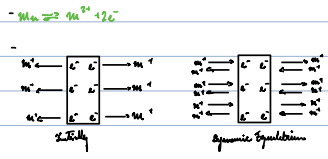


Electrochemical cells

Redox equilibria and electrochemical cells

- redox equilibria is established when a piece of metal is placed in an aqueous solution of its cations.
- the forward reaction involves some of the atoms moving to the aqueous solution as hydrated metal ions.
 - this will mean that there will be a layer of electrons on the surface of the metal.
 - this occurs at the anode.
 - E.g. $Mg \rightarrow Mg^{2+} + 2e^-$
 - 2 can also be written as "n".
- the reverse reaction involves hydrated metal ions in the solution accepting electrons from the surface of the metal.
 - they will be deposited as metal atoms on the surface of the piece of metal.
 - this is a reduction process (at a cathode).
 - E.g. $Mg^{2+} + 2e^- \rightarrow Mg$
- redox equilibrium is established when these two rates of the forward and backward reaction are equal.



- the position of the equilibrium depends on a number of factors:
 - particularly the reactivity (reducing strength) of the metal.
 - E.g. when a piece of zinc, a relatively reactive metal, is placed in an aqueous solution of zinc ions, the equilibrium lies to the right-hand side:
 - $Zn \rightleftharpoons Zn^{2+} + 2e^-$
 - this small change in the concentration of zinc, leaving the surface with a negative charge due to the presence of a layer of electrons.
 - the sum of the zinc detaches decreased due to the fact that an atom has moved to the solution as an ion.
 - this will increase the concentration of the zinc in the solution.
 - zinc reacts with copper, which is a less reactive metal than zinc, when it is placed in a solution of copper (II) ions.
 - $Cu \rightleftharpoons Cu^{2+} + 2e^-$
 - the equilibrium will be to the left.
 - the reaction involves the deposition of copper (II) ions on copper atoms, and so the copper surface will be positively charged.
 - more of copper passes in solution and concentration of the solution decreases.
 - in case of the redox equilibrium metal before, the solution and the metal will have opposite charges.
 - therefore, there will be a pd, because a non-electrode potential.
 - the pd is between the solution and the metal.
 - the metal in the solution is called an electrode.
 - when the metal is in a solution of its own ions it's called a half-cell.
 - a voltaic cell (e.g. Daniell cell) can be made by connecting two half-cells with a high-resistance voltmeter and a salt bridge.

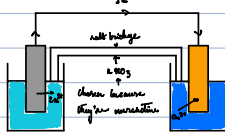
Types of half-cells

- the pd between an electrode and a solution isn't limited to metals, but also applies to non-metals.
 - there are three types of common half-cells:
 - the metal in a solution with its ions.
 - the inert electrode (e.g. graphite or platinum (they don't take part in the redox equilibrium)) immersed in an aqueous solution containing two ions from the same element.
 - E.g. ions from iron: Fe^{2+} and Fe^{3+} .
 - the gas bubbling over an inert electrode immersed in an aqueous solution containing the ions of the gas.
 - E.g. standard hydrogen electrode which has an equilibrium between hydrogen ions and hydrogen molecules.
 - two different half cells can be combined to form a voltaic cell.
 - along the flow of electrons from the reducing agent (substance being oxidised), to the oxidising agent (substance being reduced).
 - the electrode potential of an element depends on three factors:
 - the nature of the electrode.
 - the concentration of the ions in solution.
 - the temperature of the solution.
- standard thermodynamic conditions are 298K, 100kPa, and 1 mol dm⁻³.

- one amount of metal decrease affect the electrode's potential.

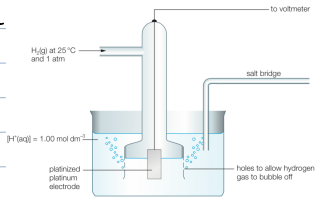
- the salt bridge

- The salt bridge is simply a piece of paper soaked in saturated potassium nitrate (KNO_3).
- The goal is that of maintaining the charges balanced in the two solutions of the Daniel cell and voltaic cells.
- The dissolution of zinc from the zinc in the Daniel cell will result in an increase in the concentration.
 - On the other hand, the deposition of copper will cause its concentration to decrease.
- The dissolution of zinc will mean that there will be a positive surplus in the solution.
 - $[Zn^{2+}]$ increases
- The deposition of copper will mean that the solution will be a negative surplus.
 - $[Cu^{2+}]$ decreases
- If it weren't for the salt bridge, then the reactions would eventually stop.
 - Therefore, the concentration of the positive ions (Zn^{2+} & Cu^{2+}) are conserved.
 - Negatively charged ions will go to the zinc solution (NO_3^- from salt solution).
 - For every two NO_3^- ions that go to the zinc solution, one Zn^{2+} ions goes to the salt bridge.
 - Positively charged ions will go to the copper solution (K^+ from the salt solution).
 - For every two K^+ ions that leave the salt bridge, one sulfate ion SO_4^{2-} ions enter the salt bridge.



- the standard hydrogen electrode (SHE)

- The pd between the solution and the electrode can't be measured.
- This is because if a voltmeter is connected to the electrode and then it's placed in the solution, then another redox equilibrium and electrode potential will be created.
- Therefore, the pd can't be between the two electrodes.

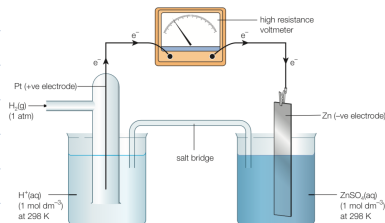


- The standard electrode known as (SHE) is hydrogen gas in equilibrium with hydrogen ions.
 - It gives a standard potential of zero.
- The SHE is maintained by a stream of pure hydrogen gas bubbling over a platinum electrode coated with platinum black, and immersed in a solution of HCl .
 - The platinum electrode has the function of:
 - It acts as an inert metal conductor to the hydrogen gas/ion equilibrium.
 - Due to platinum being unreactive.
 - The surface acts as a heterogeneous catalyst for the adsorbed hydrogen gas on its surface.
 - Allows standard electrode potentials to be measured quickly.
 - The equilibrium is set up between the gas adsorbed on the electrode and the hydrogen ions in the acid solution.

- Standard electrode potentials

- The standard electrode potential is defined as the pd between a standard hydrogen electrode and a metal immersed in a solution of its own ions

- E.g apparatus:



- Overall reaction is: $2\text{Cu} + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2$

- This gives the AEP of zinc as -0.79V .

- The negative sign is because it's the electron donor (reducing agent).

- Sign conventions

- The half-equation is written as a reduction process:

- Oxidizing agent $+ \text{e}^- \rightleftharpoons$ reduced species



- If $E^\circ > 0$, then reduction takes place.

- This means that it has a tendency to go to the right of the equation.

- If $E^\circ < 0$, then the reaction is oxidizing.

- This means a shift to the left of the equation.

- The only $E^\circ = 0$ reaction is for the standard hydrogen electrode.

- This indicates that the redox equilibrium is a "perfect" equilibrium ($\text{H}_2 + 2\text{e}^- \rightleftharpoons 2\text{H}^+$).

- Cell potential and emp

- To measure the electrode potential there must be no charge flow.

- This is so that the concentrations of the solution in the half-cells don't change.

- If charge will change the electrode potential in the half-cell.

- If high resistance voltmeter is used instead.

- This means that the current is essentially zero.

- Cell potential is: emf difference in electrode potentials (with current).

- The emp is: the potential difference between the two terminals of the voltaic cell (without current).

- em electrochemical series

- most negative E° values \rightarrow most positive E° values

readily release electrons \rightarrow readily accept electrons

best reducing systems \rightarrow best oxidizing agent

most easily oxidised \rightarrow most easily reduced

- Predicting cell reaction and voltage

- When finding the potential of a cell, one of the reactions will always have to be oxidation, and the other reduction.

- The half equation with the lowest electrode potential will be found to undergo reduction.

- Use cell potential in the name of the electrode potentials (including their signs).

- Equation: $E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

- E° in the cathode, E°_{anode} in the anode.

- Even when multiplying the electrons to cancel out, it doesn't change the E° value of the equation.

- If positive E° value implies that the reaction is favored thermodynamically.

- Cell diagrams



- Double line in the salt bridge.

- The equation shows the voltaic cell and its half equations:



- Equation for potential is: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

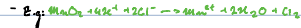
- Non-standard conditions

- Electrode potentials are only for standard conditions.

- Electrode potential for oxidizing agents in acid conditions refer to 1 mol dm^{-3} concentrations ions, 1 mol dm^{-3} (pH=0).

- Hence H^+ ion concentration measures the oxidizing strengths of the oxidizing agents.

- Subtracting the electrode potential of the half cell.



- $E^\circ_{\text{cell}} = 0.15\text{V}$

- Since the E° value is negative, that means that it's non-spontaneous under standard conditions.

- Although, with the H^+ ions the E° will become positive.

- Redox equilibrium: $\text{Ox} + e^- \rightleftharpoons \text{Red}$

- Reducing the concentration of the reduction species or increasing the concentration of oxidation species will mean that the electrode potential will become more positive.
- This is because there are less electrons.

- The Nernst equation

- The equation is to calculate the potential of non-standard cells.



$$E_{\text{cell}} = E^\ominus - \frac{2.303RT}{nF} \log_{10} \frac{[\text{M}^{n+}]}{[\text{M}]} \rightarrow E_{\text{cell}} = E^\ominus - \frac{0.059}{n} \log_{10} [\text{M}^{n+}] \rightarrow E_{\text{cell}} = E^\ominus - \frac{2.303RT}{nF} \log_{10} \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

- R is the gas constant (8.315 J mol⁻¹ K⁻¹), F is Farad constant, n: # of electrons, and T: Temp (Kelvin).

- Worked example

- Daniel cell, Temp = 298 K, $[\text{Zn}^{2+}] = 0.005 \text{ M}$, $[\text{Cu}^{2+}] = 1.5 \text{ mol dm}^{-3}$

$$E_{\text{cell}} = 1.1 - \frac{0.059}{2} \log_{10} \frac{0.005^2}{1.5^2} = 1.17 \text{ V}$$

- Concentration cells

- Concentration cells are voltaic cells that have electrodes made of the same element.
- Although, the difference is that there are different concentrations of the electrolyte in the anode & cathode.
- Cell potential is calculated with: $E = E^\ominus + \frac{0.059}{n} \log_{10} \frac{C_2}{C_1}$.
- C_2 is the concentration of the anode, while C_1 is the concentration of the cathode.

- Cell spontaneity

$$\Delta G^\ominus = -nFE_{\text{cell}}^\ominus$$

- The equation shows the spontaneity of a reaction.
- When the electrode potential of a cell is positive, the Gibbs free energy equation will be negative meaning that it's thermodynamically spontaneous.
- n = Number of electrons, F = Faraday's constant, and E^\ominus is the electrode potential of the cell.

- Predicting if a cell is spontaneous

ΔG^\ominus	E^\ominus	Reaction under standard thermodynamic conditions
Negative	Positive	Forward reaction is spontaneous, formation of products favoured, $K_c > 1$
Positive	Negative	Forward reaction is non-spontaneous, formation of reactants favoured, $K_c < 1$
Zero	Zero	Reactants and products favoured equally, $K_c = 1$

- Worked example



$$E^\ominus = 1.33 - 0.8$$

$$E^\ominus = 0.57 \text{ V}$$

- Cell is spontaneous.

- Microbial fuel cell

- A microbial fuel cell (MFC) is a bioelectrochemical system that drives a current by using and copying bacterial interactions in nature.
- It converts chemical energy to electrical energy by the catalytic reaction of micro-organisms, usually bacteria.

- MFCs can be classified into two groups:

- those that use mediators.

- The mediator is a chemical that transfers electrons from bacteria in the cell to the anode.
- E.g mediator are: humic acid, methyl blue, and thionine.

- those that don't use mediators.

- The bacteria have electron transfer proteins, such as cytochromes, on their outer membrane that can transfer electrons directly to the anode.

- Electrolysis

- Electrolysis of aqueous solutions

- Water will undergo electrolysis.

- This occurs because the water molecules will dissociate in water.



- The water's ions will compete with the ions of an electrode for the control of the ions.

- If the reduction of sodium chloride is concentrated, chlorine is produced at the anode, and hydrogen is produced at the cathode.

- If the solution is dilute, then hydrogen is produced at the cathode and oxygen is produced at the anode.

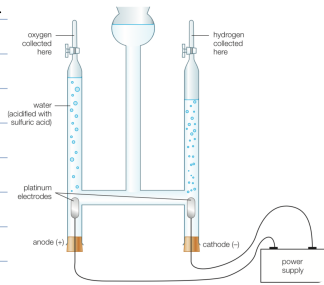
- The rules for the electrolysis of an aqueous solution are:

- Metals, if available, are discharged at the cathode.

- Hydrogen is produced at the cathode only.
- Non-noble gases from hydrogen, are produced at the anode.
- Reactive metals, metals above hydrogen, are not discharged.
- The products depend on the concentration of the electrolyte.
- If halide ions are present in reasonable concentration they will discharge faster than hydroxide ions.
- If they're not present, hydroxide ions are discharged more readily than other anions.

- In electrolysis of water:

- When very dilute sulfuric acid (H_2SO_4) is electrolysed, one volume of oxygen gas is collected over the anode, and two volume of hydrogen gas are collected over the cathode.
- At the anode, the hydroxide ions (from H_2O) are discharged in preference to the sulfate ions.
- They will form water.
- At the cathode, hydrogen ions are discharged by accepting electrons to form hydrogen molecules:
- Anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
- Cathode: $4e^- + 4H^+ \rightarrow 2H_2$
- The concentration of water decreases as time to replace the ions, increasing the concentration of H_2SO_4 .



- When inert electrodes are used during electrolysis:

- Cations with more positive E° reduction values will be discharged first at the cathode.
 - Anions with more negative E° oxidation values will be discharged first at the anode.
- or
- Anions with more positive E° oxidation values will be discharged first at the anode.
 - Cations with more negative E° reduction values will be discharged first at the cathode.

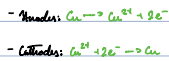
- Steps to determine the reactions:

- Write the ions present in the solution (H^+ and OH^- ions present due to water).
- Write all the reduction reactions of the ions.
- Compare the E° reduction values and identify which reactions in most likely.
- Repeat the procedure for the possible reactions occurring at the anode.
- Decide which reaction will take place by comparing the E° reduction or E° oxidation values.

- Faraday's Law

- When a solution of aqueous copper (II) sulfate is electrolysed using copper electrodes, the copper anode slowly dissolves away and the copper cathode slowly gains a deposit of copper.
- Any impurities are collected at the bottom.

- Reactions:



- Diagram:

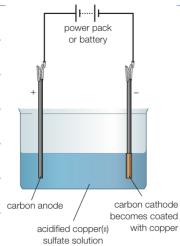


Figure 19.18 Apparatus for the electrolysis of copper(II) sulfate solution

- The amount of copper deposited depends on time for electrolysis, and the current.

- Relationship is directly proportional.

- Faraday's first law

- The mass of an element produced during electrolysis is directly proportional to the current.

- Faraday's second law

- When the same amount of electricity is passed through different electrolytes, the mass of the substance is equivalent to the substance's chemical equivalent.

- They form volume number ratios when they're divided by their common volume.

- Electroplating

- Electroplating is when an object has an external layer of a more valuable metal is placed on another substance.

- The deposit that is to be electroplated acts as the cathode.

- To have electroplating, a metal bar to be used as an anode.

- The object has to be isolated for an even electroplating.

