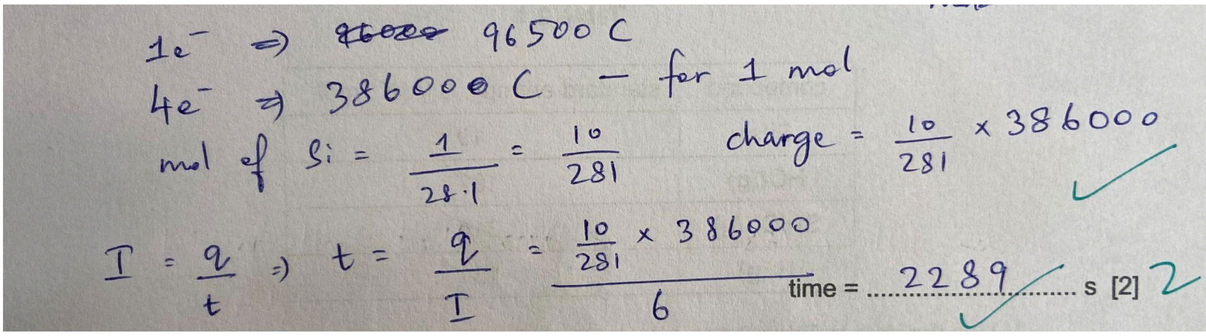
24. ELECTROCHEMISTRY

24.1 Electrolysis

Silicon can also be produced by electrolysis of SiO_2 dissolved in molten $CaCl_2$.
The relevant half-equation for the cathode is shown.

$$SiO_2 + 4e^- \rightarrow Si + 2O^{2-}$$

Calculate the time, in seconds, required to produce 1.00 g of Si by this electrolysis, using a current of 6.00 A.
Assume no other substances are produced at the cathode.


$1e^- \Rightarrow 96500\ C$

$4e^- \Rightarrow 386000\ C$ — for 1 mol

mol of Si $= \frac{1}{28.1} = \frac{10}{281}$ charge $= \frac{10}{281} \times 386000$

$I = \frac{q}{t} \Rightarrow t = \frac{q}{I} = \frac{\frac{10}{281} \times 386000}{6}$

time = ...2289.... s [2]

Fe3O4(l) can be electrolysed using inert electrodes to form Fe.
Write the half-equation for the reaction that occurs at the anode during the electrolysis of Fe3O4(l).

$2O^{2-} \rightarrow O_2 + 4e^-$

Each formula unit of Fe3O4 contains one Fe2+ and two Fe3+ ions. Fe3O4(l) can be electrolysed using inert electrodes to form Fe.
Calculate the maximum mass of iron metal formed when Fe3O4(l) is electrolysed for six hours using a current of 50A. Assume the one Fe2+ and two Fe3+ ions are discharged at the same rate.

$$2Fe^{3+} + Fe^{2+} + 4O^{2-} \longrightarrow 3Fe + 2O_2$$

$\therefore$ 8 e^- are involved

$1e^- \Rightarrow 96500\,C$

$8e^- \Rightarrow 772000\,C$

$Q = It = 50 \times 6 \times 60^2 = 1080000$

$$\frac{1080000}{772000} = \frac{270}{193}$$

mol of Fe $= 3 \times \frac{270}{193} = \frac{810}{193}$

$\therefore$ mass of Fe $= \frac{810}{193} \times 55.8 = \boxed{234.2g}$

State the possible advantages of developing cells such as lithium-ion rechargeable Batteries.

- Small size/ compact
- Low mass
- High voltage

24.2 Standard electrode potentials E⊖, standard cell potentials E⊖ cell and the Nernst equation

E^{e}_{cell} for this reaction = +1.14V

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Suggest and explain how E_{cell} value of the reaction changes with an increase in pH.

- E_{cell} value becomes less positive, as [H+] decreases and position of equilibrium shifts to LHS.

Methanoic acid, HCOOH, is being investigated as a fuel in fuel cells. When the cell operates, HCOOH is oxidised to carbon dioxide. Half-equation for reaction at cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.
In this fuel cell, the overall cell reaction is the same as that for the complete combustion of HCOOH. Deduce the half-equation for the reaction at the anode.

- 2HCOOH + O2 = 2CO2 + 2H2O
- 2HCOOH = 2CO2 + 4e– +4H+

Answer = $HCOOH \rightarrow CO_2 + 2e^- + 2H^+$

NOTE: Half equations

1. Identify what is oxidised and what is reduced (look at oxidation state)

2. Write "skeleton" half-equations: Write species being oxidised on one side and its oxidised form on the other. (same for reduced species)
3. Balance atoms (except O and H)
4. Balance oxygen atoms: Add H2O to the side that needs more oxygen.
5. Balance hydrogen atoms:
    - If acidic medium: Add H+ to the side that needs more hydrogen.
    - If alkaline medium:
        - First balance as if acidic.
        - Then add same number of OH– ions to both sides to neutralise any H+, forming water.
6. Balance charges: Add e– to the more positive side so that charges balance.
7. Combine half equations
    - Multiply each half-equation by a suitable factor so the number of electrons cancels.
    - Add the two equations together, cancelling out anything that appears on both sides.

The overall cell reaction is shown.

$$Ag_2O + Zn + H_2O \rightarrow 2Ag + Zn(OH)_2$$

Complete the half-equation for the reaction at each electrode.

at the positive electrode Ag_2O + ...

at the negative electrode Zn + ...

TiO2+ can be reduced by zinc metal in acidic conditions to form a purple solution containing Ti3+(aq). Write an ionic equation for the reduction of TiO2+ by zinc metal in acidic conditions.

Ans:

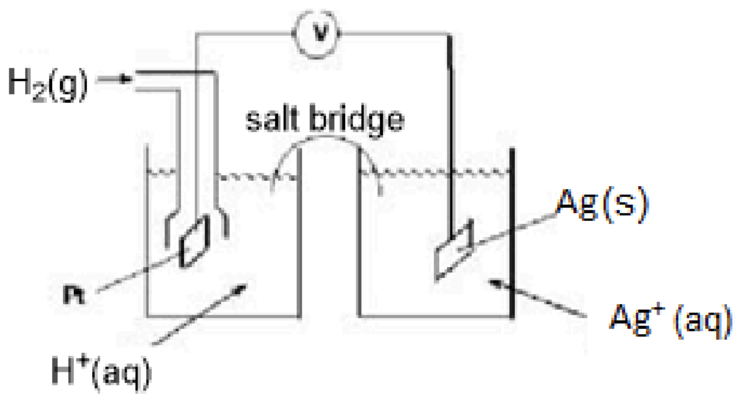
$2TiO^{2+} + 4H^{+} + Zn \rightarrow 2Ti^{3+} + 2H_2O + Zn^{2+}$

NOTE: it says a purple solution forms. So you cannot produce ZnO as one of the products, as this is a ppt.

Define standard electrode potential, including a description of standard conditions.

- Voltage of a half-cell compared to SHE.
- 1 mol dm–3 AND 101kPa AND 298K

Draw a labelled diagram of an electrochemical cell used to measure E° of Ag+(aq)/Ag(s) electrode.



M1 Pt	Ag	Ag^+
M2 gas delivery system	H_2	H^+
M3 voltmeter	salt bridge	wiring Pt to V to Ag

An electrochemical cell used to measure E° of Ag+(aq)/Ag(s) electrode. A separate electrochemical cell is set up using a lower concentration of Ag+(aq) than that in the first one. Suggest how the electrode potential, E, for the Ag+(aq)/Ag(s) electrode would change from its E° value. Explain your answer.

- E value would be more negative because $Ag^+ + e^- \rightleftharpoons Ag$ equilibrium shifts to LHS.

electrode	half-equation	$E^\ominus$/V
1	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.222
2	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.342

In a different experiment, electrode 1 is set up using a saturated solution of KCl. Saturated KCl(aq) contains 36.0g of KCl per 100cm3 of solution at 298K.

The Nernst equation for electrode 1 is:

$$E = E^\ominus + \frac{0.059}{z} \log \frac{1}{[Cl^-(aq)]}$$

Calculate the electrode potential, E, of electrode 1 under these conditions.

M1: $[Cl^-(aq)] = 10 \times 36.0 / 74.6 = 4.83\ (4.8257)\ \text{mol dm}^{-3}$

M2: $E = 0.222 + \frac{0.059}{1} \log \frac{1}{M1}$ ecf **M1**

M3: E = (+)**0.182** (V) min 2sf ecf **M1**

NOTE: Nernst equation is given for electrode 1. So use the E$^\ominus$ value of electrode 1 not E$^\ominus$cell!

Calculate the value of ΔG$^\ominus$ for the cell reaction that occurs, per mole of H2O2:

The $E^\ominus$ values for two electrode reactions are given.

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$E^\ominus$ = +1.77 V
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	$E^\ominus$ = −0.41 V

$\Delta G = -nE^\ominus_{cell}F$ [1]

$\Delta G = (-2 \times 2.18 \times 96500) = -420.7$ (kJ mol–1) [1] ecf

NOTE: Gibbs free energy is in units of joules, so remember to convert to kilojoules!!

The $E^\ominus$ values for two electrode reactions are given.

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$E^\ominus$ = +1.77 V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	$E^\ominus$ = +1.82 V

An electrochemical cell is constructed with the following half-cells.

half-cell 1 an acidified solution of H_2O_2 under standard conditions, a platinum wire

half-cell 2 a solution containing 0.020 mol dm^{-3} Co^{3+} and 2.0 mol dm^{-3} Co^{2+}, a platinum wire

(i) Use the Nernst equation to calculate the value of E, the electrode potential of half-cell 2 under these conditions.

E = ... V [2]

(ii) Write an equation for the cell reaction that occurs in this cell under these conditions.

.... [1]

Nernst: (E =) $E^{\ominus}$ + (0.059 / z)log[ox] / [red] [1] u / c
OR (E =) $E^{\ominus}$ + (RT / zF)ln[ox] / [red]
OR (E =) 1.82 + (0.059 / 1)log(0.02 / 2)

E = 1.82 + (0.059 / 1)log(0.02 / 2) = (+)1.702 (V) [1] min 2sf
OR
E = 1.82 + [(8.314 × 298 / 1) × (96 500)] ln(0.02 / 2) = (+)1.702

$H_2O_2 + 2H+ + 2Co^{2+} \rightarrow 2H_2O + 2Co^{3+}$ [1]
ECF for reverse equation from **(f)(i)** if E > 1.77 V

NOTE: In this case, E for half-cell 2 for the given conditions would be +1.70 and not +1.82. So half-cell 1 is reduction and half-cell 2 is oxidation!!

Acidified Ti^{3+}(aq) reacts with oxygen dissolved in water as shown.

$$4Ti^{3+} + O_2 + 2H_2O \rightarrow 4TiO^{2+} + 4H^+ \qquad \Delta G^{\ominus} = -436.1\ kJ\ mol^{-1}$$

The standard reduction potential, $E^{\ominus}$, of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ is +1.23 V.

Calculate the standard reduction potential, $E^{\ominus}$, in V, of the $TiO^{2+}(aq)/Ti^{3+}(aq)$ half-cell. Show your working.

$4Ti^{3+} + O_2 + 2H_2O \longrightarrow 4TiO^{2+} + 4H^+$ $\quad \Delta G^{\ominus} = -436.1\ kJ\ mol^{-1}$

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23\ V$ (red)

$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$ $\quad E^{\ominus} = x$ (ox)

$\boxed{\Delta G^{\ominus} = -nE^{\ominus}_{cell}F}$

← * ΔG is in J mol^{-1}
← * $E^{\ominus}_{cell}$ NOT $E^{\ominus}$!!
← * n refers to no. of e^- in overall cell equation, not in half-cell!

$E^{\ominus}_{cell} = \frac{-436100}{-4 \times 96500} = +1.1298\ V = 1.23 - x$

$\therefore x = 1.23 - 1.1298 = \boxed{+0.10\ V}$

The standard reduction potential, $E^{\ominus}$, of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ is +1.23 V.

Acidified $[Ti(C_6H_5O_7)_2]^{3-}$(aq) does not react with oxygen dissolved in water, unlike acidified Ti^{3+}(aq).

Suggest what this means for the value of the standard reduction potential, $E^{\ominus}$, of the following half-cell.

$$[Ti(C_6H_5O_7)_2]^{2-}(aq) + e^- \rightleftharpoons [Ti(C_6H_5O_7)_2]^{3-}(aq)$$

the $E^{\ominus}$ of the half-cell must be **greater** than +1.23 V / $E^{\ominus}$ of the $O_2|H^+$ half-cell as $E^{\ominus}_{cell} < 0$ and the reaction does not occur

Cobalt metal can be oxidised by acidified $K_2Cr_2O_7$. The relevant half-equations, and their $E^{\ominus}$ values, are shown.

$Co^{2+} + 2e^- \rightleftharpoons Co$	$E^{\ominus} = -0.28$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	$E^{\ominus} = +1.33$ V

(i) A Co^{2+}/Co electrode is constructed in which $[Co^{2+}]$ is 0.020 mol dm^{-3} at 298 K.

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is –0.33 V.

M1: Nernst equation $E = E^{\ominus} + (0.059 / z) \times \log(\frac{[\text{oxidised}]}{[\text{reduced}]})$

M2: $E = -0.28 + (0.059 / 2) \times \log(0.02)$

<u>NOTE – Nernst Equation:</u>

E = E$^{\ominus}$ + 0.059/n * log(oxidised^x/reduced^y)

E = E$^{\ominus}$ + 0.059/n * log(reactant^x/product^y)

E = E$^{\ominus}$ – 0.059/n * log(product^y/reactant^x)

Co^{2+} and Co^{3+} both form complexes with $edta^{4-}$.

half-equation	$E^{\ominus}$/V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$[Co(edta)]^- + e^- \rightleftharpoons [Co(edta)]^{2-}$	+0.38
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28

Use the data in the table to predict what happens, if anything, when separate aqueous solutions of Co^{3+} and $[Co(edta)]^-$ are left to stand in the air.

aqueous solution of Co^{3+}:

- Co3+ is reduced to Co2+
- Oxygen gas/ O2 is evolved
- E of Co3+ is <u>greater</u> than E of O2

aqueous solution of $[Co(edta)]^-$:

- No change / not feasible

The decomposition of hydrogen peroxide, H_2O_2, is catalysed by acidified IO_3^-.

H_2O_2 reduces acidified IO_3^- as shown.

$$5H_2O_2 + 2H^+ + 2IO_3^- \rightarrow I_2 + 5O_2 + 6H_2O$$

This reaction is followed by the oxidation of I_2 by H_2O_2.

half-equation	$E^{\ominus}$/V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1.19
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68

Use the data to show that the separate reactions of H2O2 with IO3– and with I2 are both feasible under standard conditions. In your answer, give the equation for the reaction of H2O2 with I2.

M1: $E^{\ominus}_{cell}$ for IO_3^-/H_2O_2 = –0.68 + 1.19 = +0.51 (∴ feasible)
M2: $E^{\ominus}_{cell}$ for H_2O_2/I_2 = +1.77 – 1.19 = +0.58 (∴ feasible)
M3: $5H_2O_2 + I_2 \rightarrow 4H_2O + 2IO_3^- + 2H^+$

Write the overall equation for the decomposition of H2O2 catalysed by acidified IO3–.

$2H_2O_2 \rightarrow 2H_2O + O_2$

NOTE: Overall reaction equation:
cathode reaction equation – anode reaction equation OR
reduction equation – oxidation equation