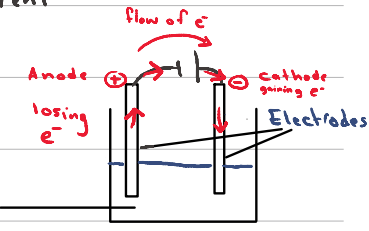
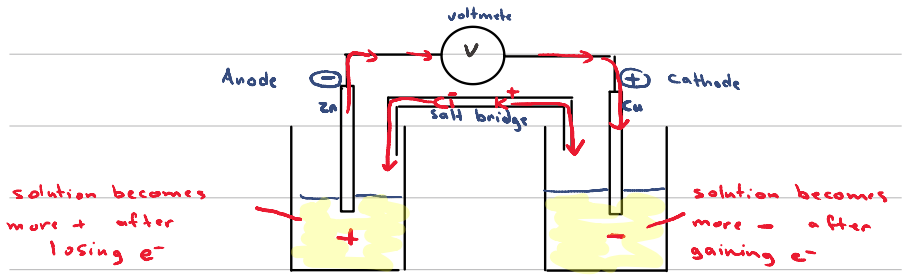
Electrochemistry A level

Electrolysis : is the decomposition of a compound into its elements by an electric current

Electrolytic cell ⇒



Galvanic cell : is an electrochemical device that converts chemical energy into electrical energy through spontaneous redox reaction



Galvanic cell generates electricity :

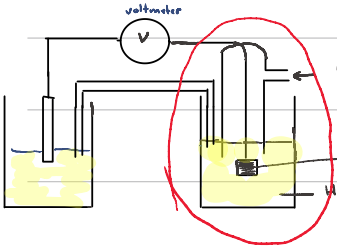
flow of e^- through wires (from anode to cathode)

flow of ions in solutions through salt bridge

* Standard Electrode Potential E°

potential difference of a half cell compared to the hydrogen electrode, under standard conditions

conc: 1 mol dm^{-3} ; 100 kpa (1 atm) ; 298 K



SHE: standard hydrogen electrode

universal reference electrode

used to measure standard reduction potential E° of other half cell

* platinium inert must be porous : to provide surface for the redox reaction and conducts electrons.

Standard cell potential E°_{cell}

the potential difference between the electrodes of a cell under standard conditions.

$E^\circ_{cell} = E_{cathode} - E_{anode}$

larger value

* half equations must be in reduction form

E° value

→ more positive → reduction / cathode

Equilibrium shifts to right →

→ less positive → oxidation / anode

Equilibrium shifts left ← and equation flips

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

↑

positive = feasible (reaction happens automatically)

Draw the electrochemical cell for the following half-cells potentials :

larger value ↙ cathode

1 : $2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$ $E^\circ = 0$ V

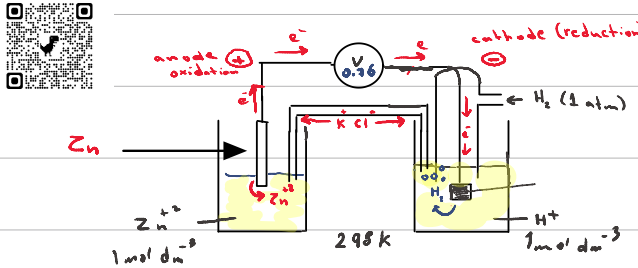
$Zn^{+2}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $E^\circ = -0.76$ V

↘ less value

$E^\circ_{cell} = E^\circ_{cath.} - E^\circ_{anode}$

$= 0 - -0.76 = 0.76$ V

anode - flip ↻



2: Br_2/Br^- and MnO_4^-/Mn^{2+}

$5 \times \left(Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)} \right)$ $(+1.09V)$ less positive (anode) flip equation

$2 \times \left(MnO_{4(aq)}^- + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{+2}_{(aq)} + 4H_2O_{(l)} \right)$ $(+1.52V)$ more positive (cathode)

rewrite equations: $10Br^- \rightleftharpoons 5Br_2 + 10e^-$

$2MnO_4^- + 16H^+ + 10e^- \rightleftharpoons 2Mn^{+2} + 8H_2O$

$10Br^- + 2MnO_4^- + 16H^+ \rightleftharpoons 5Br_2 + 2Mn^{+2} + 8H_2O$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 1.52 - 1.09 = +0.43\ V$

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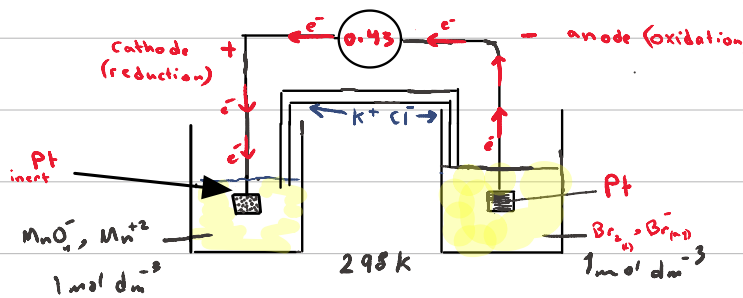
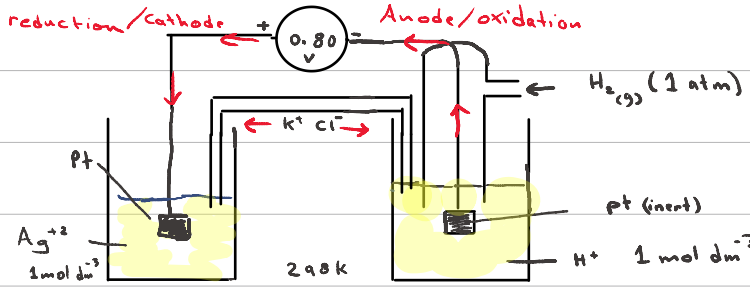


let's Analyse the following cell



$E^\circ_{cell} = E^\circ_{cath.} - E^\circ_{anode}$

$0.80 = E^\circ_{cath.} - 0$

$E^\circ_{cath.} = 0.80$

$2H^+_{(-1)} + 2e^- \rightleftharpoons H_{2(g)}$ 0 V (anode)

$Ag^{+2} + 2e^- \rightleftharpoons Ag_{(s)}$ 0.80 V (cathode)

flip anode equation: $H_{2(g)} \rightleftharpoons 2H^+ + 2e^-$

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$Ag^{+2} + 2e^- \rightleftharpoons Ag_{(s)}$

$Ag^{+2}_{(-1)} + H_{2(g)} \rightleftharpoons Ag_{(s)} + 2H^+_{(-1)}$

from reactants you can tell that we need to start with Ag^{+2} (solution) → you must use pt inert.

★ measuring feasibility :

Strongest oxidising agent

$Au^+ + e^- = Au$	+ 1.692
$Ag^+ + e^- = Ag$	+0.7996
$Cu^{2+} + 2e^- = Cu$	+0.342
$Fe^{3+} + 3e^- = Fe$	-0.037
$Pb^{2+} + 2e^- = Pb$	-0.126
$Ni^{2+} + 2e^- = Ni$	-0.257
$Cd^{2+} + 2e^- = Cd$	-0.403
$Fe^{2+} + 2e^- = Fe$	-0.447
$Zn^{2+} + 2e^- = Zn$	-0.762
$Al^{3+} + 3e^- = Al$	-1.662

Strongest reducing agent

remember to arrange E° from largest value to smallest value

rule : if stronger reducing agent (wl) reacts with stronger oxidising agent ⇒ rxn is feasible

therefore ⇒ E°_{cell} is positive

Q: will H_2O_2 reduce MnO_4^- to Mn^{+2}

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{+2} + 4H_2O$ (cathode, +1.52 V)

$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ (anode, +0.68)

MnO_4^-: stronger oxidising agent

H_2O_2: stronger reducing agent

★ H_2O_2 is stronger reducing agent and more likely to release $\bar{e}$ than Mn^{+2}

★ MnO_4^- is is stronger ox. agent and more likely to accept $\bar{e}$ than O_2 / reaction is feasible.

Q will iodine (I_2) oxidise Fe^{+2} to Fe^{+3}

(oxidising agent)

stronger oxidising agent

$Fe^{+3} + 1e^- \rightleftharpoons Fe^{+2}$ 0.77 V

$\frac{1}{2} I_2 + e^- \rightleftharpoons I^-$ 0.54 V

stronger reducing agent

Fe^{+3} is stronger oxidising agent, more likely to accept e^- than I_2 → I_2 is weaker ox. agent

I^- is better reducing agent more likely to release e^- than Fe^{+2} → weaker reducing agent

not feasible

* Non standard conditions E is used not E°

* what happens if conc. of Zn^{+2} is increased ?

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

↑↑ position of equilibrium shifts to right

therefore ⇒ more reduction → more positive E

→ more feasible

* what happens if conc. of Fe^{+2} increases ?

$$Fe^{+3} + 1e^- \rightarrow Fe^{+2} \qquad E^\circ = 0.77\ V$$

↑↑↑

equilibrium shifts to left (to the lower conc.)

→ less reduction and more oxidation of Fe^{+2} → less E → less feasible

* to calculate new potential we use

The Nernst Equation

$$E = E^\circ + \frac{0.059}{z} \log_{10} \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

E°: given

z: electrons transfer (from equation)

[oxidised species]: higher oxidation number

[reduced species]: lower oxidation number

e.g. calculate new potential of Fe^{+3}/Fe^{+2} half cell

$[Fe^{+3}]$: 0.034 mol dm^{-3} $[Fe^{+2}]$: 0.64 mol dm^{-3}

$Fe^{+3} + 1\,e^- \rightleftharpoons Fe^{+2}$ $E^\circ = 0.77$ V

0.034 ↓↓↓ ← 0.64 ↓↓

both species decrease in concentration but $[Fe^{+3}]$ decreases more, equilibrium shifts to the lower amount (to left) E must be decreased

$$E = 0.77 + \frac{0.059}{1} \log_{10} \frac{[0.034]}{[0.64]}$$ ← Fe^{+3} ← Fe^{+2}

$= 0.695$ V $E < E^\circ$ (reaction shifts to left)

remember:

if reduction half equation : shifts to right → E will increase $E > E^\circ$ (more feasible)

if reduction half equation : shifts to left ← E will decrease $E < E^\circ$ (less feasible)

* Quantitative electrolysis

mass of a substance produced at an electrode is proportional to :

1 time taken for current to pass

2 strength of the electric current

therefore we use this equation

$$Q = I \times t$$

Q : charge (coulombs) C

I : current (amperes) A

t : time (seconds) s

we also express charge in terms of Faraday F :

1 mol of electrons of a substance has 96500 coulombs

1 mol e^- : 96500 C x number of e^- transfer

Use both equations to solve depends what is given in Question

Q : Calculate mass of lead deposited on the cathode when a current of 1.5 A (current) flows through lead II bromide for 20 min. (convert to seconds) (time)

Step 1 write equation $Pb^{+2} + 2e \rightleftharpoons Pb$

Step 2 find Q from given information

$Q = I t \quad 1.5 \times 20 \times 60$

$= 1800 \text{ c}$

Step 3 use faraday ratio to find moles used up.

1 mole $\bar{e}$ = 96500 x 2

x = 1800

$x = 0.00932$ mole

Step 4 convert to mass

$\text{mole} = \frac{\text{mass}}{A_r} \qquad 0.00939 = \frac{\text{mass}}{207}$

mass = 1.93 g Pb

** you may use moles first the find current depends on questions

Q Calculate volume of oxygen produced at r.t.p when concentrated H_2SO_4 is electrolysed for 30 min using 0.5 A

$$4\,OH^-_{(aq)} \rightarrow O_{2(g)} + 2\,H_2O_{(l)} + 4e^-$$

this is the oxygen formation equation

$$Q = I\,t = 0.5 \times 30 \times 60 = 900$$

$$1\,mol\ e^- = 96500\,C \times 4\,e^-$$

$$x \quad = \quad 900\,C$$

$$x = 0.0023316\ mol$$

convert to volume at r.t.p $mol = \frac{V}{24}$

$V = 0.559\ dm^3\ O_2$

* Calculating avogadro constant L

$$L = \frac{\text{Charge of 1 mol of } e^-}{\text{charge of 1 } e^-}$$

given 1.6×10^{-19}

answer must be close to 6.02×10^{23}

Q calculate L when an electric current of 0.2 A (I) is passed throught copper ions solution for 34 min. (t) producing 0.13 grams (convert to moles) of copper on the anode.

$$Cu^{+2}_{(aq)} + 2e \leftrightarrows Cu_{(s)}$$

$$Q = It = 0.2 \times 34 \times 60 = 408\ C$$

** Don't use faraday ratio we must calculate it through moles

$$moles = \frac{mass}{Ar} = \frac{0.13}{63.5} = 0.00204724\ mol$$

Now the ratio :

$$0.00204\ mol \times 2e^- \xrightarrow{\text{produces}} 408\ C$$

$$1\ mol\ e^- \rightarrow x$$

$$x = 99646.15\ C$$

$$L = \frac{99646.15\ \cancel{C}\ mol^{-1}}{1.6 \times 10^{-19}\ \cancel{C}} = 6.2 \times 10^{23}\ mol^{-1}$$

this is close to 6.02×10^{23}

* Gibbs free energy and E°

feasible reaction is the one that has positive E and negative ΔG

$$\Delta G^\circ = -n E^\circ_{cell} F \div 1000$$

- ΔG°: because ΔG° in $J\,mol^{-1}$ ↙ to convert it to $kJ\,mol^{-1}$
- n: moles of e^- transferred
- E°_{cell}: $E^\circ_{cath} - E^\circ_{anode}$
- F: 96500 C (given)

e.g. calculate standard free energy for the following reaction between half cells

$Mg^{+2} + 2e^- \rightleftharpoons Mg \quad -2.38\,V$ anode

$Zn^{+2} + 2e^- \rightleftharpoons Zn \quad -0.76\,V$ cathode

electrons transferred = 2

$E^\circ_{cell} = -0.76 - -2.38$

$= +1.62\,V$

$\Delta G^\circ = -n E^\circ_{cell} F \div 1000$

$= -2 \times 1.62 \times 96500 \div 1000$

$= -308\ kJ\,mol^{-1}$ / feasible