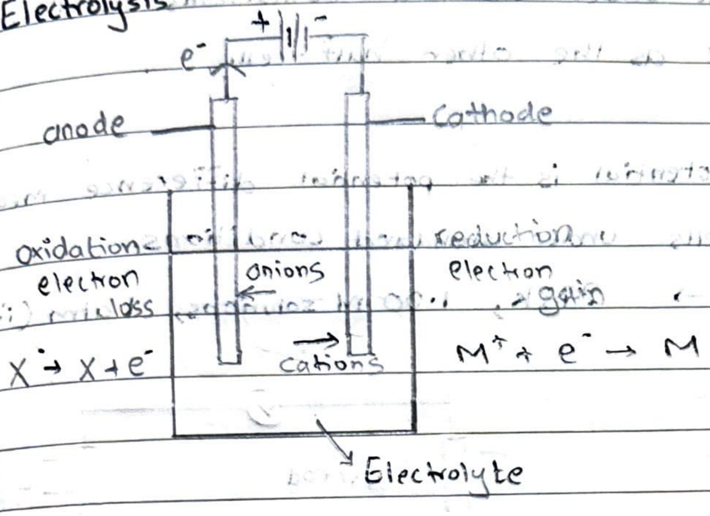
Electrochemistry

⇒ Electrolysis



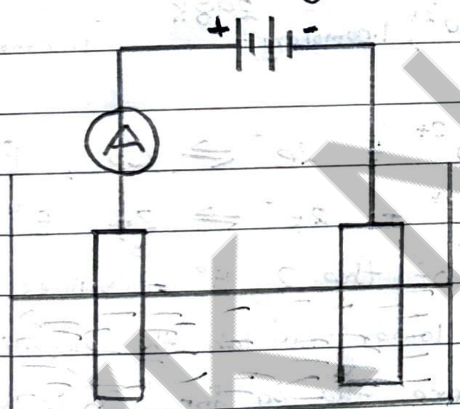
Electrolysis is the decomposition of an ionic compound into its elements by the passage of electricity.

OILRIG → oxidation is loss of e^-, Reduction is gain of e^-

ANOX → oxidation at anode

REDCAT → Reduction at cathode

⇒ Quantitative Electrolysis



To measure the amount of metal deposited or the amount of gas bubbled off in a particular time interval.

we can find charge by using

$$Q = It$$

Faraday's constant

→ 96500 C, it is the charge on one mole of electron.

$F = Le$ → F = Faraday's constant, L → avogadro's constant, e → electron charge

$\rightarrow F = 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$

$= 96500C$

$$\frac{Q}{F} = n$$ → number of moles of electrons

$Na^+ + e^- \rightarrow Na$

$2Cl^- \rightarrow Cl_2 + 2e^-$

after finding n, use that to find moles of the metal / gas and then use that to find the volume / mass

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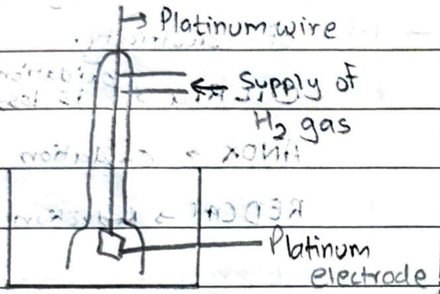
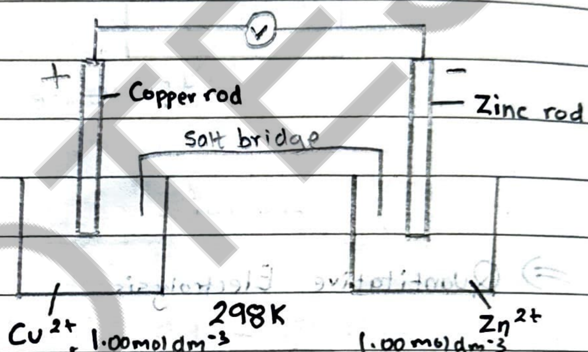
⇒ Electrode potentials

→ The standard electrode potential of a half-cell is the potential difference measured under standard conditions with a standard hydrogen electrode as the other half-cell.

→ The standard cell potential is the potential difference measured across two half cells under standard conditions.

→ Standard conditions → 298 K, 1.00 M solutions, 1 atm (if gas present)





$Cu^{2+} + 2e^- \rightleftharpoons Cu$, $E^\circ = +0.34\,V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn$, $E^\circ = -0.76\,V$

out of the 2 E° values whichever is lower switch the equation for that.

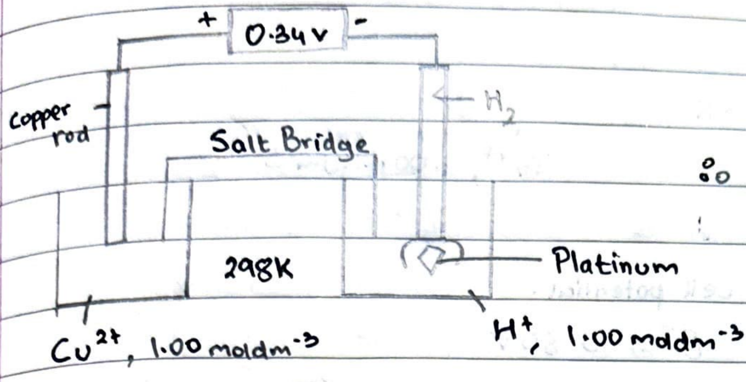
∴ here the eq for Zn is lower so:

$Zn \rightleftharpoons Zn^{2+} + 2e^-$, $E^\circ = +0.76\,V$

Now we add both E° values

∴ $+0.76 + 0.34 = 1.10\,V$

⇒ Half cells containing metal and metal ions



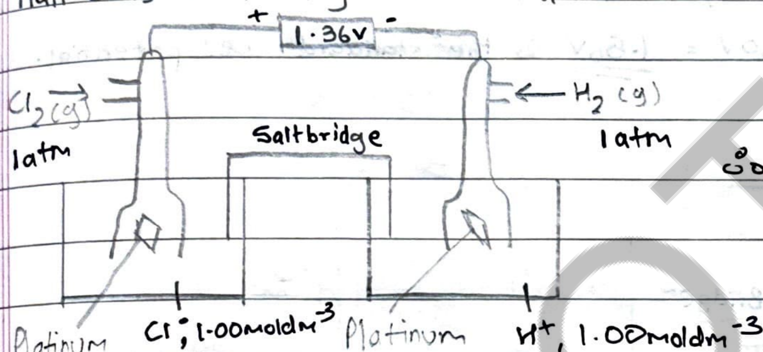
$Cu^{2+} + 2e^- \rightleftharpoons Cu$, $E^\circ = 0.34$

$2H^+ + 2e^- \rightleftharpoons H_2$, $E^\circ = 0$

∴ $H_2 \rightleftharpoons 2H^+ + 2e^-$, $E^\circ = 0v$

finally $0 + 0.34v = 0.34v$

⇒ Half cells containing non-metal and non-metal ions



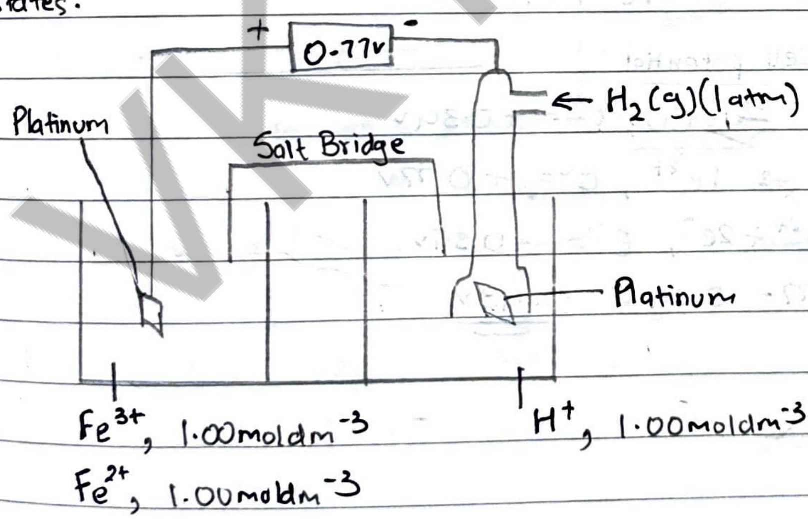
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$, $E^\circ = 1.36v$

$2H^+ + 2e^- \rightleftharpoons H_2$, $E^\circ = 0$

∴ $H_2 \rightleftharpoons 2H^+ + 2e^-$, $E^\circ = 0$

finally $0 + 1.36v = 1.36v$

⇒ Half cells containing ions of the same element in different oxidation states.



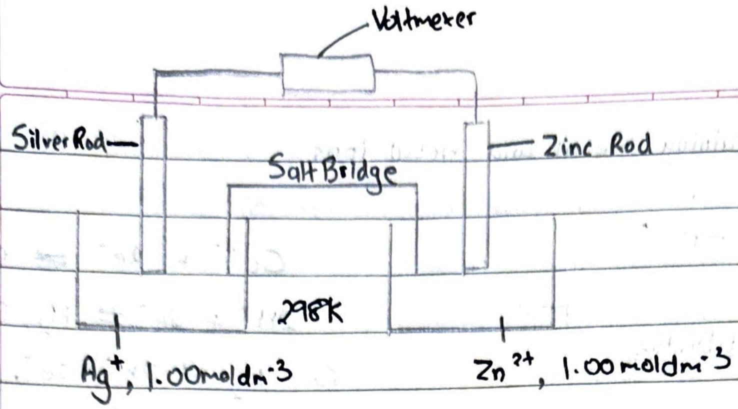
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, $E^\circ = 0.77v$

$2H^+ + 2e^- \rightleftharpoons H_2$, $E^\circ = 0$

∴ $H_2 \rightleftharpoons 2H^+ + 2e^-$, $E^\circ = 0$

Finally $0 + 0.77 = 0.77v$

Q.



Find the standard cell potential.

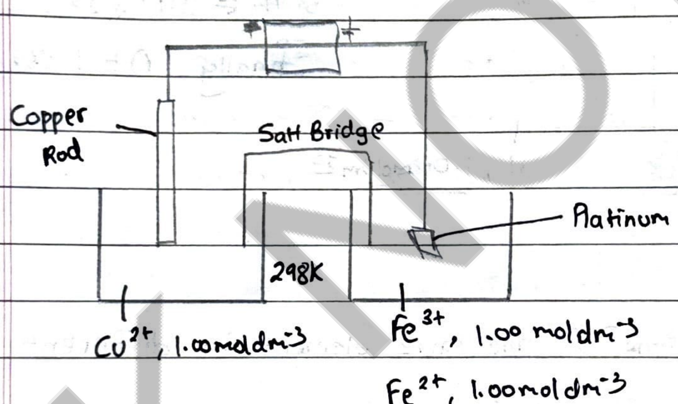
$Ag^+ + e^- \rightleftharpoons Ag$, $E^\circ = 0.80V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn$, $E^\circ = -0.76V$

$\therefore$ $Zn \rightleftharpoons Zn^{2+} + 2e^-$, $E^\circ = +0.76V$

$\Rightarrow 0.76V + 0.80V = \underline{1.56V}$ is the standard cell potential.

Q.



find standard cell potential

→ $Cu^{2+} + 2e^- \rightleftharpoons Cu$, $E^\circ = +0.34V$

→ $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, $E^\circ = +0.77V$

$\therefore$ $Cu \rightleftharpoons Cu^{2+} + 2e^-$, $E^\circ = -0.34V$

finally $0.77 - 0.34 = \underline{0.43V}$

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8. Use data from the Data Booklet to construct redox equations, and calculate the standard cell potentials for reaction between:

i → Acidified H_2O_2 (aq) and KI (aq)

→ As given in data booklet

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\circ = +1.77V$

$K^+ + e^- \rightleftharpoons K$ $E^\circ = -2.92V$

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\circ = +0.54V$

As both equations have a lesser value for E°, they both will be inverted.

When inverted they form:

$K \rightleftharpoons K^+ + e^-$ $E^\circ = 2.92V$ → here K reacts with H_2O_2

$2I^- \rightleftharpoons I_2 + 2e^-$ $E^\circ = -0.54V$ → here I^- reacts with H_2O_2

★ we want a reaction between H_2O_2 and K^+ / I^-

so as I^- is reacting in the 2^{nd} equation, we will use the E° of 2^{nd} equation to find the standard cell potential.

∴ $+1.77 - 0.54 = \underline{1.23V}$

→ The overall reaction is

→ $H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$

ii) Cl_2 (aq) and SO_2 (aq)

→ As given in the data booklet

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36V$

$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$ $E^\circ = +0.17V$

→ Inverting SO_2 eq.

$SO_2 + 2H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$ $E^\circ = -0.17V$

→ Final answer

= ~~1.36 + 0~~ 1.36 − 0.17

= ~~+1~~ $\underline{+1.19V}$

→ Overall equation

$Cl_2 + SO_2 + 2H_2O \rightarrow 2Cl^- + SO_4^{2-} + 4H^+$

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Q. Use data from the data booklet to predict the likely product of the reaction between $I_2 (aq)$ and tin metal, writing a balanced equation for the reaction.

→ As given in data booklet

③ $I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\circ = +0.54\ V$

① $Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\circ = -0.14\ V$

② $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $E^\circ = +0.15\ V$

As E° of ① < ③

we invert it = $Sn \rightleftharpoons Sn^{2+} + 2e^-$ $E^\circ = +0.14V$

As E° of ② < ③

we invert it = $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$ $E^\circ = -0.15V$

Overall equation for Sn

$Sn + \cancel{Sn^{2+}} \rightarrow \cancel{Sn^{2+}} + Sn^{4+} + 2e^- + 2e^-$

$= Sn \rightarrow Sn^{4+} + 4e^-$ $E^\circ = -0.01V$

Overall equation for I_2 and Sn

multiply ③ with 2 for balancing the eq. : $2I_2 + 4e^- \rightleftharpoons 4I^-$

$2I_2 + \cancel{4e^-} + Sn \rightarrow Sn^{4+} + \cancel{4e^-} + 4I^-$

$= 2I_2 + Sn \rightarrow Sn^{4+} + 4I^-$

Final equation

$= 2I_2 + Sn \rightarrow SnI_4$

⇒ Predicting the feasibility of a reaction using E° values
→ if $E^\circ < 0$ then not possible
→ if $E^\circ > 0$ then possible

⇒ Variation of E values with concentration of ions

→ Example

$Na^+ + e^- \rightleftharpoons Na$ $E^\circ = -2.71\ V$
$1\ mol\ dm^{-3}$

$Na^+ + e^- \rightleftharpoons Na$ $E^\circ = -3.00\ V$
$0.5\ mol\ dm^{-3}$

As the concentration of Na^+ decreases the equilibrium shifts to the left. Which means the drive to make Na decreases.
∴ the E° value decreases

→ Example 2

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\circ = +0.34\ V$
$1\ mol\ dm^{-3}$

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\circ = +0.50\ V$
$1.5\ mol\ dm^{-3}$

As the concentration of Cu^{2+} increases the equilibrium shifts to the right. Which means the drive to make Cu increases. ∴ E value increases.

⇒ Predicting if a reaction occurs under non-standard condition

→	Occurs	Does not occur
Standard	$E^\circ > 0$	$E^\circ < 0$
non-standard	$E^\circ > 0.30$	$E^\circ < 0.30$

⇒ The Nernst Equation

→ it is used to find E values in non standard conditions.

$$E = E^{\circ} + \frac{RT}{ZF} \ln\left(\frac{[\text{Oxidised form}]}{[\text{reduced form}]}\right)$$

example $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E = E^{\circ} + \frac{8.31 \times \text{Temperature}}{1 \times 96500} \times \ln\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right)$$

OR

when temperature is constant

$$E = E^{\circ} + \frac{0.059}{Z} \times \log\left(\frac{[\text{Oxidised form}]}{[\text{reduced form}]}\right)$$

example $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E = E^{\circ} + \frac{0.059}{1} \times \log\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right)$$

Important → R = gas constant = 8.31

T = temperature in kelvin

Z = no. of moles of electrons

F = Faraday's constant = 96500

[ ] = concentration of the element/ion present in brackets.

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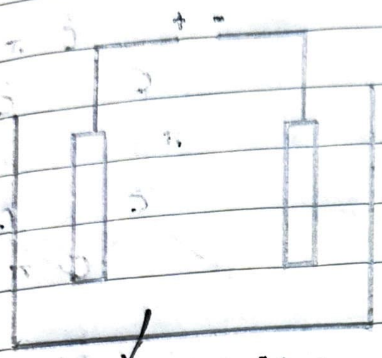
⇒ Predicting the products of the electrolysis of aqueous solutions using E° values



$Na^+(aq)$ $Cl^-(aq)$

H^+ OH^- → because aqueous solution.

To find out which metal will go on the cathode we compare their E° values. If E° value is higher then that metal will go on the cathode. Like here:

$Na^+ + e^- \rightarrow Na$ $E^\circ = -2.71\ V$

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0$

∴ H^+ ions will go to the cathode forming hydrogen gas.

To find out which negative ion will go we have a series:

Who discharges most easily

$I^- > Br^- > OH^- > Cl^- > NO_3^- > SO_4^{2-}$

∴ OH^- ions will go to the anode forming oxygen gas.

∴ NaCl will be left in the electrolyte after the reaction.