redox reactions that are important for chemical analysis (determining how much of a particular chemical is present in a sample) include those involving solutions of potassium permanganate, potassium dichromate, iron (II) salts and the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ .

The half-equations for these reactions are:

- $\text{MnO}_4^-_{(\text{aq})} + 8\text{H}^+_{(\text{aq})} + 5\text{e}^- \rightarrow \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})}$  reduction
- $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})} + 14\text{H}^+_{(\text{aq})} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}_{(\text{aq})} + 7\text{H}_2\text{O}_{(\text{l})}$  reduction
- $\text{Fe}^{2+}_{(\text{aq})} \rightarrow \text{Fe}^{3+}_{(\text{aq})} + \text{e}^-$  oxidation
- $\text{C}_2\text{O}_4^{2-}_{(\text{aq})} \rightarrow 2\text{CO}_{2(\text{g})} + 2\text{e}^-$  oxidation

### Redox Titrations

- Equivalence point of redox titration occurs when one of oxidant or reductant is used up.



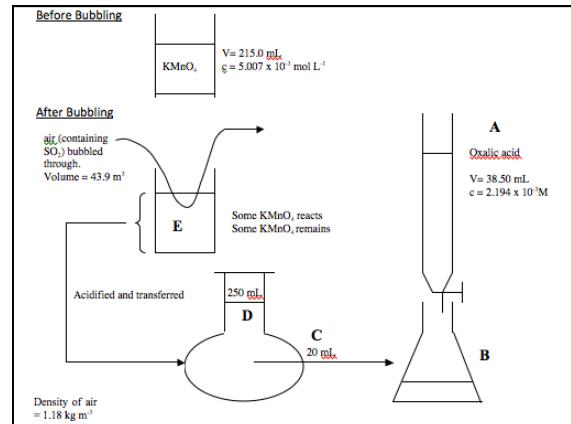
- It is possible to use indicators or voltmeters to measure the equivalence point but some of the substances involved have specific colours for example potassium permanganate is purple and iron (II) is colourless

### Back titration

- The concentration of the atmospheric pollutant sulfur dioxide ( $\text{SO}_2$ ) can be found by bubbling air through a dilute  $\text{KMnO}_4(\text{aq})$  solution of known concentration.
- $5\text{SO}_{2(\text{g})} + 2\text{MnO}_4^-_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow 5\text{SO}_4^{2-}_{(\text{aq})} + 2\text{Mn}^{2+}_{(\text{aq})} + 4\text{H}^+_{(\text{aq})}$
- The concentration of the remaining  $\text{KMnO}_4(\text{aq})$  can be found by titration with standardised oxalic acid. This allows the amount of  $\text{KMnO}_4$  reacting with sulfur dioxide to be found and thus its concentration in the air sample can be calculated.

## Procedure

- 43.9 m<sup>3</sup> of SO<sub>2</sub> polluted air was bubbled through 215.0 mL of 5.007 x 10<sup>-3</sup> mol L<sup>-1</sup> KMnO<sub>4</sub>(aq).
- The unreacted KMnO<sub>4</sub> was acidified and diluted to a volume of 250.0 mL.
- 20.00 mL samples of this KMnO<sub>4</sub> solution were titrated to equivalence with 38.50 mL of 2.194 x 10<sup>-3</sup> mol L<sup>-1</sup> oxalic acid solution.
- What is the concentration of the pollutant SO<sub>2</sub>(g) in ppm if the air has a density of 1.18 kg m<sup>-3</sup>



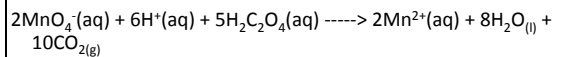
## Answer

- Before Bubbling
- n(KMnO<sub>4</sub>) = cV = 0.2150 x 5.007 x 10<sup>-3</sup> = 1.0765 x 10<sup>-3</sup> (1 mark)

## After Bubbling

$$\mathbf{A:} \quad n(\text{oxalic acid}) = cV = 0.3850 \times 2.194 \times 10^{-3} = 8.4469 \times 10^{-5}$$

Titration reaction:



$$\mathbf{B:} \quad n(\text{KMnO}_4) = (2/5) \times n(\text{oxalic acid}) = (2/5) \times 8.4469 \times 10^{-5} = 3.3788 \times 10^{-5}$$

$$\mathbf{C:} \quad c(\text{KMnO}_4) = n/V = 3.3788 \times 10^{-5} / 0.020 = 1.6894 \times 10^{-3} \text{ M} = c(\text{KMnO}_4) \text{ at}$$

$$\mathbf{D:} \quad n(\text{KMnO}_4) = cV = 1.6894 \times 10^{-3} \times 0.250 = 4.2235 \times 10^{-4} = n(\text{KMnO}_4) \text{ at E}$$

## Moles of SO<sub>2</sub> reacting

$$n(\text{KMnO}_4)_{\text{reacting with SO}_2} = n(\text{KMnO}_4)_{\text{Before Bubbling}} - n(\text{KMnO}_4)_{\text{After Bubbling}} = 1.0765 \times 10^{-3} - 4.2235 \times 10^{-4} = 6.5416 \times 10^{-4}$$

$$n(\text{SO}_2) = (5/2) \times n(\text{KMnO}_4)_{\text{reacting with SO}_2} = (5/2) \times 6.5416 \times 10^{-4} = 1.6354 \times 10^{-3}$$

$$m(\text{SO}_2) = n \times M = 1.6354 \times 10^{-3} \times 64.07 = 1.0478 \times 10^{-1} \text{ g} = 104.78 \text{ mg}$$

- This mass is contained in 43.9 m<sup>3</sup> of air

$$\text{mass(air)} = \text{density(air)} \times V = 1.18 \times 43.9 = 51.802 \text{ kg}$$

$$c(\text{SO}_2)_{\text{ppm}} = m(\text{SO}_2)_{\text{mg}} / \text{mass(air)}_{\text{kg}} = 104.78 / 51.802 = \mathbf{2.02 \text{ ppm}}$$