

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 OILRIG 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°)

STANDARD CONDITIONS:

- 298 K temperature

- 101 kPa pressure

- 1 mol dm^{-3} 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.

* H₂ gas at 101 kPa bubbles into a 1 mol dm^{-3} H⁺ ion solution.

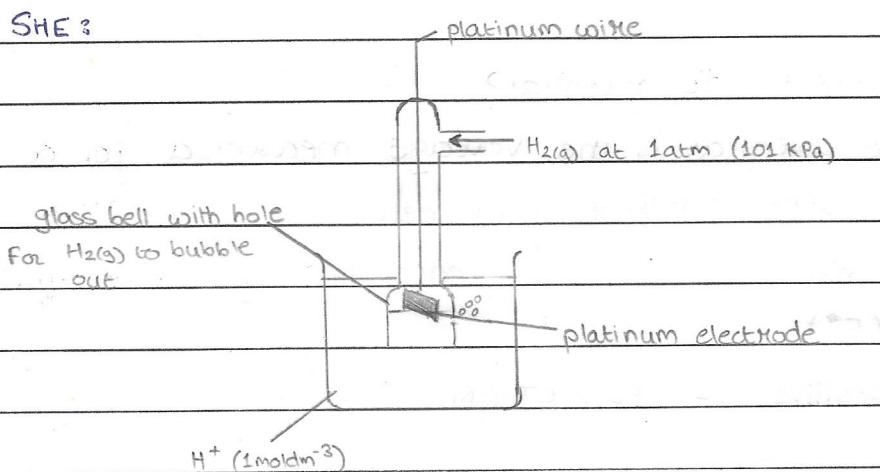
* A Platinum (Pt) electrode covered with Pt black is in contact with H₂(g) and H⁺ ions.

* The Pt black is finely divided to allow close contact of H₂(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.

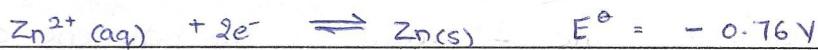
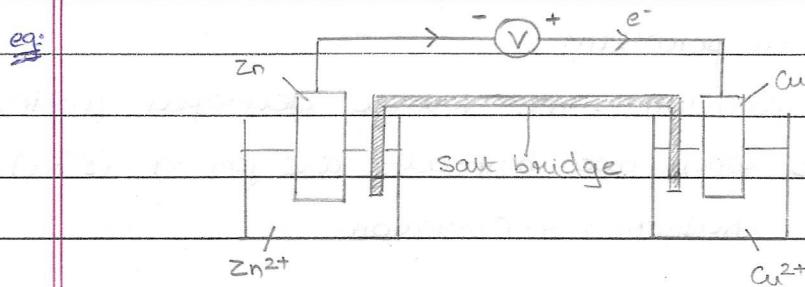
SHE:



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

Q-4) Electrochemical cells.

- > Electrochemical cells convert chemical energy to electrical energy
- > They are formed by combining two half-cells.
- Half cells are combi connected using:
 - wires connecting the metal rods in each half cells to a high resistance voltmeter. e^- flow from less positive E° to more positive E°
 - Salt bridge allows movement of ions between the 2 half-cells to maintain ionic balance. It doesn't allow movement of e^- .



* salt bridge contains KNO_3

- K^+ ions flow to Cu^{2+} to cancel out effect of e^- being sent to this half-cell.
- NO_3^- ions flow to Zn^{2+} to cancel out deficiency of 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 e^- flow:

* The 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 > 0.30V, reaction will occur.

• if oxidising agent has higher E° , 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°_{cell}).
cell potential = Reduction + Oxidation.

Q-7) The halogens as oxidising agents.

- Down the group VII, the E° 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° values.

- Under non-standard conditions, feasibility can't be predicted.
 E°_{cell} is not accurate.
e.g. change in concentration affects equilibrium position $\therefore E^\circ$ value.
- Rate of reaction can't be predicted
* Don't know when the reaction will happen.

Q-9) The Nernst Equation.

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

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

no. of e^- lost or gained. | their concentrations.

one with higher oxidation state
 one with lower oxidation state

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

Aluminium-air battery

- lightweight
- produce high voltage
- expensive
- 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

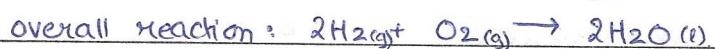
I_2 , MnO_2 on Ag_2O

Q-13) Fuel cells

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

eg: Hydrogen-oxygen fuel cell,

$H_2(g)$ and $O_2(g)$ are bubbled through two porous Pt-coated electrodes where the half-cell reactions take place.



- no harmful products (only H_2O)
- produce more energy per gram of fuel burnt than petrol engines
- they are efficient (transmission of energy from fuel to motor is direct \therefore no heat loss)
- High cost for materials.
- Manufacturing involves toxic by-products
- High pressure tanks are needed to store $H_2(g)$
- Refueling is done more often than petrol engine.
- H_2 is produced using fossil fuels.
- Don't work at a low temperature (fuel cell freezes below $0^\circ C$).

Q-14) Faraday's laws.

1st law:

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

$$Q = IT$$

2nd 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 Faraday = 96500 Coulombs.

Q-15) Faraday constant & Avogadro constant.

Faraday constant charge on an electron.

$$F = \frac{1}{N} e$$

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.

→ ∵ calculate Q on 1 mol of Cu removed.

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

use:

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

Q-16) Electrolysis.

① Molten electrolysis.

- When pure molten ionic compounds are electrolysed,

cathode = METAL

anode = NON-METAL

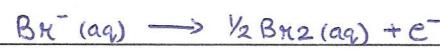
② Aqueous solutions (dilute) electrolysis.

When aqueous ionic solutions are electrolysed

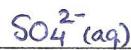
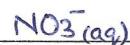
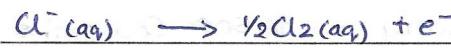
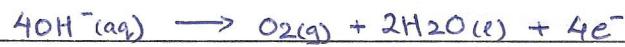
cathode = the one with the higher E° value



$\text{O}_2(\text{g})$ in case of



OH^- ions



↑
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.

$\text{O}_2(\text{g})$ in case of

↪ [same as above]

OH^- ions.