

## Electrode Potentials

Q-1) What is electronegativity?

- > It's the change of chemical energy to electrical energy in electrochemical cells. / The attraction by an atom of the  $e^-$  shared in a bond.

Q-2) What is electrode potential?

- > Electrode potential is the voltage measured for a half-cell compared with another half-cell.

\* The value tells us the ease and how far reduction occurs. (E)

more **positive** = REDUCTION

- > The standard electrode potential is the voltage measured under standard conditions with a standard hydrogen electrode as the other half-cell. ( $E^\ominus$ )

STANDARD CONDITIONS :

- 298K temperature
- 101 kPa pressure
- 1 mol dm<sup>-3</sup> concentration of ions.

Q-3) What is the Standard Hydrogen Electrode?

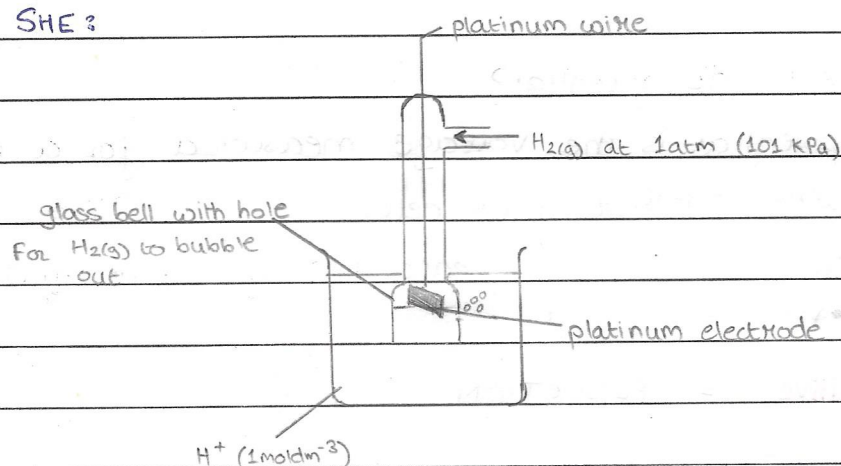
- > Standard Hydrogen Electrode (SHE) is given a value of 0.00V. All other standard electrode potentials are measured relative to this value.

- \* H<sub>2</sub> gas at 101 kPa bubbles into a 1 mol dm<sup>-3</sup> H<sup>+</sup> ion solution.
- \* A Platinum (Pt) electrode covered with Pt black is in contact with H<sub>2</sub>(g) and H<sup>+</sup> ions.
- \* The Pt black is finely divided to allow close contact of H<sub>2</sub>(g)

and  $H^+$  ions, so that equilibrium between them is established quickly.

- \* Pt collects  $H_2(g)$  by adsorption, so a high concentration of  $H_2(g)$  can be maintained at that point.
- \* Pt electrode is inert so doesn't take part in the reaction.

SHE:



SHE can act as a +ve or -ve electrode, depending on the other half-cell.

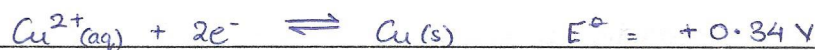
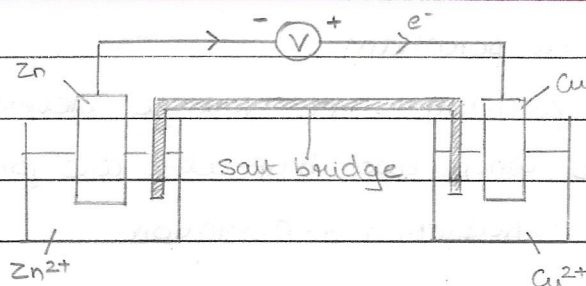
#### 0-4) Electrochemical cells.

- > Electrochemical cells convert chemical energy to electrical energy
- > They are formed by combining two half-cells.

Half cells are ~~comb~~ connected using:

- wires connecting the metal rods in each half cells to a high resistance voltmeter.  $e^-$  flow from less positive  $E^\ominus$  to more positive  $E^\ominus$
- Salt bridge allows movement of ions between the 2 half-cells to maintain ionic balance. It doesn't allow movement of  $e^-$ .

eq:



\* salt bridge contains  $\text{KNO}_3$

-  $\text{K}^+$  ions flow to  $\text{Cu}^{2+}$  to cancel out effect of  $\text{e}^-$  being sent to this half-cell.

-  $\text{NO}_3^-$  ions flow to  $\text{Zn}^{2+}$  to cancel out deficiency of  $\text{e}^-$ .

salt bridge maintains ion balance.

Q-5) Types of electrochemical cells.

① Half cell with metal rod and metal ions

② Half cell with non-metal rod and non-metal ions

↳ Platinum wire + platinum foil is used as an electrode to create electrical contact with the solution.

③ Half cells containing ions of different oxidation states.

④ Half cell with gas electrode and ions.

• Direction of  $\text{e}^-$  flow:

\* The  $\text{e}^-$  flow from -ve to +ve electrode.

∴ in this chapter

→ anode = -ve because oxidation takes place here

→ cathode = +ve because reduction takes place here.

• Predict feasibility of a reaction.

\* cell voltage = Reduction + oxidation

• if cell voltage  $> 0.30 \text{ V}$ , reaction will occur.

• if oxidising agent has higher  $E^\ominus_{\text{cell}}$ , it's more likely to be reduced and cause oxidation.



Q-6) What is standard cell potential?

- > The standard cell potential is the voltage developed under standard conditions when two half-cells are joined ( $E^\circ_{\text{cell}}$ ).  
cell potential = Reduction + Oxidation.

Q-7) The halogens as oxidising agent.

- > Down the group VII, the  $E^\circ$  values of the halogens decreases.  
 $\therefore$  the ability of the halogen ions to act as oxidising agents decreases down the group.  
(the ability of the halogen ions to act as reducing agents increases down the group).



Q-8) Limitations of  $E^\circ$  values

- ① Under non-standard conditions, feasibility can't be predicted.

\*  $E^\circ_{\text{cell}}$  is not accurate.

eg: change in concentration affects equilibrium position  $\therefore E^\circ$  value.

- ② Rate of reaction can't be predicted

\* Don't know when the reaction will happen.

Q-9) The ~~Nernst~~ <sup>Nernst</sup> Equation.

- > It's used to find electrode potential under non standard conditions.

$$E = E^\circ + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

no. of  $e^-$  lost or gained.

one with higher oxidation state  
one with lower oxidation state  
their concentrations.

Q-10) Cells and batteries.

> In primary cells, the redox reactions continue until the concentration of the reactants reaches a low value so the voltage declines and the cell can't be used anymore.

eg: Dry cell.

> In a secondary cell, the electrochemical cell can be re-charged by passing an electric current again, so the products are converted back to reactants and the cell can function again.

eg: car battery (lead storage cell) + fuel cells.

WHEN SELECTING A CELL WE NEED TO CONSIDER:

- \* is it rechargeable.
- \* the size + mass of the cell
- \* the voltage + how long it delivers maximum voltage
- \* the nature of the electrolyte.
- \* cost of the cell.

Q-11) Rechargeable cells.

Lead Storage battery (car battery)

- cheap to manufacture
- heavy

Nickel-Cadmium cell

- small size
- give low voltage
- low mass
- don't 'run down' quickly

Aluminium-air battery

- lightweight
- expensive
- produce high voltage
- Al anode has to be replaced



Q-12) Primary cells. - solid state cells

> Solid state cells (button cells) are better than Dry cells:

- small and lightweight
- give a high voltage
- give a constant voltage over time.
- they don't contain liquid or paste, so they don't leak

commonly used button cells are

-ve pole

+ve pole

Lithium or zinc.

Iodine, Manganese(IV) oxide, silver oxide.

Li or Zn

I<sub>2</sub>

MnO<sub>2</sub>

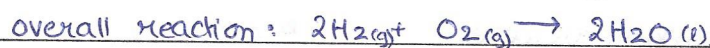
or Ag<sub>2</sub>O

Q-13) Fuel cells

> A fuel cell is an electrochemical cell in which a fuel gives up e<sup>-</sup> at one electrode, and oxygen gains e<sup>-</sup> at the other electrode.

eg: Hydrogen-oxygen fuel cell.

H<sub>2(g)</sub> and O<sub>2(g)</sub> are bubbled through two porous Pt-coated electrodes where the half-cell reactions take place.



- no harmful products (only H<sub>2</sub>O)
- produce more energy per gram of fuel burnt than petrol engines
- they are efficient (transmission of energy from fuel to motor is direct ∴ no heat loss)
- High cost for materials.
- Manufacturing involves toxic by-products
- High pressure tanks are needed to store H<sub>2(g)</sub>
- Refueling is done more often than petrol engine.
- H<sub>2</sub> is produced using fossil fuels.
- Don't work at a low temperature (fuel cell freezes below 0°C).



Q-14) Faraday's laws:

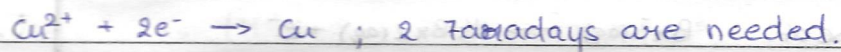
1<sup>st</sup> law:

The mass of a substance produced at an electrode is proportional to the quantity of electricity passed.

$$Q = It$$

2<sup>nd</sup> Law:

The number of Faradays required to discharge 1 mole of an ion at an electrode is equal to the charge on the ion.



$$1 \text{ Faraday} = 96500 \text{ Coulombs.}$$

Q-15) Faraday constant  $\neq$  Avogadro's constant

Faraday constant  $\neq$  charge on an electron.

$$F = n e$$

Avogadro constant

EXPERIMENT: electrolysis of Cu.

\* mass of anode at start and end is measured

\* mass of Cu removed from anode is calculated.

→ calculate  $Q = It$  for that mass of Cu removed.→  $\therefore$  calculate  $Q$  on 1 mol of Cu removed.

$[Cu^{2+} + 2e^- \rightarrow Cu]$ ; 2 moles of  $e^-$  are needed to produce 1 mol of Cu  $\therefore Q$  on 1 mol of  $e^-$  will be divided by 2.

use:

$$L = \frac{\text{charge on 1 mole of } e^-}{\text{charge on 1 } e^-}$$



Q-16) Electrolysis.

① Molten electrolysis.

- When pure molten ionic compounds are electrolysed,

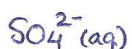
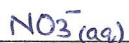
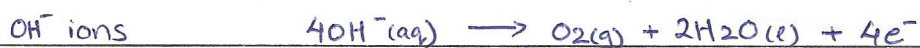
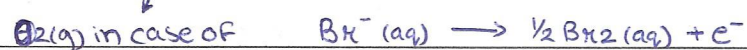
cathode = METAL

anode = NON-METAL

② Aqueous solutions (dilute) electrolysis.

When aqueous ionic solutions are electrolysed

cathode = the one with the higher  $E^\ominus$  value



↑  
increasing  
ease of  
discharge.

③ Aqueous solutions (concentrated) electrolysis

When aqueous ionic solutions are electrolysed.

cathode = ion from the salt.

anode = relative ease of oxidation series.

