

Electrochemical cells

Redox equilibrium and electrode potentials

- Redox equilibrium is established when a piece of metal is placed in an aqueous solution of its cation.
- 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.



- 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).



- Redox equilibrium is established when these 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 iron ions, the equilibrium lies to the right-hand side:



- The overall change is the dissolution of zinc, leaving the surface with a negative charge due to the presence of a layer of electrons.

- The sum of the zinc electrons removed due to the fact that an atom has moved to the solution as an ion.

- This will increase the concentration of the ion in the solution.

- An opposite will occur with copper, which is a less reactive metal than zinc, when it's placed in a solution of copper (II) ions.



- The equilibrium will lie to the left.

- The reaction involves the deposition of copper (II) ions as copper atoms, and so the copper surface will be positively charged.

- More of copper power increases and concentration of the solution decreases.

- In case of the redox equilibrium stated before, the solution and the metal will have opposite charges.

- Therefore, there will be a potentiometer or an electrode potential.

- This pot. 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 whole 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 pot. 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:

- If metal in a solution with its ions.

- The metal electrode (e.g. graphite or platinum (they don't take part in the redox equilibrium)) immersed in an aqueous solution containing the ion from the same element.

- E.g. iron from ions: Fe^{2+} and Fe^{3+} .

? - If you bubble over an metal electrode immersed in an aqueous solution containing the ion of the gas.

- E.g. standard hydrogen electrodes 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 (metals being oxidized) to the oxidizing agent (metals being reduced).

- The electrode potential of an element depends on three factors:

- The nature of the element.

- Standard Thermodynamic conditions are 298K, 100kPa, and 1 mol dm⁻³.

- The concentration of its ions in solution.

- The temperature of the solution.

- the amount of metal disolve affect the electrode potential.

- the salt bridge

- the salt bridge is simply a piece of paper soaked in saturated potassium nitrate (KNO_3).

- the goal is that maintaining the charges balanced in the two solutions of the Daniell cell and voltaic cells.

- the dissolution of zinc from the zinc in the Daniell cell will result in an increase in the concentration

- on the other hand, the deposition of copper will cause its ion concentration to decrease.

- the dissolution of zinc will mean that there will be a positive napher in the solution.

- $[Zn^{2+}]$ increases

- the deposition of copper will mean that the solution will be a negative napher.

- $[Cu^{2+}]$ decreases

- if it wasn't for the salt bridge, then the reaction would eventually stop.

- therefore, the concentration of the positive ions (Zn^{2+} & Cu^{2+}) are constant.

- 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+} ion goes to the salt bridge.

- positively charged ions will go to the copper solution (Cu^+ from the salt solution).

- for every two Cu^+ ions that leave the salt bridge, one sulfate ion (SO_4^{2-}) ion enters the salt bridge.

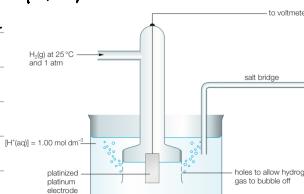


- the standard hydrogen electrode (SHE)

- the pd between the solution and the electrodes can't be measured.

- this is because if a voltmeter is connected to the electrodes 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 (NHE) is hydrogen gas in equilibrium with hydrogen ions

- this gives a electrode potential of zero.

- the NHE 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 connector to the hydrogen gas/ion equilibrium.

- due to platinum being inert.

- the surface acts as a heterogeneous catalyst for the adsorbed hydrogen gas on its surface.

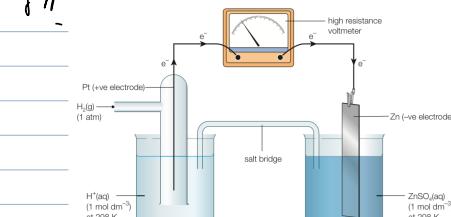
- allows standard electrode potential to be measured quickly.

- 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.

- Eg apparatus:



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

- this gives the ΔE° of zinc or -0.79V .

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

- half-reactions

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

- Oxidizing species + $\text{e}^- \rightarrow$ 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 ($K_\infty = 1$): $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$

- cell potential and emf

- 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.

- it doesn't affect the electrode potential in the half-cell.

- if high current is applied it will distort.

- this means that the current is essentially zero.

- cell potential is the difference in electrode potentials (with current).

- the emf is the potential difference between the terminals of the voltaic cell (without current).

- non-electrochemical series

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

Readily reduce electrons \rightarrow Readily accept electrons

Best reducing system \rightarrow best oxidizing agent

Most easily oxidized \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-reaction with the lowest electrode potential will be forced to undergo reduction.

- the cell potential is the sum of the electrode potentials (including their signs).

- Equation: $E^\circ = E_{\text{cath}}^\circ - E_{\text{anode}}^\circ$

- E_{cath}° 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.

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

- cell diagram

- E.g.: $2\text{Zn}^{2+} + 2\text{e}^- \parallel \text{Cu}^{2+} + 2\text{e}^-$

- Double bar in the salt bridge

- the equation shows the voltage cell and its half-equations:



- Equation for potential is: $E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{anode}}$ (more cathode) - E°_{anode} (less anode).

- non-standard conditions

- Electrode potentials are only for standard conditions.

- Electrode potentials for oxidizing agents in acid conditions refer to 1 mol dm^{-3} concentration zinc, 1 M cup (pH=0).

- More H^+ ion concentration increases the oxidizing strength of the oxidizing agent.

- Increasing the electrode potential of the half-cell.

- Eq: $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2$

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

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

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

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

- 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.



$$- E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \log_{10} \left[\frac{P_{\text{H}_2}}{P_{\text{H}_2}^{(l)}} \right] \rightarrow E_{\text{cell}} = E^{\circ} - \frac{0.059}{nF} \log_{10} P_{\text{H}_2} \rightarrow E_{\text{cell}} = E^{\circ} - \frac{0.059}{nF} \log_{10} \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{(l)}} \quad [\text{Standard form}]$$

- R is the gas constant ($8.315 \text{ J mol}^{-1} \text{ K}^{-1}$), F is Faraday's constant, n = # of electrons, and T = temp (kelvin).

- Worked example

- Daniel cell, temp = 298 K , $a_{\text{H}_2} = 0.005 \text{ M}$, copper (II) = 1.5 mol dm^{-3}

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

- Concentration cells

- Concentration cells are certain 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: $E = E^{\circ} + \frac{0.059}{n} \log_{10} \frac{C_{\text{O}}}{C_{\text{A}}}$.

- C_{O} is the concentration of the anodes, while C_{A} is the concentration of the cathode.

- Cell spontaneity



- 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 is thermodynamically spontaneous.

- n = Number of electrons, F = Faraday's constant, and E° is the electrode potential of the cell.

- Predicting if a cell is spontaneous

ΔG°	E°	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



$$- E^{\circ} = 1.23 \text{ V}$$

$$- E^{\circ} = 0.57 \text{ V}$$

- Cell in spontaneous

- Microbial fuel cells

- A microbial fuel cell (MFC) is a biochemical system that derives a current by using and copying bacterial interactions in nature.

- It converts chemical energy to electrical energy by the catalytic action of micro-organisms, usually bacteria.

- MFCs can be classified into two groups:

- Those that are mediators.

- The mediator is a chemical that transfers electrons from bacteria in the cell to the anode.

- E.g. mediator are: humic acids, methylviologen, and thiosulfate.

- Those that don't use mediators.

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

- Biotinylation

- Electrolysis of aqueous solutions

- Water will undergo electrolysis.

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



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

- If the solution 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.

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

- Oxidation, i.e. reduced, are observed at the anode.

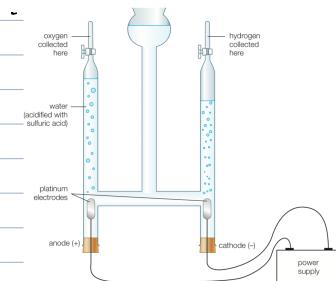
- Hydrogen is produced at the cathode only.
- Non-metals, apart from hydrogen, are produced at the anode.
- Reactive metals, metals above hydrogen, are not discharged.
- The products depend on the concentration of the electrolyte.
- If halide ions are present in appreciable concentrations they will discharge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

- The electrolysis of water

- When pure dilute sulphuric acid (H_2SO_4) is electrolysed, one volume of oxygen gas is collected over the anode, and two volumes of hydrogen gas are collected over the cathode.
- At the anode, the hydroxide ions (from H_2O) are discharged in preference to the sulfate ion.
- They will form water.
- "In the cathode, hydrogen ions are discharged by accepting electrons to form hydrogen molecules:



- The concentration of water increases according 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 anode.
- Anions with more negative E° reduction values will be discharged first at the cathode.

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

- Steps to determine the reaction:

- 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 reaction is 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.

- Foucault's Law

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

- Reactions:



- Diagram:

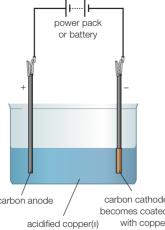


Figure 19.18 Apparatus for the electrolysis of copper(II) sulfate solution

- 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 electrodes, the mass of the substance is equivalent to the substance's molar equivalent.

- They form whole number ratios when they're divided by a common & lowest common st.

- Electroplating

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

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

- To have electrolysis, a metal has to be used as an anode.

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

