

Electrochemistry

$$\rightarrow \text{charge of } 1 e^- = 1.60 \times 10^{-19} C$$

$$\rightarrow \text{charge of } 1 \text{ mol of } e^- = 6.02 \times 10^{23} \times 1.60 \times 10^{-19}$$
$$= 96320 \text{ C mol}^{-1}$$
$$\approx 96500 \text{ C mol}^{-1}$$

↳ Faraday Constant

$$\hookrightarrow 1F = 96500 \text{ C mol}^{-1}$$

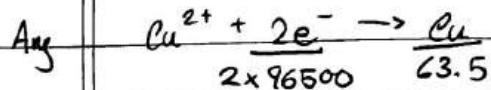
$$2F = 2 \times 96500 \text{ C mol}^{-1}$$

→ The ~~mass~~ amount of product formed at each electrode is directly proportional to the amount of current supplied and the time it takes to electrolyse the ionic compound.

$$\hookrightarrow Q = It \therefore \text{amount of product} \propto Q$$

$$\frac{\text{amount}_1}{Q_1} = \frac{\text{amount}_2}{Q_2} \quad *$$

Q. A solution of CuSO_4 is electrolysed for 40 minutes. Given that a constant current of 4A is supplied. Find the mass of Cu formed at the cathode.



$$Q = It$$

$$= 4 \times 40 \times 60$$

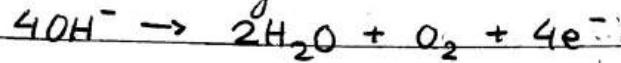
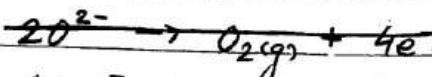
$$= 9600 \text{ C}$$

$$2 \times 96500 \text{ C} = 63.5 \text{ g}$$

$$1 \text{ C} = \frac{63.5}{96500 \times 2} \text{ g}$$

$$\therefore 9600 \text{ C} = \frac{9600 \times 63.5}{96500 \times 2} = 3.16 \text{ g}$$

a. Calculate the ^{amount} of current required to form ~~300~~ 3600 cm^3 of $\text{O}_2(\text{g})$ when dilute H_2SO_4 is electrolysed for 30 minutes.



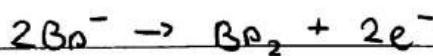
$$\frac{3600}{24000} = \frac{x \times 30 \times 60}{4 \times 96500}$$

$$\therefore x = 32.2 \text{ A}$$

$$\rightarrow L = \frac{F}{e} \quad \text{where: } L = \text{Avogadro's Constant}$$

$e = \text{charge of } 1 \text{ e}^-$

b. Molten PbBr_2 is electrolysed. Given that 3.90 A of current is required to form 10 g of Br_2 , within, 30 minutes. Find the value of Avogadro's constant correct to 2 d.p.



$$\frac{10}{79.9 \times 2} = \frac{3.9 \times 30 \times 60}{2 \times A \times 1.60 \times 10^{-19}}$$

amount ₁	=	amount ₂
A_1		A_2

$$A = 3.51 \times 10^{23}$$

→ Define Standard Electron Potential (E°)

↳ It is the voltage measured of a half cell with with standard hydrogen electrode of the other half cell under standard conditions (2 marks)

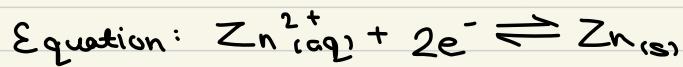
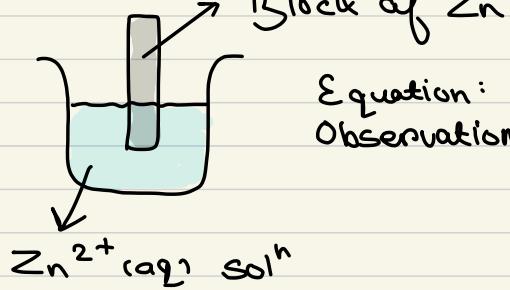
↳ By standard conditions we mean : 298 K temperature

- : For any solⁿ, the concⁿ of the sol must be 1 mol dm⁻³
- : For any gas present, the pressure of the gas must be 1 atm (1 mark)

Electrode Potential

Metal ion / Metal half-cell

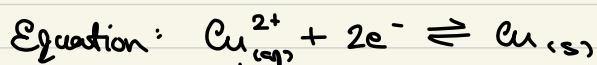
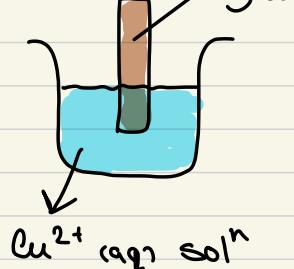
a) Block of Zn



Observations: None

: Reactⁿ is in equilibrium, rate of forward and reverse reactⁿ equal thus no observable change

b) Block of Cu



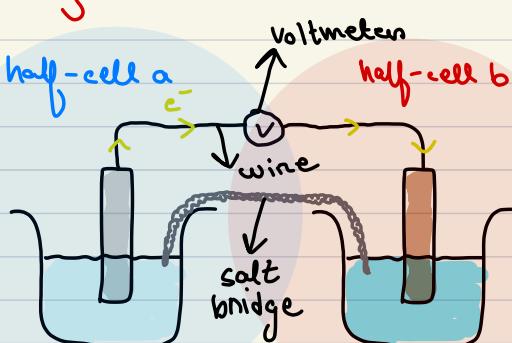
Observations: None

: Reactⁿ is in equilibrium, rate of forward and reverse reactⁿ equal thus no observable change

More reactive metals give up e⁻ more readily than less reactive metals

The ions of less reactive metals accept e⁻ more readily than ions of more reactive metals

a+b)



Zn atoms can give up e⁻ more readily than Cu atoms

Cu²⁺ ion can accept e⁻ more readily than Zn²⁺ ion

When a wire is used to connect the two half cells, Zn atoms start to release e⁻ more readily as the Cu²⁺ ion accept e⁻ more readily than the Zn²⁺ ion. (and vice versa from the perspective of the Cu²⁺ ion)

The salt bridge is used to complete the circuit by facilitating the flow of ions from 1 cell to another

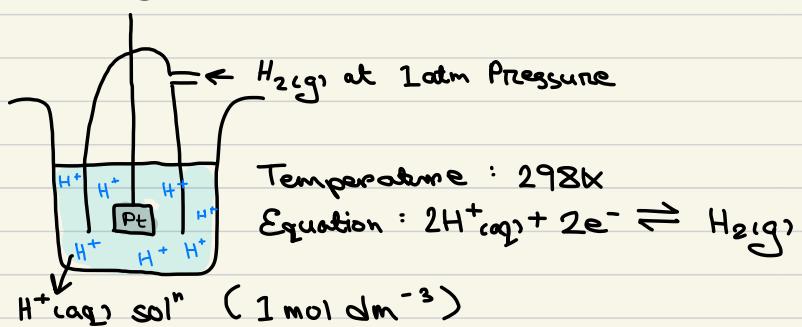
↳ In cell a, the equation:
 $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$
 shifts to the left

↳ In cell b, the equation:
 $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ shifts to the right

↳ This voltmeter reading is called Electrode Potential

A salt bridge is a filter paper soaked in KNO_3 or $NaNO_3$ soln. This is because ions of reactive metals do not accept e⁻ readily and are thus quite unreactive. NO_3^- ion have the lowest precedence of discharge in our syllabus thus also unreactive. Hence the salt bridge will not affect the experiment

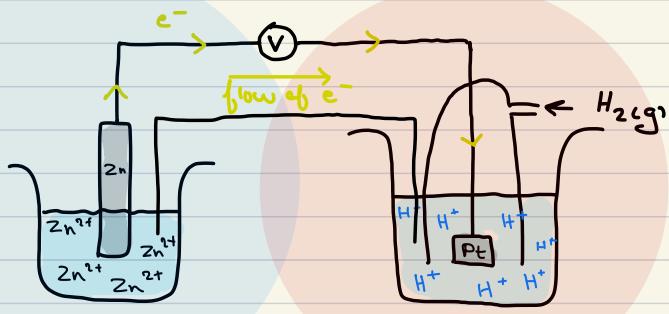
Standard Hydrogen half-cell



- # The Pt electrode provides an interface (for the $\text{H}_2(\text{g})$ to come into contact with the $\text{H}^{+}(\text{aq})$ ions) between the $\text{H}_2(\text{g})$ and $\text{H}^{+}(\text{aq})$
- # Pt is used as the electrode as it is highly unreactive

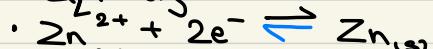
Standard E(c)lectron Potential (E°)

→ When finding the E° of a substance, its corresponding half-cell is connected to a Standard Hydrogen half-cell



$$E^\circ (\text{Zn}^{2+}/\text{Zn}) = -0.76$$

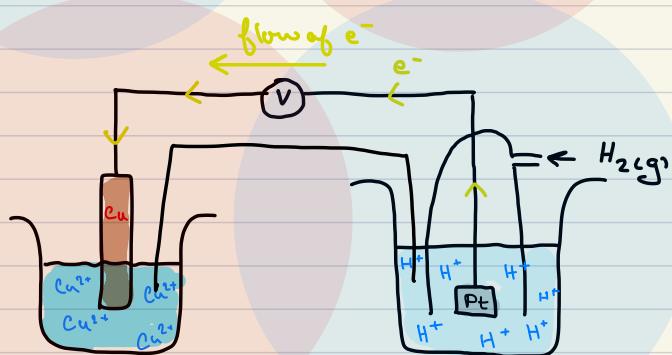
Equations



↳ Reverse reaction, Oxidation, is favoured



↳ Forward reaction, Reduction, is favoured

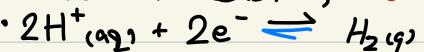


$$E^\circ (\text{Cu}^{2+}/\text{Cu}) = +0.34$$

Equations



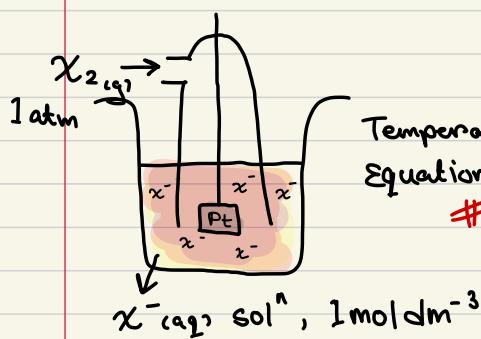
↳ Forward reaction, Reduction, is favoured



↳ Reverse reaction, Oxidation, is favoured

- # When writing any electrode potential equation, the forward reactⁿ must Always be Reduction
- # When a substance has a +ve E° : its reactⁿ will favour the forward reactⁿ
 - : Oxidation will occur in the standard hydrogen half cell
 - : e^{-} will flow away from the standard hydrogen half cell
 - : reduction occurring in the cell being measured
- # # The more reactive a substance // the more readily a substance can give e^{-} // the stronger the Reducing Ability of a substance, the more negative its E°
 - (metal)
 - : reducing agent // oxidised readily

Non-metal / Non-metallic ion half-cell

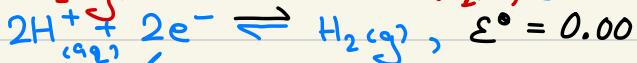
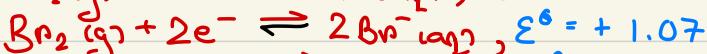
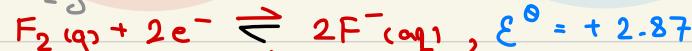
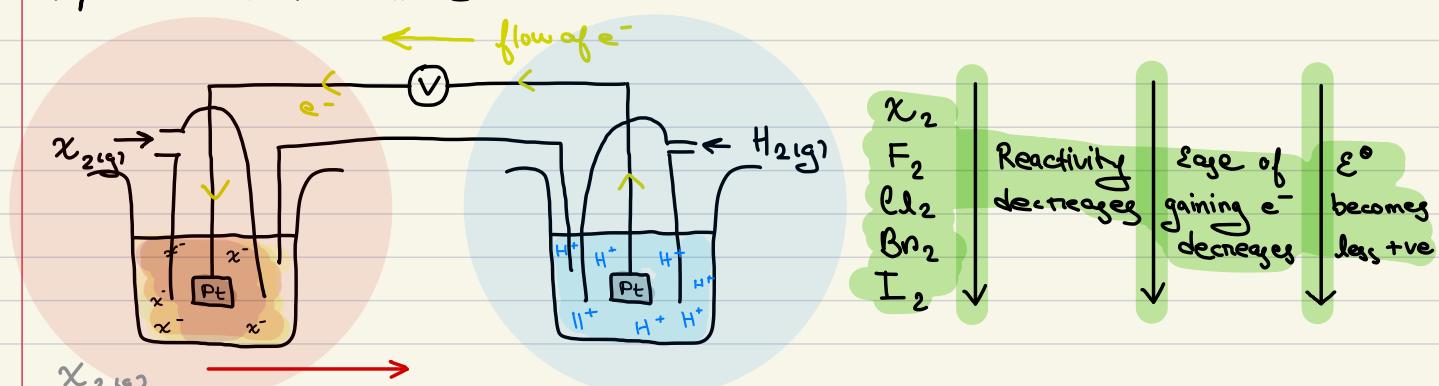


Temperature : 298K



both half cells must be under standard conditions when finding E°

Whenever the reacting species in a half-cell is a non-metal, we must use a platinum (Pt) electrode

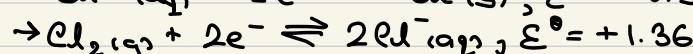
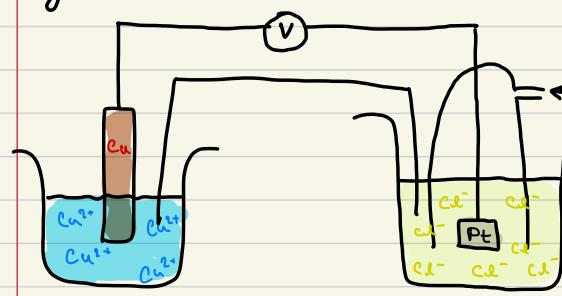


$X_{2(g)}$ acts as the oxidising agent and is reduced in the reacⁿ

The species on the L.H.S. of the electrode potential equation is always an oxidising agent as the forward reacⁿ is always a reduction reacⁿ where this species accepts e^{-}

The species on the R.H.S. of the electrode potential equation is always a reducing agent as the reverse reacⁿ is always an oxidation reacⁿ where this species gives e^{-}

The less positive (+ve) or more negative (-ve) the E° value, the species on the R.H.S. of the electrode potential equation acts as a more powerful reducing agent than $H_{2(g)}$



↳ $E^{\circ}(Cu^{2+}/Cu) < E^{\circ}(Cl_2/Cl^-)$

Alt. ↳ Cu stronger reducing agent than Pd⁻

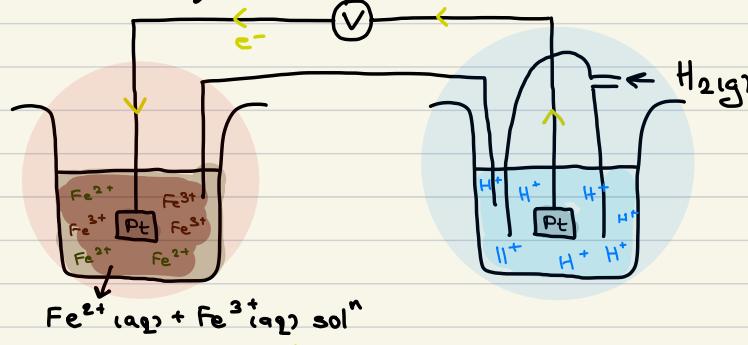
↳ Cl₂ stronger oxidising agent than Cu

1) $\therefore Cu^{2+} + 2Cl^{-} \rightarrow NO REAC^n$

2) $\therefore Cu + 2Pd \rightarrow Cu^{2+} + 2Pd^{-}$

Alt. The forward reaction of Cl₂ is more favourable than the forward reacⁿ of Cu²⁺. The reverse reaction of Cu is more favourable than the reverse reacⁿ of Cl⁻. Thus Cu and Cl₂ WILL react but Cu²⁺ and Cl⁻ will NOT

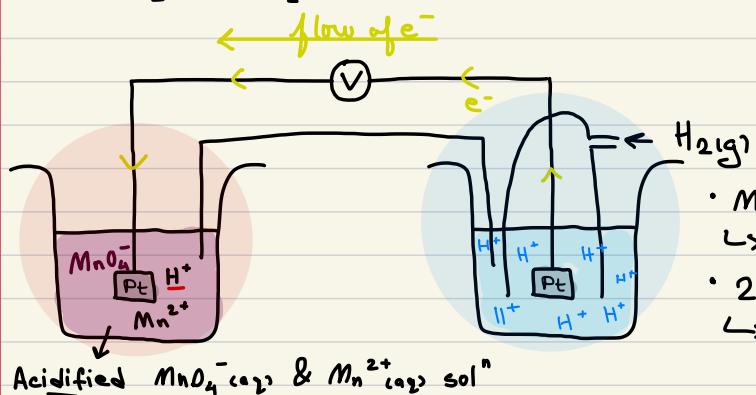
Ion / Ion half-cell



$$\mathcal{E}^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77$$

Equations

- $\text{Fe}^{3+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})}$
 - Forward reacⁿ, Reduction, is favoured
- $2\text{H}^{+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$
 - Reverse reacⁿ, Oxidation, is favoured



$$\mathcal{E}^\circ (\text{MnO}_4^{-}/\text{Mn}^{2+}) = +1.52$$

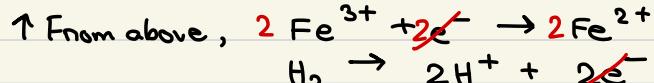
Equations

- $\text{MnO}_4^{-}_{(\text{aq})} + 8\text{H}^{+}_{(\text{aq})} + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})}$
 - Forward reacⁿ, Reduction, is favoured
- $2\text{H}^{+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$
 - Reverse reacⁿ, Oxidation, is favoured

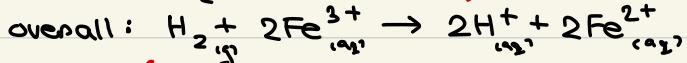
$\hookrightarrow \text{H}^+$ ions are in the solⁿ because it is Acidified // to provide Acidified conditions

Overall Equations

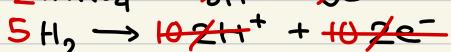
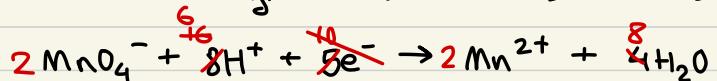
Favoured equation 1
+



Favoured equation 2



= Overall equation



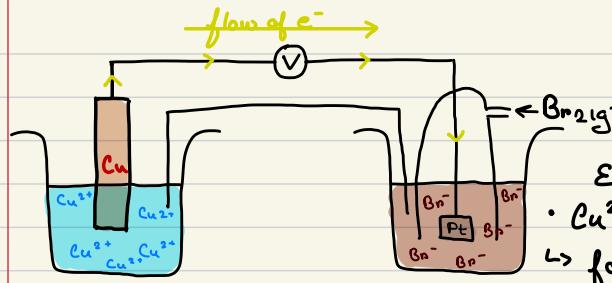
When finding overall equations, use full reaction arrows (\rightarrow) for the favoured equations as well as the overall equation

Electrochemical Cell Voltage ($\mathcal{E}^\circ_{\text{cell}}$)

\hookrightarrow When neither of the half-cells are a standard hydrogen electrode, we call call the voltmeter reading Electrochemical Cell Voltage ($\mathcal{E}^\circ_{\text{cell}}$)

$$\begin{aligned} \mathcal{E}^\circ_{\text{cell}} &= \mathcal{E}^\circ_{\text{reduction}} - \mathcal{E}^\circ_{\text{oxidation}} \\ &= \text{more +ve } \mathcal{E}^\circ - (\text{less +ve } \mathcal{E}^\circ) \end{aligned}$$

P.T.O.

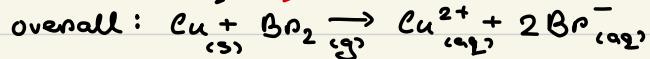
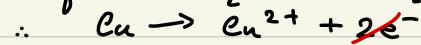
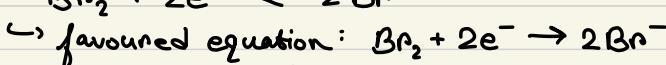
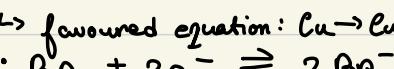
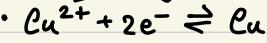


$$\mathcal{E}^\circ (\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$$

$$\mathcal{E}^\circ (\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$$

Since $\mathcal{E}^\circ (\text{Cu}^{2+}/\text{Cu}) < \mathcal{E}^\circ (\text{Br}_2/\text{Br}^-)$, forward reaction of Br_2 will be favoured and reverse reaction

Equations



$$\begin{aligned}\mathcal{E}^\circ_{\text{cell}} &= \mathcal{E}^\circ (\text{Br}_2/\text{Br}^-) - \{\mathcal{E}^\circ (\text{Cu}^{2+}/\text{Cu})\} \\ &= 1.07 - (0.34) \\ &= 0.73 \text{ V}\end{aligned}$$

- # If there is any change in the condition of equilibrium, the position of equilibrium will change
 \hookrightarrow If reactant decreases, rate of forward reaction (reduction) decreases. The equilibrium shifts to the left to oppose the change. Thus E becomes less +ve

Nernst Equation

$$\Sigma = \Sigma^\circ + \frac{RT}{ZF} \ln \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

where : Σ = Electrode Potential under non-standard conditions

R = Molar Gas Constant = 8.31

T = Temperature / K

Z = no. of mol's of e^- in the standard equation

F = Faraday Constant = 96500 C mol⁻¹

species that gets reduced

$[\text{oxidised form}] = \text{conc}^n$ of product of oxidation // oxidising agent

$[\text{reduced form}] = \text{conc}^n$ of product of reduction // reducing agent

for non-aqueous products, we take the concⁿ of 1

Species that gets oxidised

- # Electrode Potential always written to 2 d.p.

(cathode)

+ve electrode receives e^- from wine

-ve electrode gives e^- to wine
 (anode)

- a) Calculate the electrode potential of an Ag/Ag^+ electrode at 298K, where $[\text{Ag}^+]$ is $2 \times 10^{-4} \text{ mol dm}^{-3}$

$$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}, \quad \Sigma = \Sigma^\circ + \frac{8.31 \times 298}{1 \times 96500} \ln \frac{2 \times 10^{-4}}{1}$$

$$= +0.58 \text{ V}$$

Misc. Notes

- # When $\Sigma^{\circ}_{\text{cell}} > 0$, forward reactⁿ is favoured, $[\text{products}] > [\text{reactants}]$, equilibrium shifts to the right
 $\Sigma^{\circ}_{\text{cell}} = \frac{\text{reduction - oxidation}}{\text{forward - backward}}$
 \therefore when $\Sigma^{\circ}_{\text{cell}} > 0$, forward reactⁿ more favoured than backward
- # A reactⁿ is feasible if Σ_{cell} is +ve
- # Remember to add salt bridge to diagram
- # The terminal / electrode that receives e^- is called the +ve terminal / positive electrode / cathode
- # Reducing agent or
Increasing concⁿ of oxidising agent (species being reduced) makes its Σ more +ve because it becomes more likely to be reduced.
- # Nernst Equation
 - i) For Σ_{cell} : $\Sigma_{\text{cell}} = \Sigma^{\circ}_{\text{cell}} + \frac{RT}{ZF} \ln \frac{[\text{oxidised form}]}{[\text{Reduced form}]}$
 - ii) For Σ : $\Sigma = \Sigma^{\circ} + \frac{RT}{ZF} \ln \frac{[\text{oxidising/reducing agent}]}{1}$
(half cell/electrode)
 - L) If the concⁿ of the reduced form decreases, Σ_{cell} should become more positive, thus the Σ of that reduced form should be more negative as $\Sigma_{\text{cell}} = \Sigma_{\text{oxidised form}} - \Sigma_{\text{reduced form}}$