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ELECTROCHEMISTRY:

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TYPES OF ELECTROCHEMICAL RXNS:

1. Electrical $\rightarrow$ Chemical energy:
 - ↳ electrical current passed through solution.
 - ↳ process called **electrolysis**.
 - ↳ Δ chemical makeup of solution.
 2. Chemical $\rightarrow$ Electrical energy:
 - ↳ chemical rxn bet. chemicals.
 - ↳ production of electrical current.
 - ↳ takes place in batteries
- both involve a transfer of electrons

TYPES OF ELECTROCHEMICAL CELLS:

1. **Electrolytic cells:**
 - ↳ device that converts electrical energy into chemical potential by means of a **non-spontaneous** redox rxn.
 - ↳ electrical energy required to start rxn.
 - ↳ electrode rxns sustained by supply of electrical energy
 - ↳ convert to chemical
2. **Galvanic / voltaic cells:**
 - ↳ device that converts chemical energy to electrical energy as a result of **self-sustaining** spontaneous electrode rxns.

ELECTROLYTIC CELLS:

ELECTROLYSIS:

- ↳ process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them.
- in order for electrolysis to work; ions must be free to move
- **electrode:** electrical conductor used to make contact w/ nonmetallic part of circuit
- **electrolyte:** substance that can conduct electricity by forming free ions when molten or dissolved in a solution.

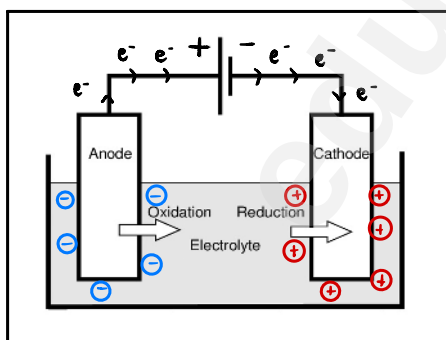


Diagram showing an electrolytic cell.

- **+** ions attracted to **- electrode**
- **-** ions attracted to **+** electrode
- ions (l) or (aq) move freely which allows for flow of current

- electrode made of a solid substance which has delocalised e^- ; e.g. metal and graphite

- this is for a **non-spontaneous rxn**.
- delocalised e^- move throughout electrodes.

- in electrolytic cells: The cathode is always negative and the anode is always positive

USES OF ELECTROLYSIS:

1. extraction of metals (aluminium from bauxite, magnesium, sodium).
2. Preparation of halogens (e.g. chlorine)
3. Refining of metals (e.g. Cu; Zn)

ELECTRODES: part of process that transfers electrons

- **inert:** does not take place in rxn (e.g. carbon, platinum)
- **active:** takes place in rxn (e.g. Cu electrode in $CuCl_2(aq)$)
- **Positive ions move to negative electrode**
 - ↳ metal | hydrogen ions $\oplus$:: metal | $H_2(g)$ produced

- **Negative ions move to positive electrode**
 - ↳ non-metal ions $\ominus$:: non-metals produced

REDCAT

- ↳ reduction occurs at cathode

ANOX

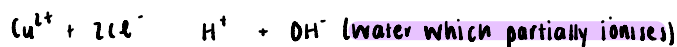
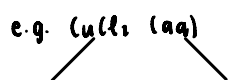
- ↳ oxidation occurs at anode

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ELECTROLYSIS OF AQUEOUS SOLUTIONS IDENTIFYING PREDOMINANT HALF-RXNS:

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Aqueous solutions mixture of two electrolytes: compound + water



$\therefore \text{Cu}^{2+}$ and H^+ attracted to negative electrode

$\therefore 2\text{Cl}^-$ and OH^- attracted to positive electrode

Preferential discharge will be carried out (certain ions would be selected to carry out predominant rxn).

FACTORS AFFECTING PREFERENTIAL DISCHARGE:

1. Position of ions in reactivity / electrochemical series:

Stronger oxidising agent ↓
↑ Stronger reducing agent

At anode (ANOX):

At cathode (RED(CAT):

if element is stronger RA (higher)
 $\therefore$ is oxidised at anode.

if element is stronger OA (lower)
 $\therefore$ is reduced at cathode.

But: if concentration is high; the more concentrated substance undergoes rxn

2. Concentration of ions:

2 ions in similar reactivity are in competition $\therefore$ relative concentration of ions becomes factor

$\therefore$ if concentration of a substance is higher than the other; that substance undergoes rxn.

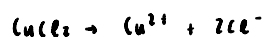
3. Type of electrodes:

use of inert / active electrodes influences which rxn is predominant at electrode e.g. Cu electrode in CuCl_2 solution

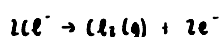
inert electrodes $\rightarrow$ mainly halogen formed. (e.g. Carbon / platinum)

EXAMPLES OF ELECTROLYTIC CELLS:

Electrolysis of copper (II) chloride using inert electrodes:

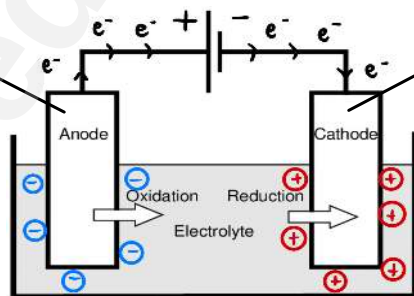
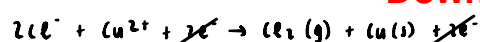
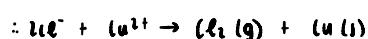
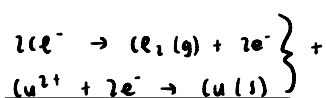


negative Cl^- ions attracted to positive anode and are oxidised.

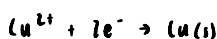


Oxidation $\frac{1}{2}$ rxn.

Full redox rxn:



positive Cu^{2+} ions attracted to negative cathode and are reduced.



Reduction $\frac{1}{2}$ rxn.

chlorine given off anode as gas bubbles.

if taken at STP, can calculate no. mol.

using $n = \frac{V}{V_m}$

Cu deposited on cathode $\therefore$ mass of cathode $\uparrow$

colour of CuCl_2 solution blue (presence of Cu^{2+} ions).

As rxn proceeds, $[\text{Cu}^{2+}] \downarrow$ as they are reduced at cathode to form $\text{Cu}(\text{s})$

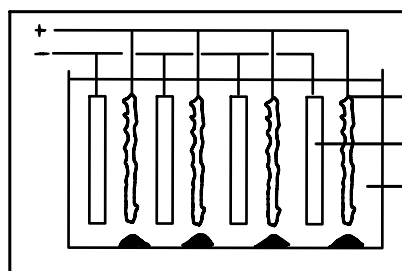
$\therefore$ solution becomes lighter in colour.

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Electrolysis of Cu(II) salt using active electrodes

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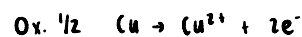
- used in electroplating of copper (refining of copper).



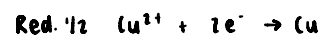
blister (impure) copper anode: $\text{Cu} \rightarrow \text{Cu}^{2+}$
 pure copper cathode: $\text{Cu}^{2+} \rightarrow \text{Cu}$
 copper(II) sulphate
 solution (electrolyte)

- Copper passes from anode $\rightarrow$ cathode
- leaves impurities (Ag, Au, Pt etc.) $\rightarrow$ forms slime which sinks to bottom
- The $[\text{Cu}^{2+}]$ will not change $\therefore$ no Δ colour.

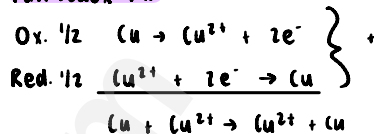
Anode:



Cathode:



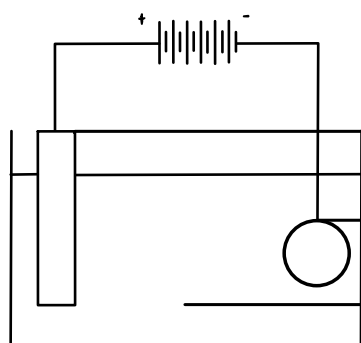
Full redox rxn:



- Cu (impure) $\rightarrow$ Cu (pure)

Electroplating of silver using active electrodes

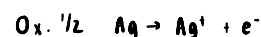
- electroplating: depositing thin layer metal on another for protection / appearance



pure Ag anode
 object to be electroplated (cathode)
 Solution of AgNO_3 and potassium cyanide

- $[\text{Ag}^+]$ ions remains the same (both being made + used up)
- Cyanide ensures + $[\text{Ag}^+]$ ions $\rightarrow$ best plating results
- But: expensive + harmful

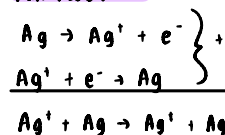
Anode:



Cathode:

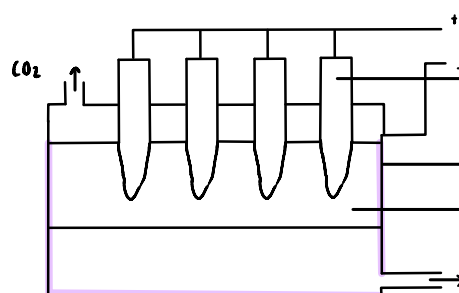


Full redox rxn:



- $\text{Ag (s)} \rightarrow \text{Ag (s)}$

Electroplating in industry: recovery of aluminium



Carbon anode

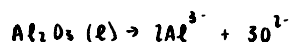
Carbon cathode

molten Al_2O_3 (alumina)

+ mineral cryolite (Na_3AlF_6)

lower melting point ($1045 \rightarrow 950^\circ\text{C}$)

Al Hall-Héroult process



- O_2 gas formed attacks C anodes $\rightarrow$ form CO_2

$\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \therefore$ must be regularly replaced

- Al forms at cathode. Heavier than $\text{Al}_2\text{O}_3 / \text{Na}_3\text{AlF}_6$ mixture $\therefore$ sinks to bottom + collected

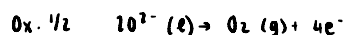
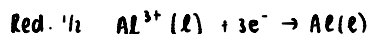
- But: has fluorides

toxic to environment

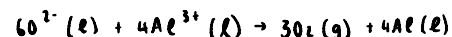
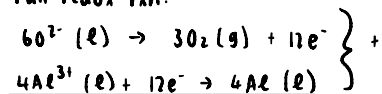
must be thoroughly cleaned

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harmful gases

Anode:**Cathode:**

Full redox rxn:



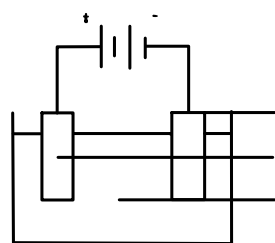
Standardising on electron transfer

Why not a solution of Al_2O_3 ?

• Financial + resource costly

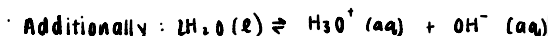
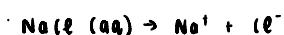
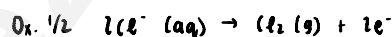
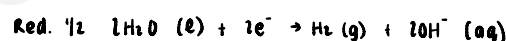
• Al^{3+} ions weaker oxidising agent than H_2O • releases O_2 (greenhouse gas).• $\therefore$ water will be reduced at cathode, not Al^{3+} ions.**Electrolysis in industry: production of chlorine:**• production of chlorine gas (Cl_2) + sodium hydroxide (NaOH) via electrolysis of NaCl (brine)

• Chlorine: water + sewage treatment, production of plastics (PVC), pesticides + insecticides

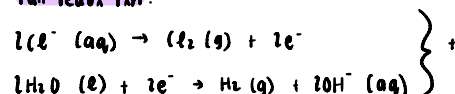
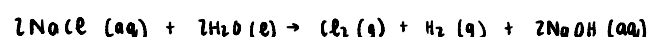
• NaOH : chemicals (organic/inorganic compound synthesis), metallurgy/alumina/aluminium industry, pulp + paper industry, textile industry, soaps + surfactants, water treatment

Positive anode

Negative cathode

 $\text{NaCl}(\text{aq})$ a.k.a. brine which is the electrolyte**Anode:**• Cl^- + OH^- ions attracted.• Easier to get OH^- ions, but $[\text{Cl}^-]$ ions $\uparrow$ $\therefore$ Cl^- ions formed• $\text{Cl}_2(\text{g})$ contaminated w/ $\text{O}_2(\text{g})$ - rxn w/ hydroxyl ions:• $[\text{Cl}^-]$ ions $\uparrow$; $\therefore$ Cl_2 gas formed• $[\text{Cl}^-]$ ions $\downarrow$; $\therefore$ O_2 gas formed• $\therefore$ $\text{Cl}_2(\text{g})$ purified from oxygen**Cathode:**• Na^+ + H_3O^+ ions attracted• $\text{Na}(\text{s})$ does not form:• H_2O stronger oxidising agent than Na^+ (lower on redox table) $\therefore$ reduced at cathode• effect: OH^- ions formed + build-up of Na^+ ions at cathode $\therefore$ NaOH formed at cathode.**Anode:****Cathode:**

Full redox rxn:

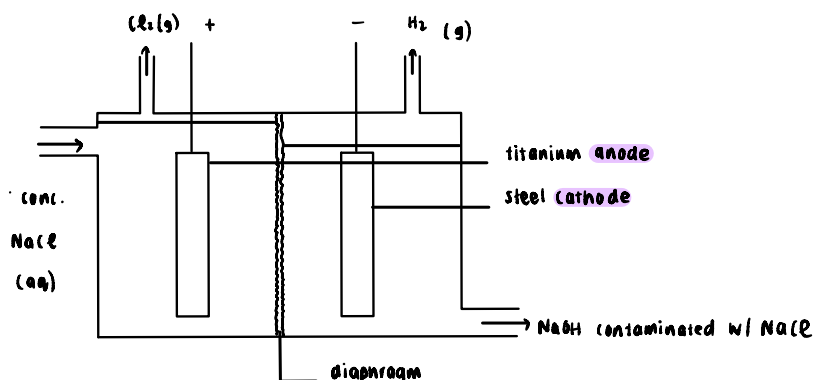
NB: Na^+ ions are present in the solution; $\therefore$ if we add Na^+ :**Why are products formed kept separate?**• $\text{Cl}_2(\text{g})$ and $\text{H}_2(\text{g})$ react explosively

• dangerous

• destroys product

• Cl_2 reacts w/ NaOH to form bleach

Diaphragm cell:



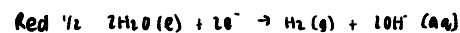
- asbestos dangerous + toxic
- asbestos + polymers
- pressure anode side = liquid flow left to right
- prevents NaOH from flowing back.

- 50% concentration
- NaCl crystallises ∴ separated + dissolved + process repeated
- Small % NaCl remains
- 1400 - 2700 kWh per metric ton of chlorine

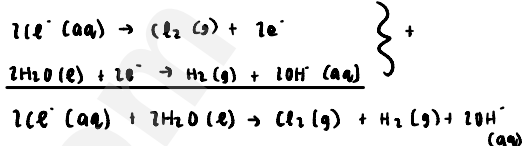
Anode:



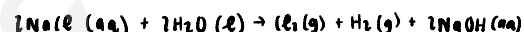
Cathode:



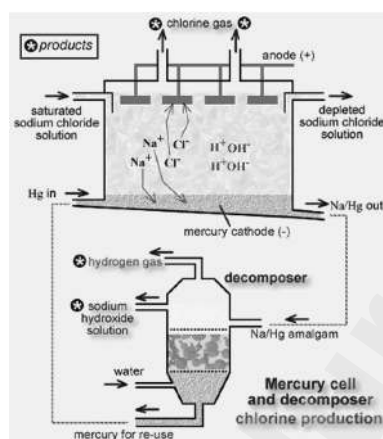
Full redox rxn:



Add Na:



Mercury / Castner-Kelner cell:



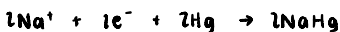
Anode:



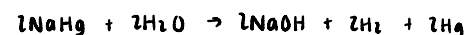
Cathode:



- Amalgam (substance formed by rxn of mercury with another metal) between aluminium + mercury:



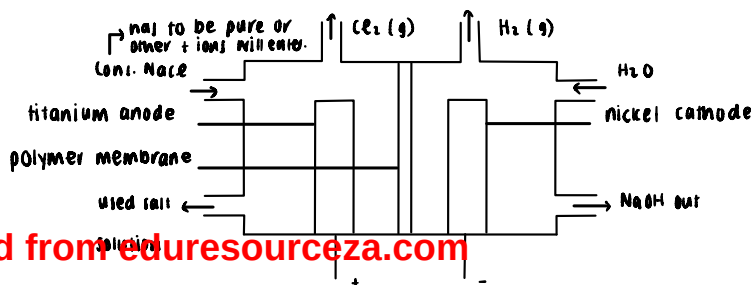
- Pumped into decomposer w/ water + graphite catalyst to recycle mercury:

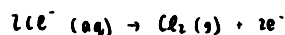
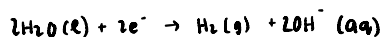
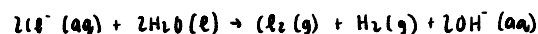
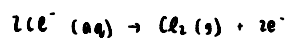
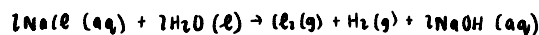


- ↑ purity + not as contaminated (50%)
- mercury poisoning
- ↑ energy consumption
- environmental pollution (mercury vapour)

Membrane cell:

- membrane: only allows positive (Na^+) ions through and not Cl^- ions
- ∴ no contamination



Anode:**Cathode:****Full redox rxn:****Add Na:**

- Only 33% NaOH production
- lowest energy consumption
- does not require lots of space
- very little contamination

ELECTROLYSIS AND THE MOLE: FARADAY'S CONSTANT:

amt substance deposited depends on:

- charge on ion
- current in circuit
- time

$$q = nF$$

$$q = I \times \Delta t$$

• q = charge (in C)

• q = charge (in C)

• n = no. of moles (in mol)

• I = current (in A)

• F = Faraday's constant

• Δt = time (in s)

• Charge of 1 mole of electrons = no. electrons in 1 mol $\times$ charge of electron

$$= 6.022 \times 10^{23} \times 1.6 \times 10^{-19} = 96352 \text{ C}$$

• Faraday's constant = 96500 C

e.g. The electrolysis of molten lead (II) bromide - PbBr_2 produces lead at the cathode and bromine at the anode. A current of 10 amps is allowed to flow through molten lead bromide for 5 hours. What mass of lead is deposited at the cathode?

Given:

$$I = 10 \text{ A}$$

$$m_{\text{lead}} = ?$$

$$\Delta t = 5 \times 60 \times 60$$

$$q = ?$$

3. Calculate the charge and no. mol e^- .

$$q = I \Delta t$$

$$= (10)(5 \times 60 \times 60)$$

$$= 180000 \text{ C} \quad \text{— how much charge used in rxn}$$

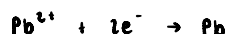
$$q = nF$$

$$180000 = n(96500)$$

$$\therefore n = 1.87 \text{ mol}$$

↑ how much mol e^- you have

1. Write half rxn for electrolysis (redox table)



• if asked for Br, use Br formula

4. Calculate no. mol substance or mass (if asked).

$$n_{\text{Pb}} = \frac{1}{2} \times 1.87$$

$$= 0.933 \text{ mol}$$

2. Write out your mol ratio

$$n_{\text{e}^-} : n_{\text{Pb}}$$

$$2 : 1$$

$$1 : \frac{1}{2}$$

$$m_{\text{Pb}} = nM$$

$$= (0.933)(207)$$

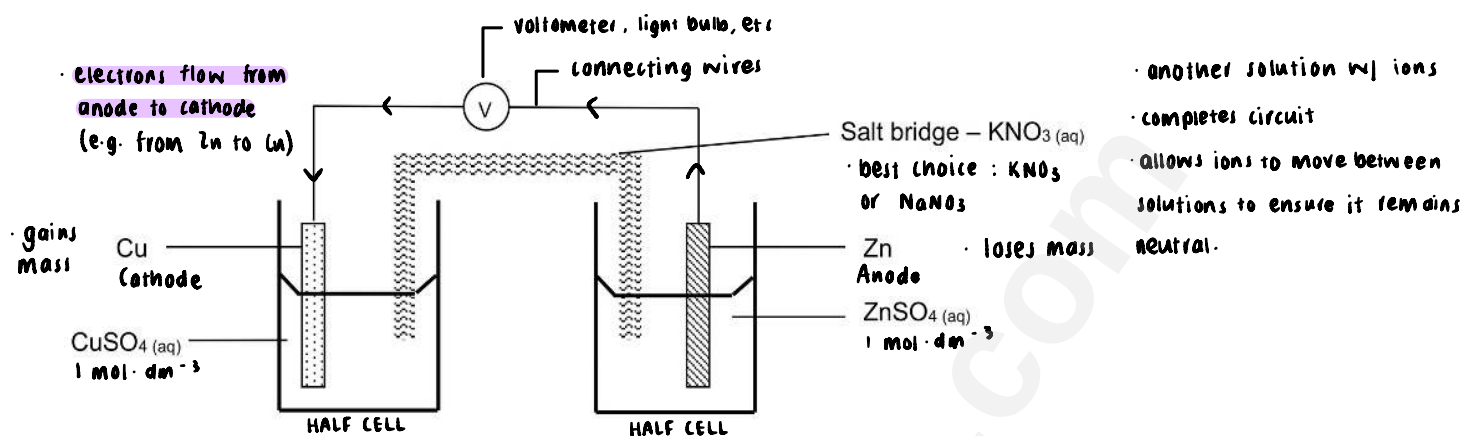
$$= 193.13 \text{ g}$$

GALVANIC/VOLTAIC CELLS:

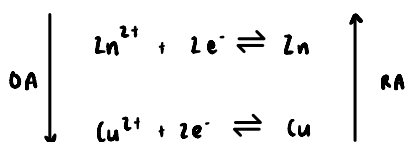
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SETUP OF A SIMPLE GALVANIC CELL:

e.g. Copper-zinc galvanic cell:



Looking at the 2 redox rxns (from redox table):



· Metal electrodes placed in solutions of their own salts:

- Enables metal ions to dissolve + drift
- completes circuit
- other solutions used: metals react + form side products

- Zn is higher on the table ∴ it is oxidised (stronger RA)
- ∴ Zn electrode is the anode.
- Cu lower on the table ∴ it is reduced (stronger OA)
- ∴ Cu electrode is the cathode.

NB: BaCl_2 - forms insoluble salts with SO_4^{2-} and CO_3^{2-}

AgNO_3 - forms insoluble salts w/ every anion besides NO_3^-

· formation of precipitate hampers working of salt bridge ∴ ↓ [solutions]

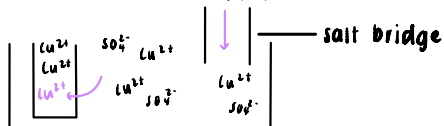
Function of salt bridge in each half cell:

· anions move into anode half



- Zn^{2+} ions leave Zn electrode and into the solution, making the solution positive.
- Thus, negative ions will flow into the anode half-cell.

· cations move into cathode half



- Cu^{2+} ions leave the solution and become attached to the Cu electrode, making the solution negative.
- Thus, positive ions will flow into the cathode half-cell.

Why do we need inert electrodes?

1. Half-cells that don't have electrodes to transfer e^- from anode to cathode
2. If there's an eqm between 2 ions (e.g. $\text{Sn}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$)
3. Eqm between gas and ion

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CELL NOTATION:

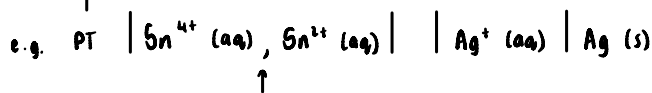
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Always:

- ① Anode ② Salt bridge ③ Cathode



This indicates that the substances are in separate states.



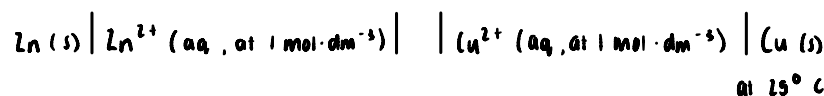
indicates they are in same phase.

Sn^{4+} and Sn^{2+} are ions $\therefore$ not solid

$\therefore$ an inert electrode like platinum/graphite must be added.

Standard conditions:

if asked to give phase indicators and standard conditions:

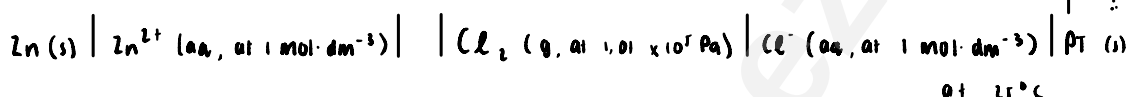


pressure of 1 atmosphere / $1.01 \times 10^5 \text{ Pa}$ (for gases)

concentration of $1 \text{ mol} \cdot \text{dm}^{-3}$ (for aq solutions)

Temperature of 25°C .

if given gases:



none of the substances are solid

$\therefore$ platinum used as inert electrode

CALCULATING EMF:

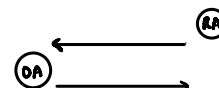
- $E^\circ (\text{cell}) = E^\circ (\text{cathode}) - E^\circ (\text{anode})$
- $E^\circ (\text{cell}) = E^\circ (\text{oxidising agent}) - E^\circ (\text{reducing agent})$
- $E^\circ (\text{cell}) = E^\circ (\text{reduction } \frac{1}{2} \text{ rxn}) - E^\circ (\text{oxidation } \frac{1}{2} \text{ rxn})$

on data sheet

$E^\circ (\text{cell}) > 0$; $\therefore$ spontaneous rxn

$E^\circ (\text{cell}) < 0$; $\therefore$ non-spontaneous rxn
OR

if RA is above and to right of OA (redox table)



RELATION OF CURRENT AND CELL POTENTIAL TO RATE AND EQUILIBRIUM:

Cell potential and equilibrium:

- Once eqm in cell is reached; the voltage of the cell is zero.
- factors that favour the forward rxn $\uparrow$ the voltage
- factors that favour the reverse rxn $\downarrow$ the voltage

κ does not affect emf

Cell voltage and current related to rxn rate:

- Once eqm in a cell is reached; the current stops flowing in the cell.
- $\uparrow$ rxn rate + $\uparrow$ amt reacting substance ; $\uparrow$ current
- $\uparrow$ surface area terminals ; $\uparrow$ rxn rate + $\downarrow$ int. r $\therefore$ $\uparrow$ current
- Wider + shorter + more conductive salt bridge ; $\downarrow$ int. r

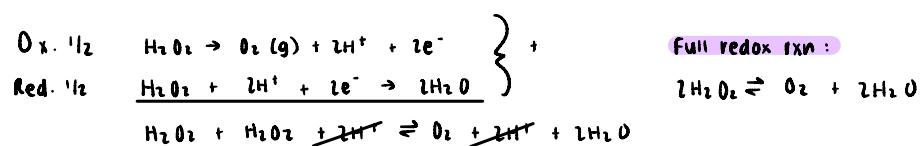
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AUTO-REDOX:

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· reaction of a substance with itself in which it acts both as an oxidising + reducing agent.

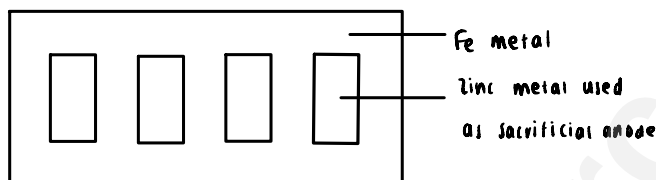
e.g. H_2O_2 :



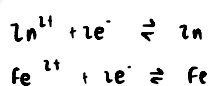
SACRIFICIAL ANODES:

- Use of another more reactive metal to protect another metal + prevent it from corrosion
- $\therefore$ use of a metal that is a stronger RA
- will be preferentially oxidised
- protects other metal

e.g.



↓
OA



↑
RA

- Zn stronger RA than Fe
- $\therefore$ will oxidise
- $\therefore$ Fe will not oxidise + not corrode.

BATTERIES:

- device consisting of one or more electrochemical cells, which store chemical energy and make it available in an electrical form.
- environmental concern: toxic metal pollution

· primary batteries used once

· irreversible reaction

· secondary batteries used more than once

· reversible reaction

· recharged: current ran through battery but in opposite direction of discharged current.

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