

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.

OILRIG

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⁻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.

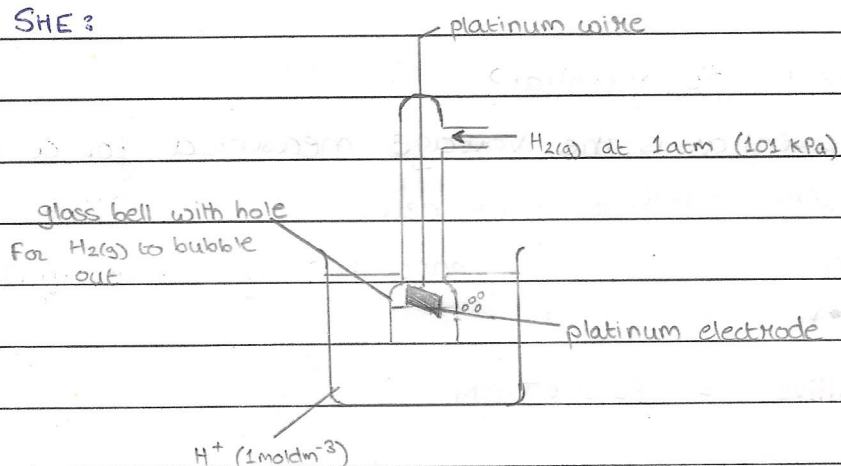
* A Platinum (Pt) electrode covered with Pt black is in contact with H₂(g) and H⁺ ions.

* 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.

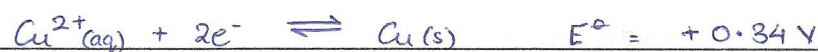
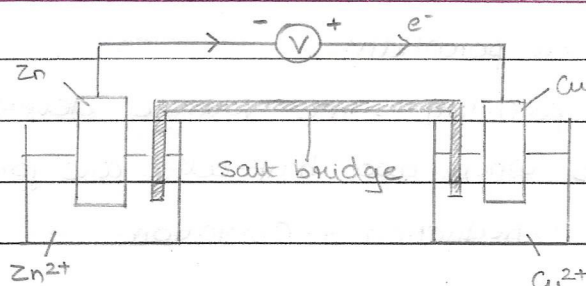
0-4) Electrochemical cells.

- > 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 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 $> 0.30 \text{ V}$, reaction will occur.

• if oxidising agent has higher E^\ominus_{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°_{cell}).
- cell potential = Reduction + Oxidation.

Q-7) The halogens as oxidising agent.

- > 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

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

* E°_{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~~ ^{Nernst} 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. | 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

I₂

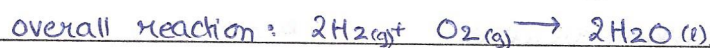
MnO₂ or Ag₂O

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 H₂O)
- 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_{2(g)}
- Refueling is done more often than petrol engine.
- H₂ is produced using fossil fuels.
- Don't work at a low temperature (fuel cell freezes below 0°C).



Q-14) Faraday's Laws:

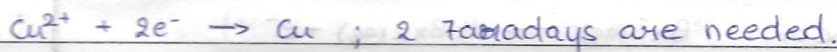
1st Law:

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.



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

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.

$[\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}]$; 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,

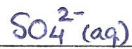
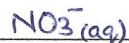
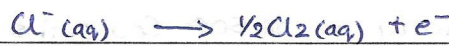
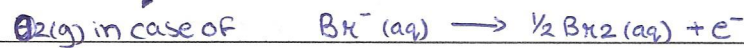
cathode = METAL

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.

