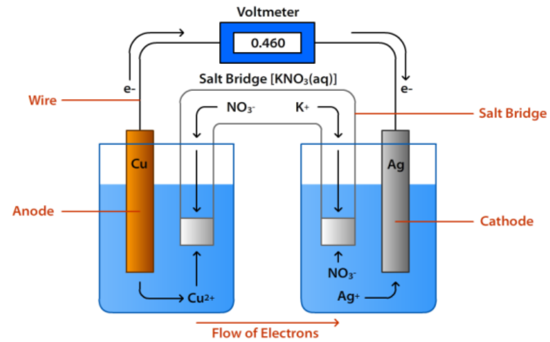
Name: ______________________ Date: __________ Period: ______

HL Chemistry 9.1_ Redox - Guided Notes

Slide 3: Voltaic cell

- A voltaic cell generates an ____________ **force (EMF)** resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the **cell potential ($E^\ominus$)**.

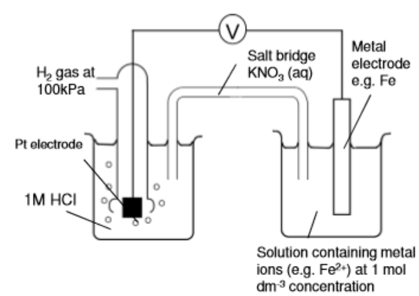


Slide 4: Standard Hydrogen Electrode

- The standard hydrogen ____________ (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K.
- The **standard electrode potential** (aka **standard reduction potential**) (**$E^\ominus$**) is the potential (voltage) of the reduction half-equation under standard ____________ measured relative to the SHE.
- $E^\ominus$ for the SHE is 0V.

Slide 5: Standard Hydrogen Electrode

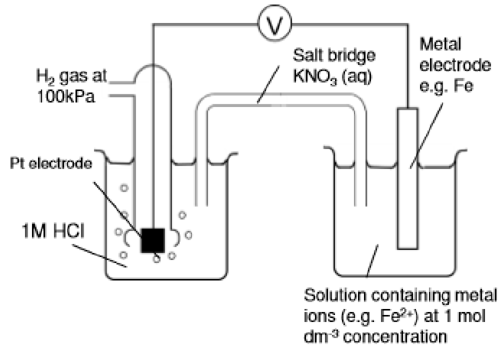
- To measure electrode ____________, a cell has to be connected to another half-cell of **known potential**, and the potential difference between the two half-cells measured.
- We use the **standard hydrogen ____________**.
- It has a standard ____________ ($E^\ominus$)of exactly **0V**.
- **Hydrogen gas is bubbled into a solution of H^+ ions**. A **platinum** ____________ is used as a platform for oxidation and reduction.



Slide 6: Standard Hydrogen Electrode

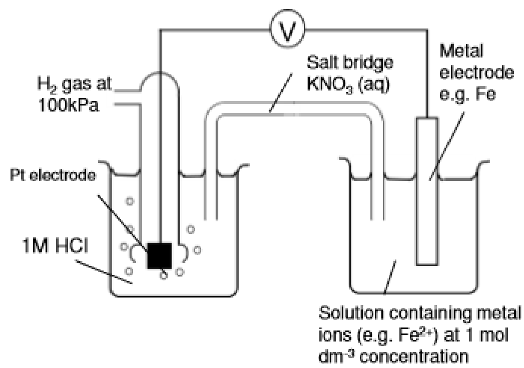
- Platinum is a suitable ____________ because it is fairly inert, will not ionize, and acts as a catalyst for the reaction of proton reduction.

- $Pt|H_2|H^+||Fe^{2+}|Fe$



Slide 8: Importance of conditions

- Half-cells under these ____________ are **standard half-cells**
- **298 K**
- **100 kPa**
- **pure ____________ at 1.0 mol dm^{-3}**
- **Pt used as ____________ if half-cell doesn't include a solid metal**



Slide 9: International-mindedness

- Microbial fuel cells (MFCs) (Also termed biological fuel cells) can generate electricity from the degradation of organic material.
- Sewage bacteria oxidize organic compounds at the anode, which flow through a circuit to the cathode, generating electricity.
- **What implications do MFCs have in terms of "green" energy as well as the environment in general?**

Slide 10: The voltmeter for the copper and zinc electrochemical cell displays the standard cell potential.

Standard cell potential

$E^{\circ}cell = +1.10V$

- Rule for calculating $E^{\circ}cell$?
- **Calculating cell potential**
- The more positive the E°**, the more readily the half-cell is reduced**
- reduction
- oxidation
- ϴ
- ϴ
- ϴ

Slide 11: Rule for calculating $E^{\circ}cell$?

- Work out which species is being oxidised and reduced
- Draw the conventional diagram for this cell
- Calculate the e.m.f of the cell overall
- **Calculating cell potential**
- ϴ
- ϴ
- ϴ

Slide 12: Rule for calculating $E^{\circ}cell$?

- Mg is being oxidised as has most negative electrode potential
- **Calculating cell potential**
- **$E^{\ominus}$cell = 0.34 - (-2.37)**
- **= + 2.71 V**
- Note: always use $E^{\ominus}$ values **exactly as given** in the data table (reduction values). The subtraction in the $E^{\ominus}$cell equation for the half-cell undergoing oxidation reverses its sign, so you don't have to!
- $^{\ominus}$
- $^{\ominus}$
- $^{\ominus}$

Slide 13: You Try

Slide 14: Answers

Slide 15: Determining Spontaneity of a Reaction

- **$E^{\ominus}$values can be used to predict whether or not a redox reaction will occur ____________.**
- **$E^{\ominus}$cell > 0, reaction is ____________**
- **$E^{\ominus}$cell < 0, reaction is non-____________**
- A voltaic cell will always run in the ____________ that gives a **positive $E^{\ominus}$cell value.**

Slide 16: Example

Use $E^{\ominus}$ values to determine whether the reaction

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

will occur spontaneously under standard conditions.

Slide 17: Example Solution

The data values are as follows:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E^{\ominus} = -0.26\ V$$

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad E^{\ominus} = -1.18\ V$$

In the reaction given, Ni is being oxidized and Mn^{2+} is being reduced.

Substituting in the equation:

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{Mn^{2+}} - E^{\ominus}_{Ni^{2+}} = -1.19 - (-0.26) = -0.93\ V$$

The negative sign for $E^{\ominus}_{cell}$ tells us that this reaction will not happen spontaneously. In this mixture the reaction that occurs will be the reverse reaction,

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

Slide 18: Nernst Equation

- $\Delta G^{\ominus} = -nFE^{\ominus}$
- Number of moles of electrons ____________
- Faraday ____________ (96,500 C mol^{-1})
- Gibbs free energy
- Cell potential
- The more positive $E^{\ominus}$**, the more ____________ favorable the reaction**

Slide 19: You Try

- Calculate the standard free-energy change at 298K for the zinc-coper voltaic cell, which has a standard cell potential of +1.10 V.

Slide 20: Nuggets of Wisdom

- Electrons always flow from anode to cathode (____________)
- ____________ always tend to flow towards the half-cell with the highest $E^{\ominus}$ value.
- The higher the value of $E^{\ominus}$, the stronger the ____________ agent (gets reduced)
- The lower the value of $E^{\ominus}$, the ____________ the reducing agent (gets oxidized)
- These are at the **top** of the ____________ potential chart
- ____________ **reducing agents** are at the anode
- Stronger ____________ **agents** are at the cathode

Slide 21: You Try

- A solution containing potassium manganate (VII) and concentrated hydrochloric acid reacts to form chlorine gas. Identify the strongest oxidizing agent in the solution and calculate the standard cell potential.

Slide 22: Things to Consider

- Cell potential data gives no ____________ on the **rate** of a reaction
- Redox reactions predicted to be ____________ may not occur if the activation energy is too high.
- Standard cell potential ($E^{\ominus}$) relate only to **standard** ____________.
- Asdf
- ____________ flow towards the half-cell with the **highest** $E^{\ominus}$ value.

Slide 23: Electrolytic Cells

- ____________ **Cells** are the **reverse** of voltaic cells
- **Voltaic Cells**
- ____________ redox reactions
- Convert chemical energy to ____________ energy
- **Reactive** metal ____________ connected by salt bridge
- **Electrolytic Cells**
- Uses external energy source to perform ____________ redox reactions
- Convert ____________ energy to chemical energy
- **Inert or reactive** metal electrodes are placed in an ____________
- Liquid ____________, usually molten/solution of an ionic compound

Slide 24: Electrolytic Cells

- Power source produces an electric current that passes through the electrolyte, causing the ions to undergo redox reactions at the electrodes **(usually metals or graphite)** and form ____________ neutral products
- ____________ is used to extract metals from ores such as Al_2O_3 and NaCl
- There are no good ____________ agents able to reduce these ions since $E^\ominus$ values are so low

Slide 25: Electrolytic Cells

- Longer line: ____________ terminal
- Shorter line: ____________ terminal
- Battery
- Power source pushes ____________ towards negative electrode (cathode)
- Current is passed through the ____________ via ions. Electrons are released at the positive electrode (anode) and returned to the source

Slide 26: Electrodes in Electrolytic Cells

- Even though the **anode is positive** and the **cathode is negative**, ____________ still occurs at the **anode** and **reduction** still occurs at the **cathode**.
- This happens because **cations are ____________** to the **negative electrode (cathode)**, where they accept electrons and **reduction occurs**. **Anions are attracted** to the **positive electrode (anode)**, where they donate electrons and **oxidation occurs**.
- Cathode (____________): $M^+ + e^- \rightarrow M$
- Anode (____________): $A^- \rightarrow A + e^-$

Slide 27: You Try

- Magnesium metal is produced by the electrolysis of molten magnesium chloride using inert electrodes.
- Make a fully labelled drawing of the electrolytic cell, including the charges on the electrodes and the direction of electron and ion migration.

Slide 28: Example:

- Describe the reactions that occur at the two electrodes during the electrolysis of molten lead (II) bromide. Write an equation for the overall reaction and comment on any likely changes that would be observed.
- $PbBr_2(l) \rightarrow Pb^{2+}(l) + 2Br^-(l)$
- To cathode

- To anode
- $2Br^-(l) \rightarrow Br_2(l) + 2e^-$
- $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$
- $Pb^{2+}(l) + 2Br^-(l) \rightarrow Pb(l) + Br_2(l)$
- Brown liquid with a strong smell (Br_2) will form at anode and grey metal (Pb) will form at cathode.

Slide 29: You Try:

- Describe what you would expect to observe during the electrolysis of molten copper (II) chloride. Explain your answer in terms of the redox reactions occurring at the electrodes, including equations in your answer.

Slide 30: Voltaic cell vs electrolytic cell

Slide 31: Summary

Slide 32: Economical Implications

- Most ionic compounds have high melting points, so sometimes other compounds are added to lower the melting point to make electrolysis more economical
- Example: $CaCl_2$ is added to NaCl to lower the melting point, but the added compound can't interfere with discharge of the metal ion
- Electrode potentials used to check if the added compound can be used
- $Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $E^{\ominus} = -2.87$ V
- $Na^+(aq) + e^- \rightarrow Na(s)$ $E^{\ominus} = -2.71$ V
- Since Na^+ has a higher electrode potential, it will be reduced in preference to Ca^{2+} (no interference)

Slide 33: Electrolysis of Aqueous Solutions

- Predicting the products at electrodes is more difficult when ____________ occurs in aqueous solutions because water can be oxidized or reduced.
- When aqueous solutions are ____________, water can be oxidised to oxygen at the anode and reduced to hydrogen at the cathode.
- $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
- $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
- Reduction at cathode
- Oxidation at anode
- ____________ **discharge** depends on:
- ____________ $E^\ominus$ values of ions
- Relative ____________ of ions in electrolyte
- Nature of the ____________

Slide 34: FOLLOW MY WORDS OF WISDOM

- If there are 2 possible reactions that can occur at the ____________…
- Smaller (more negative) $E^\ominus$ ____________ oxidized.
- Larger (more positive) $E^\ominus$ ____________ reduced.
- Even though we are writing some of these as ____________ reactions,
- DON'T FLIP THE SIGNS OF ELECTRODE ____________…..EVER!!!!
- IT MAKES ____________ MORE CONFUSING!!!!!!!!!

Slide 35: A note about the half-reaction for the reduction of water

- Your Data Booklet lists these as the half-____________ for the reduction of water:
- $2H^+(aq) + \frac{1}{2} O_2(g) + 2e^- \rightarrow H_2O(l)$ $E^\ominus = +1.23$ V
- $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^-(aq)$ $E^\ominus = -0.83$ V
- This will occur at the cathode (as ____________)
- This will occur at the anode (as ____________)
- Remember, electrolytic cells are ____________ **(so the half-reaction with the smaller reduction potential is forced to be reduced)**

Slide 36: One small caveat…

- If there are 2 options for a reaction at the cathode, the larger number will be ____________ reduced
- If there are 2 options for a reaction at the anode, the smaller number will be ____________ oxidized

Slide 37: Example of Electrolysis of Water

- Describe the electrolysis of water with additional sodium hydroxide added.
- Ions present:
- Possible electrode reactions:
- Cathode:

- Anode:
- Overall balanced equation:
- Observed changes at the electrodes: O_2 gas released at anode, H_2 gas released at cathode, 2 mol H_2 gas released for every 1 mol of O_2 gas, pH decreases at anode, pH increases at cathode
- $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
- $Na^+(aq) + e^- \rightarrow Na(s)$ $E^\ominus = -2.71$ V
- $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V
- $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$ $E^\ominus = +0.40$ V
- $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $E^\ominus = +1.23$ V
- $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
- Larger number reduced
- Smaller number oxidized

Slide 38: Example of Electrolysis of NaCl(aq)

- Describe the electrolysis of aqueous sodium chloride (brine)
- Ions present:
- Possible electrode reactions:
- Cathode:
- Anode:
- Overall balanced equation:
- Observed changes at the electrodes: Cl_2 gas released at anode, H_2 gas released at cathode, Cl_2 causes strong smell and bleaching effect, pH increases due to release of OH^-
- $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$
- $Na^+(aq) + e^- \rightarrow Na(s)$ $E^\ominus = -2.71$ V
- $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V
- $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $E^\ominus = +1.36$ V
- $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $E^\ominus = +1.23$ V
- $2NaCl(aq) + 2H_2O(l) \rightarrow H_2(g) + Cl_2(g) + 2Na^+(aq) + 2OH^-(aq)$
- Cl^- is preferentially oxidized due to keeping the concentration of NaCl > 25%

Slide 39: You Try:

- Deduce the products formed during the electrolysis of an aqueous solution of potassium fluoride. Write an equation for the reaction at the anode and explain your reasoning.

Slide 40: Example of Electrolysis of CuSO4(aq)-inert electrodes

- Describe the electrolysis of aqueous copper sulfate (blue)
- Ions present:
- Possible electrode (graphite) reactions:
- Cathode:
- Anode:
- Overall balanced equation:
- Observed changes at the electrodes: pink-brown copper deposited at cathode, O_2 gas released at anode, pH decreases due to release of H^+, loss of blue color
- $CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$
- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\ominus = +0.34$ V
- $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V
- $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $E^\ominus = +1.23$ V
- $2CuSO_4(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq) + 2SO_4^{2-}(aq)$
- Note: The sulfur in SO_4^{2-} has a maximum oxidation state so cannot be oxidized any further.

Slide 41: Example of Electrolysis of CuSO4(aq)-copper electrodes

- Describe the electrolysis of aqueous copper sulfate (blue)
- Ions present:
- Possible electrode (copper) reactions:
- Cathode:
- Anode: copper is oxidized
- Cu^{2+} is produced at the anode and moves to the cathode, where it is discharged as Cu(s).
- Observed changes at the electrodes: pink-brown copper deposited at cathode, disintegration of the copper anode, no change in pH, no change in blue color
- $CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$
- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\ominus = +0.34$ V

- $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V
- $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
- Note: The sulfur in SO_4^{2-} has a maximum oxidation state so cannot be oxidized any further.

Slide 42: Example of Electrolysis of CuSO4(aq)-copper electrodes

- **Amount of products formed depends on:**
- The current
- The duration of the electrolysis
- The charge on the ion

Slide 43: Calculating Amounts Produced from Electrolysis

- $Q = I \times t$
- Charge, ____________ in coulomb (C)
- Current, ____________ in amperes (A)
- Time, ____________ in seconds (s)
- ____________, F = 96500 C mol^{-1}
- ____________ (*I*), time (t)
- Charge (*Q*)
- Moles of electrons
- Moles of product (*n*)
- Mass of product (*m*)
- $Q = I \times t$
- $F = Q$
- 96500
- Use mole ratio
- $m = n \times M$

Slide 44: Example: Calculating Amounts Produced from Electrolysis

- How many grams of copper are deposited on the cathode of an electrolytic cell containing $CuCl_2$(aq) if a current of 2.00 A is run for 15.0 minutes?
- Q = 2.00 A × (15.0 × 60s) = 1800 C
- F = 1800 C/96500 C mol-1 = 0.01865 mol e^-
- Cu^{2+}(aq) + 2e^- → Cu(s) 2 mol e^-: 1 mol Cu
- 0.01865 mol e^- × 0.5 = 0.00933 mol Cu
- *m* = 0.00933 mol × 63.55 g mol^{-1} = 0.583 g Cu
- How would the amount differ if the same conditions were applied using CuCl(aq) instead?
- Cu^+(aq) + e^- → Cu(s) 1 mol e^-: 1 mol Cu
- 0.01865 mol e^- = 0.01865 mol Cu
- *m* = 0.01865 mol × 63.55 g mol^{-1} = 1.19 g Cu

Slide 45: You Try:

- If a current of 2.00 A is passed through a solution of $AgNO_3$ for 10 minutes it is found that 0.0124 moles of Ag are formed.
- How much would form if a current of 1.00 A is passed through the same solution for 30 minutes?
- What amount of Cu (in mol) would form if the quantity of electricity in (a) was passed through a solution of $CuSO_4$?

Slide 46: Electroplating

- Using ____________ to deposit a layer of a metal on top of another metal or other conductive object.
- ____________ has metal ions to be deposited
- Cathode ____________ object to be plated
- Anode has same metal which is to be coated so it is oxidized to replenish ions in ____________
- Sometimes metals such as iron are coated with a thin layer of zinc to protect the metal underneath it from corrosion (know as ____________)