

24. ELECTROCHEMISTRY

24.1 Electrolysis

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Learning outcomes

Candidates should be able to:

- 1 predict the identities of substances liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration
- 2 state and apply the relationship $F = Le$ between the Faraday constant, F , the Avogadro constant, L , and the charge on the electron, e
- 3 calculate:
 - (a) the quantity of charge passed during electrolysis, using $Q = It$
 - (b) the mass and/or volume of substance liberated during electrolysis
- 4 describe the determination of a value of the Avogadro constant by an electrolytic method

Electrolysis

The breaking down of a compound into its elements using an electric current. It is carried out in an electrolytic cell.

Uses of Electrolysis

- To extract metals from their metal ores when the metals cannot be extracted by heating their ores with carbon.
- To purify metals.
- To produce non-metals such as fluorine

Electrolytic Cell

Electrolysis is carried out in an electrolytic cell. It consists of:

1. Electrolyte:
 - the compound that is broken down during electrolysis.
 - molten ionic compound OR concentrated aqueous solution of ions.
2. 2 electrodes:
 - metal or graphite rods that conduct electricity to the electrolyte and away from the electrolyte.
 - positive electrode = anode.
 - negative electrode = cathode.
3. Power supply – direct current

Electrolysis of Molten Electrolytes

At cathode	At anode
Cations (+ve charged ions) move to -ve charged cathode.	Anions (-ve charged ions) move to +ve charged anode.
Cations gain electrons at cathode.	Anions lose electrons at anode.
Reduction takes place at cathode	Oxidation takes place at anode.
Examples: <ul style="list-style-type: none"> - $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ - $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ 	Examples: <ul style="list-style-type: none"> - $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
Observations: <ul style="list-style-type: none"> - If metal is formed at cathode, a layer of metal is deposited on cathode OR a molten layer forms in the cell. - If hydrogen gas is formed at cathode, bubbles are seen. 	

Examples:

Compound	Cathode product	Anode product
Al_2O_3	Al	O_2
HCl	H_2	Cl_2

Electrolysis of Aqueous Solutions

- Aqueous solutions have more than one cation and anion in solution due to presence of water.
- Water is a weak electrolyte and splits into H^+ and OH^- ions:

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$
- Actual ions discharged during electrolysis will depend on:
 1. Relative electrode potential of the ions
 2. Concentration of the ions

Relative Electrode Potential (E^\ominus) of Ions

Describes how easily an ion is discharged during electrolysis.

Positively charged cation with most positive E^\ominus will be discharged at the cathode, as this is the cation that is most easily reduced.	Negatively charged anion with most negative E^\ominus will be discharged at the anode, as this is the anion that is most easily oxidised.
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<p>Example: Concentrated aqueous solution of NaF will contain H^+ and Na^+ ions.</p> <ul style="list-style-type: none"> - $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ $E^\ominus = 0.00 \text{ V}$ - $\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$ $E^\ominus = -2.71 \text{ V}$ <p>Since E^\ominus of $\text{H}^+ > E^\ominus$ of Na^+, H_2 is formed at cathode instead of Na.</p>	<p>Example: Concentrated aqueous solution of NaF will contain OH^- and F^- ions.</p> <ul style="list-style-type: none"> - $4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$ $E^\ominus = -0.40 \text{ V}$ - $2\text{F}^-(\text{aq}) \rightarrow \text{F}_2(\text{g}) + 2\text{e}^-$ $E^\ominus = -2.87 \text{ V}$ <p>Since E^\ominus of $\text{F}^- < E^\ominus$ of OH^-, F_2 is formed at anode.</p>
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Concentration of Ions

- Ions that are present in higher concentrations are more likely to be discharged.
- In electrolysis of concentrated aqueous solution of NaF, F^- ions are in much higher concentration, so more fluorine is formed at anode.
- In electrolysis of a very dilute aqueous solution of NaF, F^- ions are in much lesser concentration, so more oxygen and less fluorine is formed at anode. In reality, a mixture of both oxygen and fluorine gas is formed.

Faraday's Law & Avogadro

Faraday's Law

Amount of substance formed at an electrode during electrolysis is proportional to:

1. The time for which a constant electric current passes through the electrolyte.
2. The total electric charge, in coulombs, that passes through the electrolyte (strength of electric current).

$$Q = I t$$

- Q = charge (coulombs, C)
- I = current (amperes, A)
- t = time (seconds, s)

Faraday Unit

- Can be used to express the amount or quantity of electricity.
- One faraday = amount of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions.
- 1 faraday = 96500 C mol^{-1}

$$F = L e$$

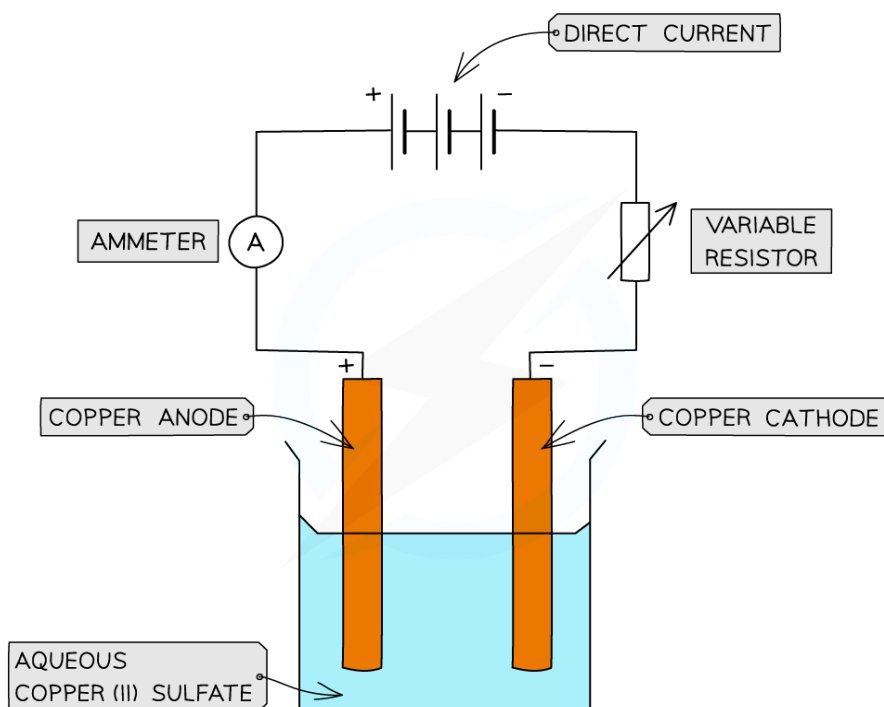
- F = Faraday's constant (96500 C mol⁻¹)
- L = Avogadro's constant (6.02 x 10²³ mol⁻¹)
- e = charge on an electron (1.60 x 10⁻¹⁹ C)

Examples:

$\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$	1 faraday of electricity (96500 C) is required to deposit 1 mol of Ag.
$\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu} (\text{s})$	2 moles of electrons are needed to produce 1 mole of copper from Cu ²⁺ . Thus 2 faradays of electricity (96500 x 2 C) is required to deposit 1 mol of Cu.
$2\text{Cl}^- (\text{aq}) \rightarrow \text{Cl}_2 (\text{g}) + 2\text{e}^-$	2 moles of electrons are released when 1 mole of Cl ₂ is formed. Thus 2 faradays of electricity (96500 x 2 C) is required to produce 1 mol of Cl ₂ .
$4\text{OH}^- (\text{aq}) \rightarrow \text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) + 4\text{e}^-$	4 moles of electrons are released when 1 mole of O ₂ is formed. Thus 4 faradays of electricity (96500 x 4 C) is required to produce 1 mol of O ₂ .

Determining Avogadro's Constant by Electrolysis

$$L = \frac{\text{charge on 1 mol of electrons}}{\text{charge on 1 electron}}$$



Method

- Pure copper anode and pure copper cathode are weighed.
- Variable resistor is kept at constant current.
- Electric current is passed through for certain time interval.
- Anode and cathode are removed, washed with distilled water, dried with propanone, and reweighed.

Results

- Cathode has increased in mass as copper is deposited.
- Anode has decreased in mass as copper goes into solution as copper ions.

Calculation

- Current = 0.20 A
- Time interval for which current is passed = 34 min
- Initial mass of copper anode = 56.53 g
- Final mass of copper anode = 56.40 g

Mass of copper removed from anode = $56.53 - 56.40 = 0.13$ g
$Q = I t$ $= 0.2 \times 34 \times 60 = 408$ C
<ul style="list-style-type: none">- To deposit 0.13g of copper = 408 C- To deposit 1 mol of copper (63.5g) = $(63.5/0.13) \times 408$ C
<ul style="list-style-type: none">- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$- 2 moles of electrons are needed to produce 1 mole of copper.- So, charge on 1 mole of electrons = $(63.5/0.13) \times 408 \times 0.5 = 99646$ C.
$L = \frac{\text{charge on 1 mol of electrons}}{\text{charge on 1 electron}}$ $= 99646 / (1.6 \times 10^{-19}) = 6.23 \times 10^{23} \text{ mol}^{-1} \sim 6.02 \times 10^{23} \text{ mol}^{-1}$

Electrolysis Calculations

Faraday's constant can be used to calculate:

1. Mass of a substance deposited at an electrode.
2. Volume of gas liberated at an electrode

Calculating the mass of a substance deposited at an electrode

- Write half-equation at electrode.
- Determine number of coulombs needed to form one mole of substance at the specific electrode using Faraday's constant.
- Calculate charge transferred during electrolysis.
- Use simple proportion and relative atomic mass of substance to find mass.

Example: Calculate the amount of magnesium deposited when a current of 2.20 A flows through the molten bromide for 15 minutes.

Half equation at cathode:



Number of coulombs needed to deposit 1 mole of Mg at cathode:

- 1 mole of electrons = 96500 C mol^{-1}
- Each mole of Mg involves 2 electrons, so $96500 \times 2 = 193000 \text{ C mol}^{-1}$

Charge transferred during electrolysis:

- $Q = It = 2.20 \times 15 \times 60 = 1980 \text{ C}$

Mass of Mg deposited:

Charge (C)	Amount of Mg deposited (mol)	Amount of Mg deposited (g)
193000	1	24.3
1980	0.0103	0.250

0.25 g of Mg is deposited.

NOTE: quicker formula to determine amount of substance formed at an electrode:

$$m = \frac{MQ}{nF}$$

- m = mass of substance formed/deposited (g)
- M = molar mass of substance (g mol^{-1})
- Q = total charge passed (C)
- n = number of electrons involved per ion
- F = Faraday's constant (96500 C mol^{-1})

Calculating the volume of gas liberated at an electrode

- Write half-equation at electrode.
- Determine number of coulombs needed to form one mole of substance at the specific electrode using Faraday's constant.
- Calculate charge transferred during electrolysis.
- Use simple proportion and the relationship 1 mol of gas occupies 24.0 dm^3 at room temperature.

Example: Calculate the volume of oxygen gas produced at room temperature, when a concentrated aqueous solution of H_2SO_4 is electrolysed for 35.0 minutes using a current of 0.75 A.

Half equation at anode:



Number of coulombs needed to produce 1 mole of O_2 at anode:

- 1 mole of electrons = 96500 C mol^{-1}
- Each mole of O_2 involves 4 electrons, so $96500 \times 4 = 386000 \text{ C mol}^{-1}$

Charge transferred during electrolysis:

- $Q = It = 0.75 \times 35 \times 60 = 1575 \text{ C}$

Mass of Mg deposited:

Charge (C)	Amount of O_2 liberated (mol)	Amount of O_2 liberated (dm^3)
386000	1	24
1575	4.08×10^{-3}	0.0979

0.0979 dm^3 of O_2 is liberated.

24.2 Standard Electrode Potentials (E^\ominus), Standard Cell Potentials (E^\ominus_{cell}) and the Nernst Equation

24.2 Standard electrode potentials E^\ominus , standard cell potentials E^\ominus_{cell} and the Nernst equation

Learning outcomes

Candidates should be able to:

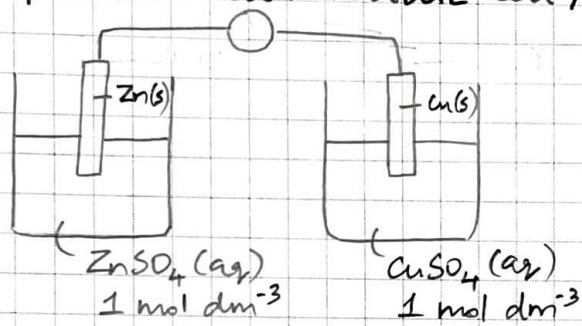
- 1 define the terms:
 - (a) standard electrode (reduction) potential
 - (b) standard cell potential
- 2 describe the standard hydrogen electrode
- 3 describe methods used to measure the standard electrode potentials of:
 - (a) metals or non-metals in contact with their ions in aqueous solution
 - (b) ions of the same element in different oxidation states
- 4 calculate a standard cell potential by combining two standard electrode potentials
- 5 use standard cell potentials to:
 - (a) deduce the polarity of each electrode and hence explain/deduce the direction of electron flow in the external circuit of a simple cell
 - (b) predict the feasibility of a reaction
- 6 deduce from E^\ominus values the relative reactivity of elements, compounds and ions as oxidising agents or as reducing agents
- 7 construct redox equations using the relevant half-equations
- 8 predict qualitatively how the value of an electrode potential, E , varies with the concentrations of the aqueous ions
- 9 use the Nernst equation, e.g. $E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$,
to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$, $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
- 10 understand and use the equation $\Delta G^\ominus = -nE^\ominus_{\text{cell}} F$

ELECTROCHEMISTRY

- 1) Chemical \rightarrow Electrical (Electrochemical cell)
- 2) Electrical \rightarrow Chemical (Electrolytic cell / Electrolysis)

ELECTROCHEMICAL CELL \rightarrow Spontaneous reactions

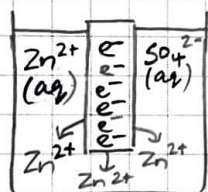
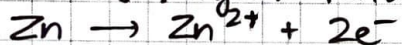
Galvanic Cell / Voltaic Cell / Daniel Cell



○ ammeter / bulb / high-resistance voltmeter

|| electrodes

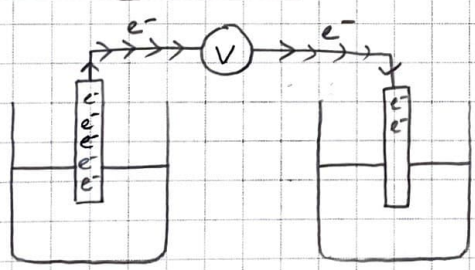
\rightarrow Zn rod has higher tendency to lose e^- and undergoes oxidation.



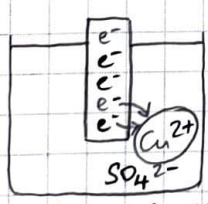
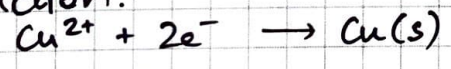
ANODE (-ve)

$\text{Zn} \rightarrow \text{Zn}^{2+} \therefore$ anode shrinks

oxidation half cell (OHC)



$\rightarrow e^-$ move to Cu rod, and Cu^{2+} ions accept the e^- and undergoes reduction.



CATHODE (+ve)

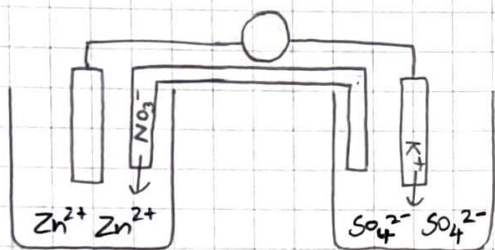
relatively +ve due to lower e^- density

$\text{Cu}^{2+} \rightarrow \text{Cu} \therefore$ cathode inc. in size

reduction half cell (RHC)

\rightarrow over time, Zn^{2+} builds up in OHC. Inc +ve charge of solution strongly attracts e^- and prevents them from moving to cathode.

There is unequal distribution of charge in both. To prevent this, a salt bridge is used.



Salt Bridge

- inert electrolyte
- molten state
- electrolyte dissociates
- ions formed from dissociation will neutralise charge imbalance

inert \rightarrow ions in electrolyte won't form ppt with ions in the half cells. eg. KNO_3

LOANI

left side = oxidation
anode = negative
(only for electrochemical cell)

Red Cat

Reduction on Cathode always

E_{Cell} \rightarrow any conc. / temp.

E°_{Cell} \rightarrow stp

E°_{cell} \Rightarrow standard cell potential

- temp 25°C
- conc 1 mol dm^{-3}
- pressure 1 atm

Factors that affect how much voltage:

- \rightarrow conc.
- \rightarrow temp.
- \rightarrow metal

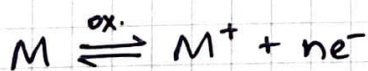
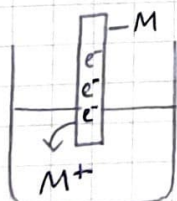
Salt Bridge

- 1) Maintains charge balance between both half cells.
- 2) Maintains electrical neutrality
- 3) Completes internal circuit by allowing the flow of ions.

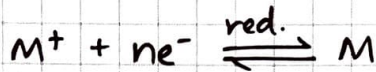
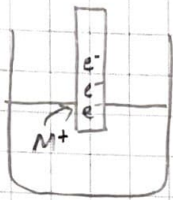
ELECTRODE POTENTIAL

Tendency of any given electrode to either lose or accept e^- .

- \rightarrow can only be measured under equilibrium.
- \rightarrow p.d b/w metal electrode and its ions in solution; measured in volts



oxidation electrode potential
 E°_{oxid}



reduction electrode potential
 E°_{red}

* electrode potential is measured using standard hydrogen electrode (SHE)
 Inert electrode

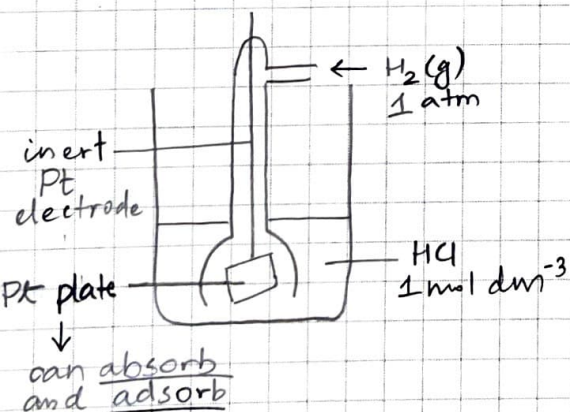
Inert electrode: doesn't undergo oxidation/reduction
Active electrode: undergoes

- provides surface area
- conducts electricity

Types of electrode potential

- 1) metal (s) dipped in its own metal ion (aq)
 → metal(s) / metal ion (aq) eg. Zn in $ZnSO_4$
- 2) non-metal dipped in its own non-metal ion
 → non-metal / non-metal ion OR gas/ion electrode eg. SHE
- 3) ion/ion
 eg. Fe^{2+}, Fe^{3+}

Reference Electrode Potential (SHE)



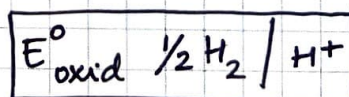
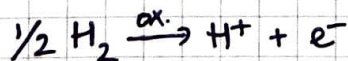
1) reversible: can be ox. half cell or red. half cell

2) $E^\circ_{\text{oxid}} = 0$
 $E^\circ_{\text{red}} = 0$

* value for SHE is always 0. Value on voltmeter shows electrode potential of the half cell it is connected to.

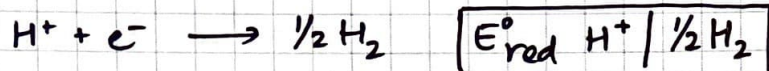
- Pt provides surface area for H_2 gas bubbles to adsorb on its surface.

- H^+ ions in solution and H_2 gas undergo reaction:



cell notation: $Pt(s) \mid \frac{1}{2} H_2(g) \mid H^+(aq)$
 $1 \text{ atm} \quad 1 \text{ mol dm}^{-3}$

• if SHE = RHC, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$



cell notation: $\text{H}^+(\text{aq}) \mid \frac{1}{2}\text{H}_2(\text{g}) \mid \text{Pt}(\text{s})$
 $1 \text{ mol dm}^{-3} \quad 1 \text{ atm}$

* E° is always expressed in standard reduction potential.

$$\boxed{E_{\text{cell}}^{\circ} = E_{\text{HC}}^{\circ} \text{oxid} + E_{\text{HC}}^{\circ} \text{red}}$$

anode cathode

E_{cell}° = p.d btwn the
2 electrodes / half
cells.

$$E_{\text{cell}}^{\circ} = -E_{\text{red}}^{\circ} + E_{\text{red}}^{\circ}$$

$$\boxed{E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}}$$

↳ NERNST EQUATION

→ used to calculate E_{cell} at any given temp, pressure, conc.

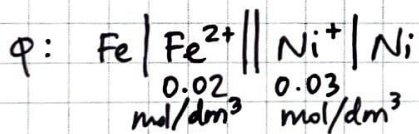
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303}{nF} \log_{10} \frac{[P]^x}{[R]^y}$$

- n : total electrons lost/gained
- F : Faraday's constant $\sim 96500 \text{ C}$
- $[P]$: conc. of product
- $[R]$: conc. of reactant
- x : coefficient of product in balanced eq.
- y : coefficient of reactant in balanced eq.

$$\frac{2.303}{nF} = \frac{0.059}{n}$$

*

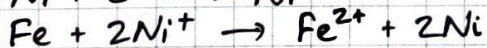
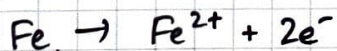
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log_{10} \frac{[P]^x}{[R]^y}$$



$$E^{\circ} \text{Fe}^{2+} | \text{Fe} = 0.9$$

$$E^{\circ} \text{Ni}^{2+} | \text{Ni} = 0.7$$

$$E^{\circ}_{\text{cell}} = \cancel{0.9} - \cancel{0.7} = -0.2 \quad 0.7 - 0.9 = -0.2$$



NERNST EQUATION (contd.)

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \times 2.303 \times \log_{10} \frac{[P]^x}{[R]^y}$$

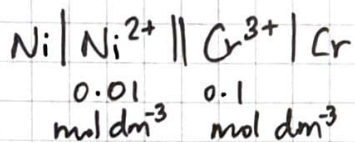
R = gas constant

T = temperature

n = total no. of e^- lost/gained

F = Faraday constant

Q: 1)

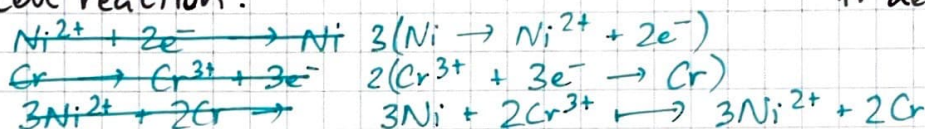


$$E^{\circ}_{\text{Ni}^{2+} \mid \text{Ni}} = -0.25$$

$$E^{\circ}_{\text{Cr}^{3+} \mid \text{Cr}} = -0.74$$

* anode & cathode are already given \therefore don't look at E°_{cell} values given to decide oxid/red.

i) Cell reaction:



$$\text{ii) } E^{\circ}_{\text{cell}} = 0.74 - (-0.25) = -0.49$$

$$\text{iii) } n = 6$$

$$\text{iv) } E_{\text{cell}} = -0.49 - \frac{0.059}{6} \log_{10} \frac{[0.01]^3}{(0.1)^{3 \cdot 2}} = \boxed{-0.451}$$

$$2) E^{\circ}_{\text{Fe}^{2+} \mid \text{Fe}} = -0.49 \text{ V}$$

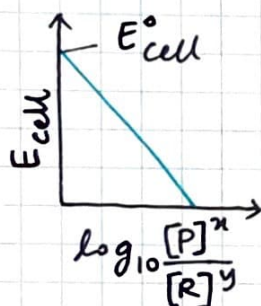
find $E_{\text{Fe}^{2+} \mid \text{Fe}}$ conc. of $\text{Fe}^{2+} = 0.79 \text{ mol dm}^{-3}$

$$-0.49 - \frac{0.059}{2} \log_{10} \frac{1}{0.79} = \boxed{-0.493}$$

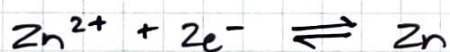
Nernst Equation Graph

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log_{10} \frac{[P]^x}{[R]^y}$$

$y = -mx + c$



EQUILIBRIUM CONSTANT



If conc. of $\text{Zn}^{2+} \uparrow$:

- equilibrium shifts to RHS
- Zn^{2+} is more likely to undergo reduction
- E°_{cell} increases; becomes more +ve OR less -ve
- Zn^{2+} behaves as a stronger O.A.

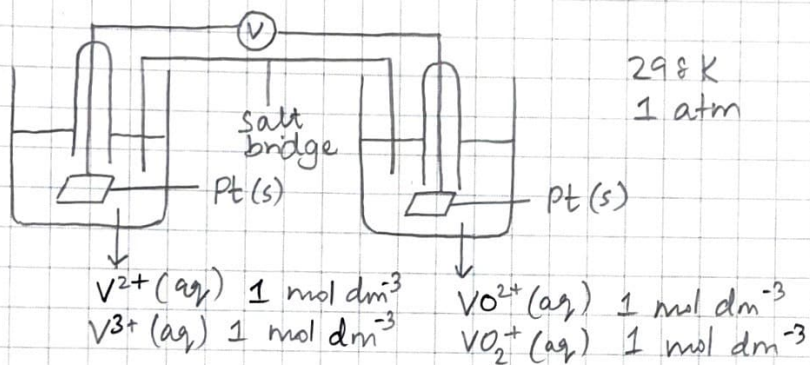
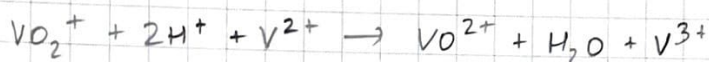
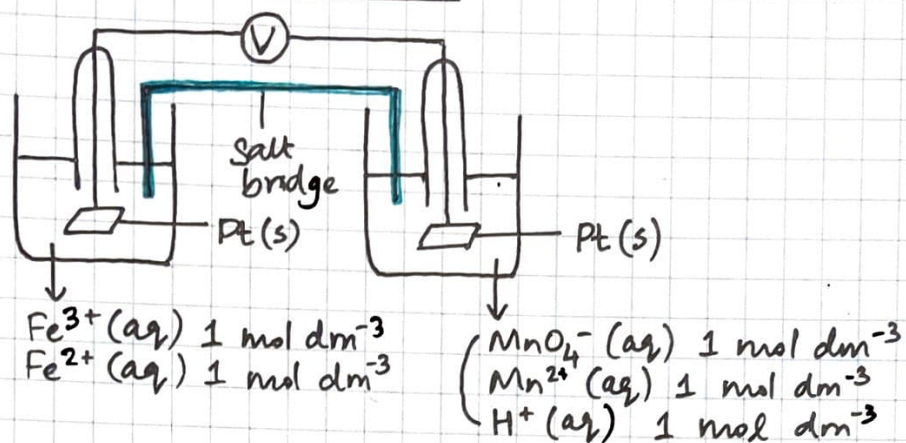
GIBB'S FREE ENERGY

↳ parameter that tells you if reaction is feasible/
Spontaneous.

- $\Delta G = -ve$: spontaneous
- $\Delta G = +ve$: non-spontaneous
- $\Delta G = 0$: reaction is at equilibrium

$\Delta G = -nFE_{\text{cell}}$	$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$
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Metal ion / Metal ion



$\text{V}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$

$\text{VO}^{2+}(\text{aq})$ and Fe^{3+}

↓
note the state
if V it would be (s)

< 0.3 NOT feasible !!

Q: aq. solution of CuSO_4 is electrolysed using Cu electrodes.
Current of 1.5A for 3hrs. 5.09 g of Cu deposited on cathode.

$$\begin{aligned} & (\text{charge on } 1e^- = -1.60 \times 10^{-19} \text{ C}) \\ & \text{Mr of Cu} = 63.5 \end{aligned}$$

$$Q = It = 1.5 \times 3 \times 60 \times 60 = 16200 \text{ C}$$

$$\text{no. of } e^- = \frac{16200}{1.6 \times 10^{-19}} = 1.0125 \times 10^{23}$$

$$\text{mol of Cu} = \frac{5.09}{63.5} = 0.08$$

$$1 \text{ mol of Cu} \Rightarrow \frac{16200}{\frac{5.09}{63.5}} : 202102.1611 \text{ C} \Rightarrow 2 \text{ mol } e^-$$

$$\therefore 1 \text{ mol of } e^- \Rightarrow 101051.0806 \text{ C}$$

$$\therefore \frac{101051.0806}{1.6 \times 10^{-19}} = 6.32 \times 10^{23} \approx 6.023 \times 10^{23}$$

Rules for what gets discharged at each electrode:

1) E° value

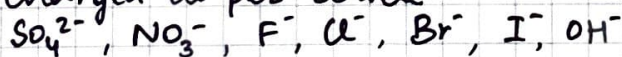
↳ higher \Rightarrow gets reduced

2) Less Reactivity of cation

↳ less reactive cation gets discharged at cathode

3) Anion

↳ discharged as per series:



—————→

NOTE:

