PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

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ELECTROCHEMISTRY

COMPLETE NOTES

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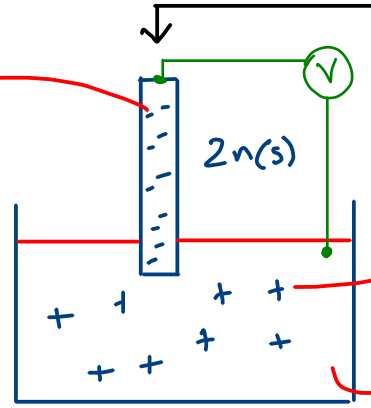
Electrochemistry:-

Metal / Metal ion Equilibrium:- If a metal is dipped into a solution containing its ions, it will produce an equilibrium between the solid metal and its solution

$$M^{2+} + 2e^- \rightleftharpoons M_{(s)}$$

if equilibrium towards left side => metal is reactive/good reducing agent

if equilibrium towards right side => metal is unreactive/weak reducing agent

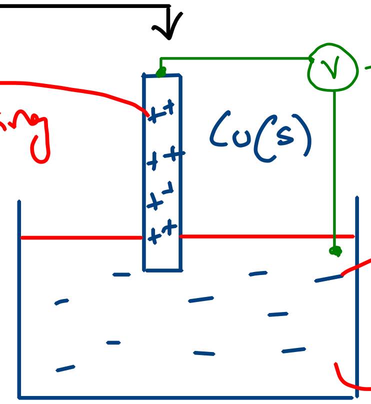


→ if we would connect a voltmeter like this, it would give us -ve potential (-ve potential = reactive metal)

→ Zn^{2+} ions

→ $ZnSO_4$ (aq)

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$$



Cu^{2+} ions gain $2e^-$ creating an electron deficiency

→ if we would connect a voltmeter like this, it would give us a +ve potential (+ve potential = unreactive metal)

→ solution in turn becomes negative as Cu^{2+} ions become less (more SO_4^{2-} ions in solution)

→ $CuSO_4$ (aq)

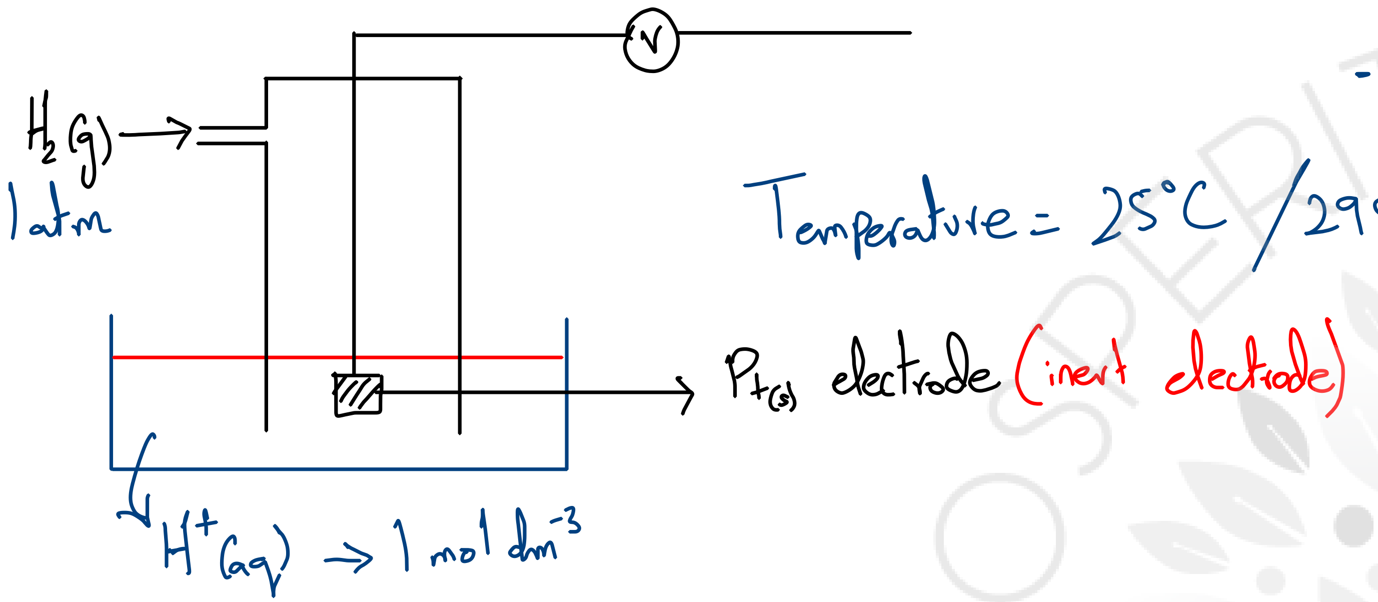
$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$

- We cannot connect the voltmeters as shown, they are only to demonstrate theory...
  - ↳ because the wires of the voltmeter would themselves establish equilibrium with solution
  - ↳ they might react with the solution

We will use standard hydrogen electrode to solve this problem!

Standard Hydrogen Electrode:-

- The standard hydrogen electrode has a potential of 0.0V
- $[H^+] = 1 \text{ mol dm}^{-3}$, 1 atm $H_{2(g)}$, 298K, Pt electrode are must!
- $2H^+ + 2e^- \rightleftharpoons H_{2(g)}$
- used to measure standard electrode potential ($E^\ominus$) of other species



Temperature = 25°C / 298 K

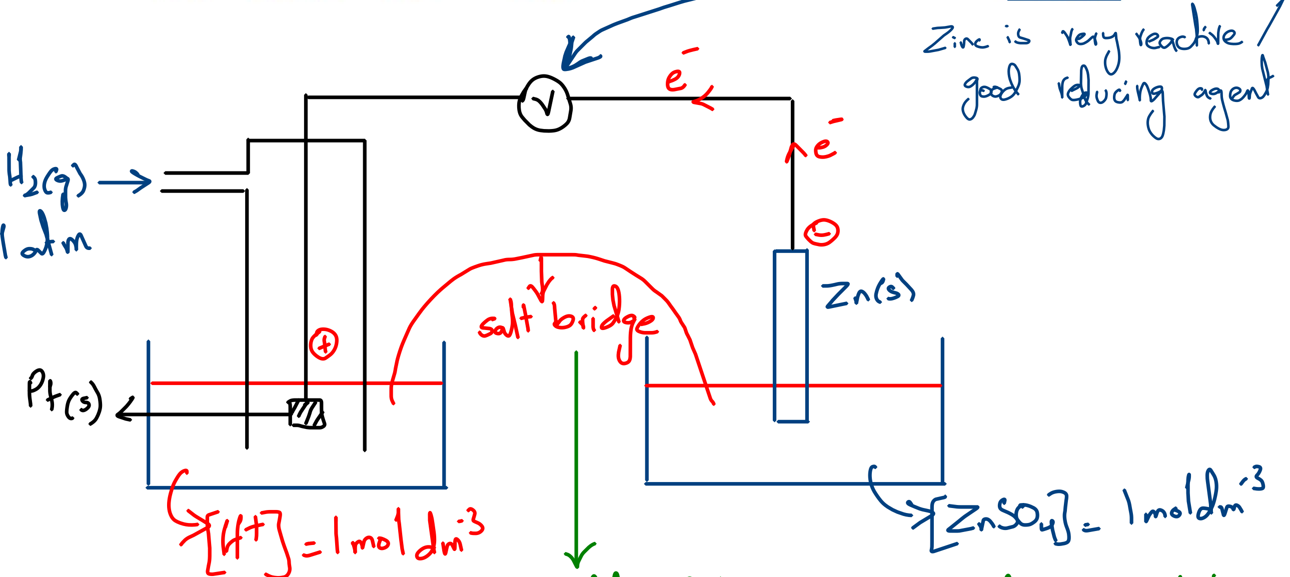
Using the standard Hydrogen electrode to measure $E^\ominus$.

$E^\ominus$ – Standard electrode/reduction potential:- The potential difference between a half cell containing 1 mol dm^{-3} of all of its ions and the standard hydrogen electrode, all measured at 25°C.

For metals:- e.g. Zinc

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

Zinc is very reactive / good reducing agent

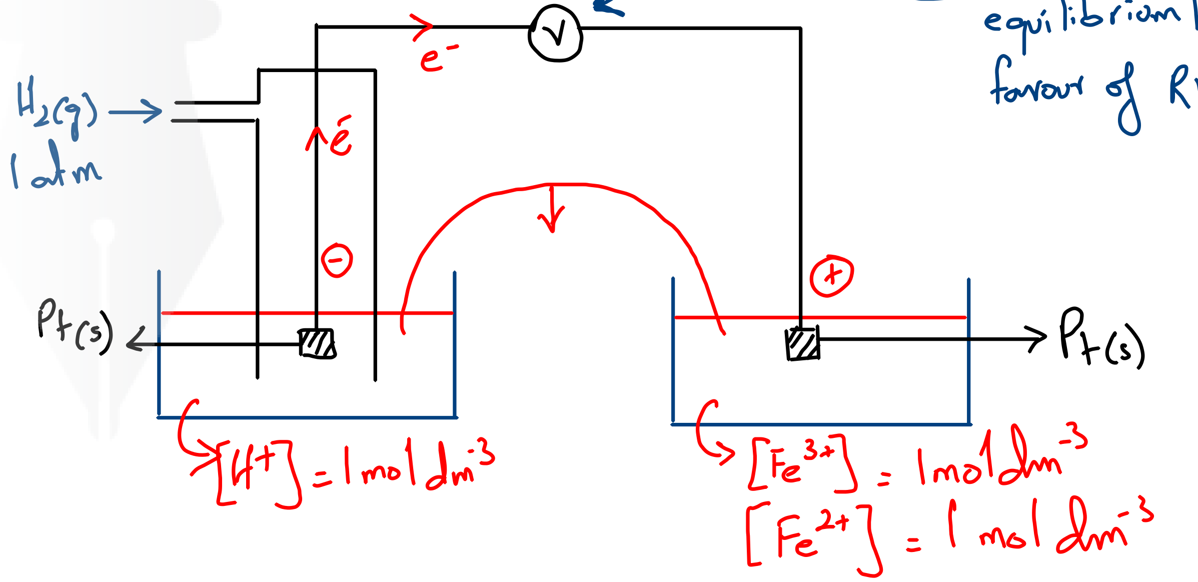


usually filter paper dissolved in KNO_3
to complete circuit by providing free moving ions

For ions:- e.g. Fe^{3+}/Fe^{2+}

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

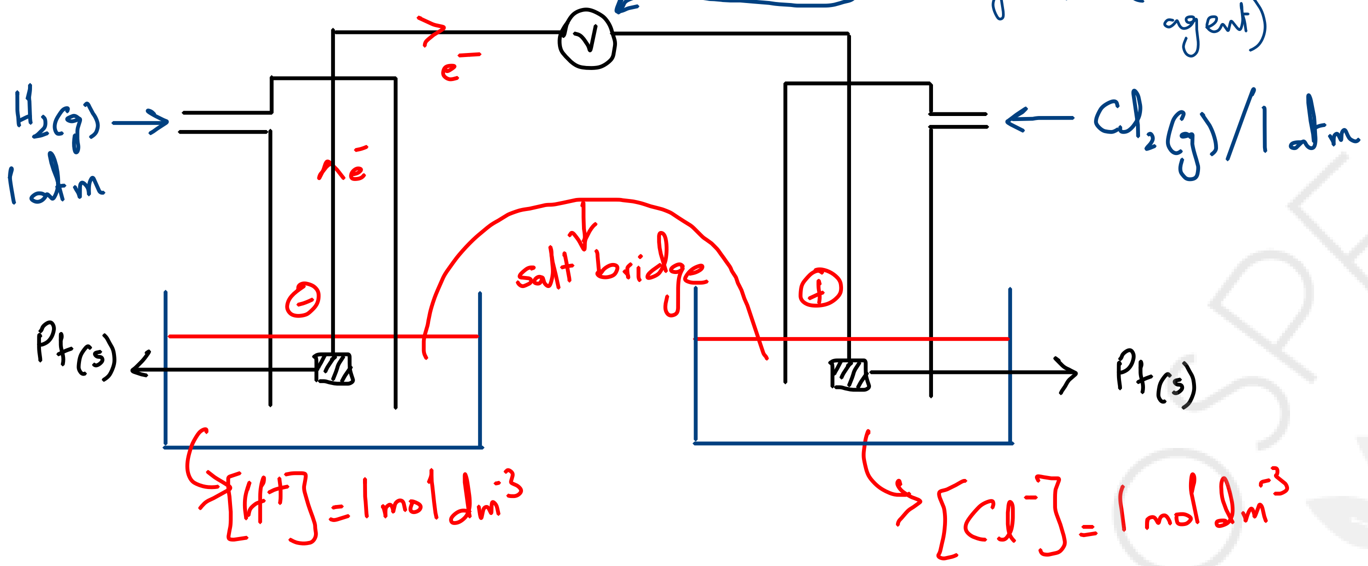
equilibrium lies in favour of RHS (Fe^{2+} is a bad reducing agent)



For gases:- e.g. $Cl_2(g)$

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ +1.36

equilibrium lies in favour of RHS (Cl^- is a bad reducing agent)



- $-ve$ $E^\ominus$ values show that equilibrium lies in favour of left hand side. The reactant on the right is more reactive / a good reducing agent (easily loses electrons)
- $+ve$ $E^\ominus$ values show that equilibrium lies in favour of right hand side. The reactant on the right is unreactive / a bad reducing agent.

Q. Identify the best and worst reducing agents from the list below:-

$Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^\ominus = +0.80$ → most +ve → worst reducing agent

$Co^{2+} + 2e^- \rightleftharpoons Co(s)$ $E^\ominus = -0.28$

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$

$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76$ → most -ve → Zn is the best reducing agent

↑ reactivity   ↓ reactivity

Rank of reactivity of the metals:- $Zn(s)$, $Co(s)$, $Cu(s)$, $Ag(s)$

$E^{\ominus}$ **in alphabetical order**

Electrode reaction			
$Ag^+ + e^-$	⇌	Ag	+0.80
$Al^{3+} + 3e^-$	⇌	Al	−1.66
$Ba^{2+} + 2e^-$	⇌	Ba	−2.90
$Br_2 + 2e^-$	⇌	$2Br^-$	+1.07
$Ca^{2+} + 2e^-$	⇌	Ca	−2.87
$Cl_2 + 2e^-$	⇌	$2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^-$	⇌	$Cl_2 + 2H_2O$	+1.64
$ClO^- + H_2O + 2e^-$	⇌	$Cl^- + 2OH^-$	+0.89
$Co^{2+} + 2e^-$	⇌	Co	−0.28
$Co^{3+} + e^-$	⇌	Co^{2+}	+1.82
$[Co(NH_3)_6]^{2+} + 2e^-$	⇌	$Co + 6NH_3$	−0.43
$Cr^{2+} + 2e^-$	⇌	Cr	−0.91
$Cr^{3+} + 3e^-$	⇌	Cr	−0.74
$Cr^{3+} + e^-$	⇌	Cr^{2+}	−0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇌	$2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^-$	⇌	Cu	+0.52
$Cu^{2+} + 2e^-$	⇌	Cu	+0.34
$Cu^{2+} + e^-$	⇌	Cu^+	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^-$	⇌	$Cu + 4NH_3$	−0.05
$F_2 + 2e^-$	⇌	$2F^-$	+2.87
$Fe^{2+} + 2e^-$	⇌	Fe	−0.44
$Fe^{3+} + 3e^-$	⇌	Fe	−0.04
$Fe^{3+} + e^-$	⇌	Fe^{2+}	+0.77
$[Fe(CN)_6]^{3-} + e^-$	⇌	$[Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^-$	⇌	$Fe(OH)_2 + OH^-$	−0.56
$2H^+ + 2e^-$	⇌	H_2	0.00
$2H_2O + 2e^-$	⇌	$H_2 + 2OH^-$	−0.83
$I_2 + 2e^-$	⇌	$2I^-$	+0.54
$K^+ + e^-$	⇌	K	−2.92
$Li^+ + e^-$	⇌	Li	−3.04
$Mg^{2+} + 2e^-$	⇌	Mg	−2.38

Electrode reaction			
$Mn^{2+} + 2e^-$	⇌	Mn	−1.18
$Mn^{3+} + e^-$	⇌	Mn^{2+}	+1.49
$MnO_2 + 4H^+ + 2e^-$	⇌	$Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^-$	⇌	MnO_4^{2-}	+0.56
$MnO_4^- + 4H^+ + 3e^-$	⇌	$MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^-$	⇌	$NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^-$	⇌	$HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^-$	⇌	$NH_4^+ + 3H_2O$	+0.87
$Na^+ + e^-$	⇌	Na	−2.71
$Ni^{2+} + 2e^-$	⇌	Ni	−0.25
$[Ni(NH_3)_6]^{2+} + 2e^-$	⇌	$Ni + 6NH_3$	−0.51
$H_2O_2 + 2H^+ + 2e^-$	⇌	$2H_2O$	+1.77
$HO_2^- + H_2O + 2e^-$	⇌	$3OH^-$	+0.88
$O_2 + 4H^+ + 4e^-$	⇌	$2H_2O$	+1.23
$O_2 + 2H_2O + 4e^-$	⇌	$4OH^-$	+0.40
$O_2 + 2H^+ + 2e^-$	⇌	H_2O_2	+0.68
$O_2 + H_2O + 2e^-$	⇌	$HO_2^- + OH^-$	−0.08
$Pb^{2+} + 2e^-$	⇌	Pb	−0.13
$Pb^{4+} + 2e^-$	⇌	Pb^{2+}	+1.69
$PbO_2 + 4H^+ + 2e^-$	⇌	$Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^-$	⇌	$SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^-$	⇌	$2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^-$	⇌	$2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^-$	⇌	Sn	−0.14
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	+0.15
$V^{2+} + 2e^-$	⇌	V	−1.20
$V^{3+} + e^-$	⇌	V^{2+}	−0.26
$VO^{2+} + 2H^+ + e^-$	⇌	$V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^-$	⇌	$VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^-$	⇌	$VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^-$	⇌	Zn	−0.76

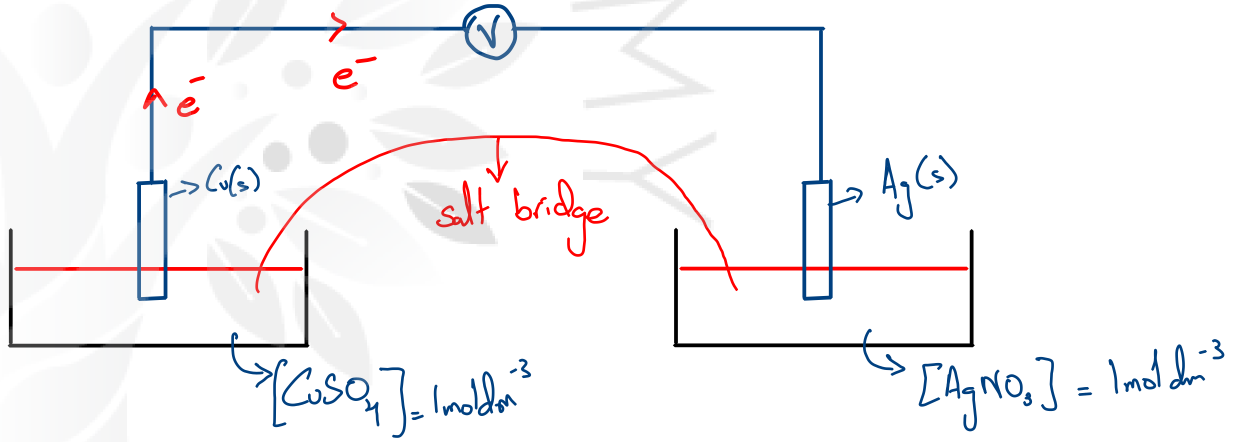
Combining Half cells:-

- $\boxed{E^\ominus_{cell} = E^\ominus_{red} + E^\ominus_{ox}}$ – reverse the $E^\ominus$ sign of the more negative electrode and add both $E^\ominus$

- Electrons flow from more negative $E^\ominus$ to more positive $E^\ominus$
- When combining equations, flip the equation with the more negative $E^\ominus$ and then combine
- Balance electrons before combining

Q. a) Draw a fully labelled diagram to show a cell consisting of a Cu^{2+}/Cu half cell and Ag^+/Ag half-cell.
b) Calculate its standard cell potential
c) Write down its equation
d) Show the electron flow

a) 298K: Temp



b) $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $+0.34$

$2Ag^+ + 2e^- \rightleftharpoons 2Ag(s)$ $+0.80$

$E^\ominus = 0.80 - (+0.34) = 0.46V$

c) $2Ag^+ + \cancel{2e^-} + Cu(s) \rightleftharpoons Cu^{2+} + \cancel{2e^-} + 2Ag(s)$

$2Ag^+_{(aq)} + Cu(s) \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$ $+0.46V$

E and ion concentration:-

- If equilibrium shifts to RHS, E↑
- If equilibrium shifts to LHS, E↓

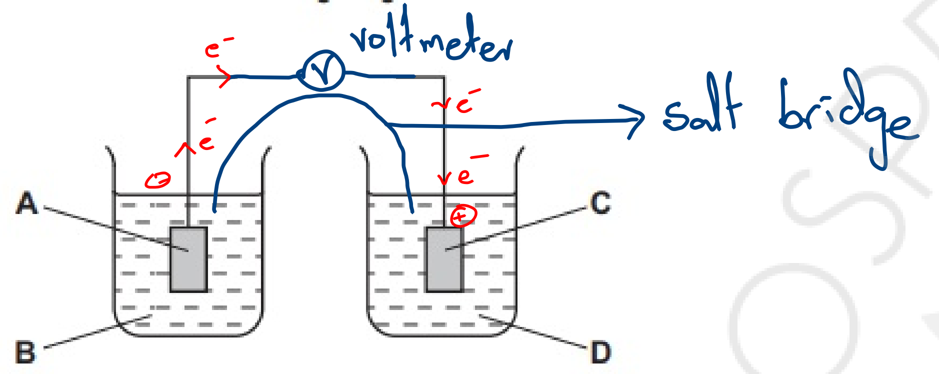
Q. $Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

a. What happens to E, if $[Cr_2O_7^{2-}]$↑? eqm to RHS, E↑
b. What happens to E, if $[H^+]$↓? eqm to LHS, E↓
c. What happens to E, if $[Cr^{3+}]$↑? eqm to LHS, E↓

4 (a) (i) Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

The potential difference obtained between 2 half cells each containing an ion in equilibrium with 1 mol dm^{-3} solution of its ion all at 25°C. [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E^{\ominus}_{cell}$ for a cell composed of the Fe^{3+}/Fe^{2+} and Ag^{+}/Ag half-cells.



(ii) Complete the diagram, labelling the components you add. [1]

(iii) Identify the components A-D.

A Pt(s)

B Fe^{3+}(aq), 1 mol dm^{-3} and Fe^{2+}(aq), 1 mol dm^{-3}

C Ag(s)

D Ag^{+}(aq), 1 mol dm^{-3} [3]

(b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in (a) are connected by a wire and the circuit is completed.

$Ag^{+}_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$ [1]

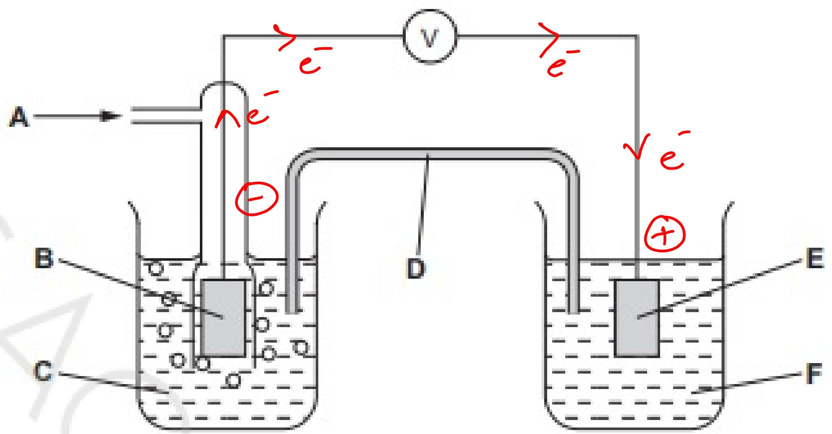
$Ag^{+} + e^{-} \rightleftharpoons Ag$ +0.80

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

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

$0.80 - 0.77 = 0.03$ V

3 (a) The diagram shows the apparatus used to measure the standard electrode potential, $E^{\ominus}$, of $Fe^{3+}(aq)/Fe^{2+}(aq)$.



(i) Identify what the letters A to F represent.

A H_2(g), 1 atm

B Pt(s)

C H^{+}(aq), 1 mol dm^{-3}

D Salt bridge

E Pt(s)

F Fe^{2+}(aq), Fe^{3+}(aq), both 1 mol dm^{-3} [3]

(ii) Label the diagram to show

- which is the positive electrode,
- the direction of electron flow in the external circuit.

Use the *Data Booklet* to help you. [1]

(b) In another experiment, an $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell was connected to a $Cu^{2+}(aq)/Cu(s)$ half-cell.

Determine the standard cell potential, $E^{\ominus}_{cell}$, when these two half-cells are connected by a wire and the circuit is completed.
Use the *Data Booklet* to help you.

$2(Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+})$ +0.77

$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$ +0.34 reverse

$= 0.77 - 0.34$
$= 0.43$ V

$2Fe^{3+} + Cu \rightleftharpoons 2Fe^{2+} + Cu^{2+}$

$E^{\ominus}_{cell}$ = 0.43 V [1]

(c) (i) The $E^{\ominus}$ of $Ni^{2+}(aq)/Ni(s)$ is –0.25 V. $Ni^{2+} + 2e^{-} \rightleftharpoons Ni$ –0.25

State and explain how the electrode potential changes if the concentration of $Ni^{2+}(aq)$ is decreased.

The equilibrium will shift to the left hand side and therefore the $E^{\ominus}$ will become more negative. [1]

(ii) Use standard electrode potential, E°, data from the *Data Booklet* to calculate the E°_{cell} for the following reaction.

$$Cl_2 + 2OH^- \rightleftharpoons Cl^- + ClO^- + H_2O$$

$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$ +0.89 reverse

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ +1.36

$\cancel{Cl^-} + 2OH^- + Cl_2 + \cancel{2e^-} \rightleftharpoons \cancel{2}Cl^- + ClO^- + H_2O + \cancel{2e^-}$

$2OH^- + Cl_2 \rightleftharpoons Cl^- + ClO^- + H_2O$

$1.36 - 0.89 = +0.47$

E°_{cell} = +0.47 V [2]

(iii) The [OH^-] was increased and the E_{cell} was measured.

Indicate how the value of the E_{cell} measured would compare to the E°_{cell} calculated in **(ii)** by placing **one** tick (✓) in the table.

E_{cell} becomes less positive than E°_{cell}.	
E_{cell} stays the same as E°_{cell}.	
E_{cell} becomes more positive than E°_{cell}.	✓

Explain your answer.

Increasing [OH] shifts equilibrium to right hand side that is why E° becomes positive

[2]

(c) A half-equation involving bromate(V) ions, BrO_3^-, and bromide ions is shown.

$$BrO_3^-(aq) + 3H_2O(l) + 6e^- \rightleftharpoons Br^-(aq) + 6OH^-(aq) \qquad E^{\circ} = +0.58\,V$$

reverse

(i) An alkaline solution of chlorate(I), ClO^-, can be used to oxidise bromide ions to bromate(V) ions.

Use the *Data Booklet* and the half-equation shown to write an equation for this reaction.

$3(ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-)$ +0.89

$Br^- + \cancel{6OH^-} + 3ClO^- + \cancel{3H_2O} + \cancel{6e^-} \rightleftharpoons \cancel{6e^-} + \cancel{3H_2O} + BrO_3^- + 3Cl^- + \cancel{6OH^-}$

$Br^-_{(aq)} + 3ClO^-_{(aq)} \rightleftharpoons BrO^-_{3(aq)} + 3Cl^-_{(aq)}$ [1]

(ii) Calculate the E°_{cell} for the reaction in **(i)**.

$0.89 - 0.58 = 0.31$

E°_{cell} = 0.31 V [1]

(iii) When a concentrated solution of bromic(V) acid, $HBrO_3$, is warmed, it decomposes to form bromine, oxygen and water only.

Write an equation for this reaction. The use of oxidation numbers may be helpful.

$2HBrO_{3(aq)} \longrightarrow Br_{2(l)} + \frac{5}{2}O_{2(g)} + H_2O_{(l)}$ [1]

[Total: 10]

Feasibility of the Reaction :-

+ve $E^\ominus$ are feasible
-ve $E^\ominus$ are not feasible

- A reaction may be feasible but may not occur due to high activation energy.
- Generally an $E^\ominus \geq 0.30$ will occur at standard conditions.

Gibbs free energy and $E^\ominus_{cell}$:-

$$\boxed{\Delta G = -n E^\ominus_{cell} \times F}$$ $\longrightarrow$ -ve: feasible , +ve: not feasible

- n is number of electrons transferred in reaction
- F is 9.65×10^4 C mol^{-1} (Faraday's constant = charge carried by 1 mol of electrons)
- Divide ΔG by 1000 to get ΔG in KJ mol^{-1}

4 An electrochemical cell consists of a half-cell containing V^{3+}(aq) and V^{2+}(aq) ions and another half-cell containing VO_2^+(aq) and VO^{2+}(aq) ions.

(a) **(i)** Use data from the *Data Booklet* to calculate a value for the $E^\ominus_{cell}$.

$E^\ominus_{cell} = 1 - (-0.26)$
1.26

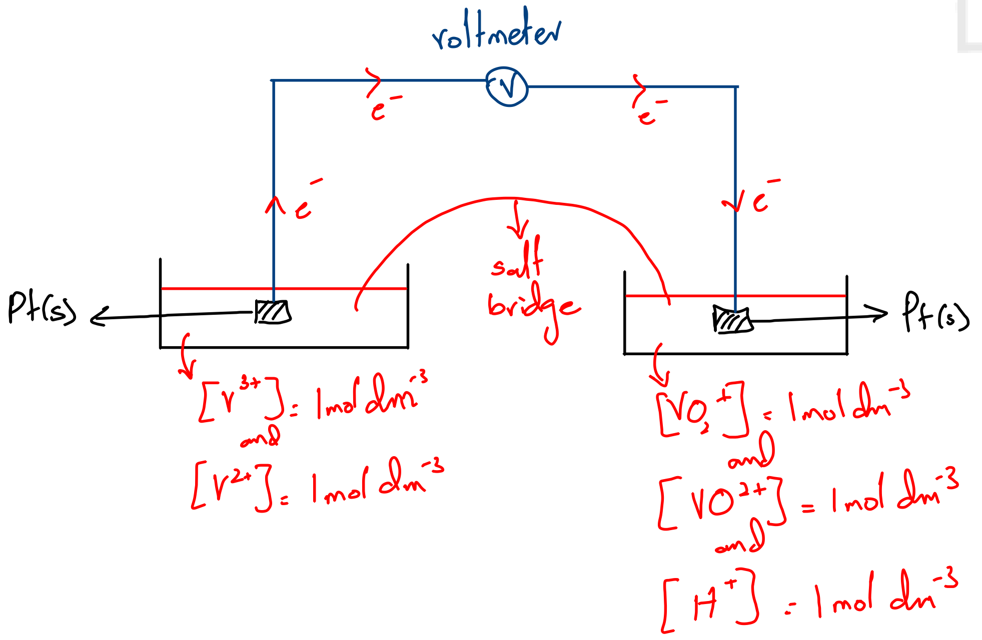
$E^\ominus_{cell}$ = ...1.26.......... V [1]

(ii) Write the ionic equation for the cell reaction.

			reverse
$V^{3+} + e^-$	⇌	V^{2+}	-0.26
$VO_2^+ + 2H^+ + e^-$	⇌	$VO^{2+} + H_2O$	$+1.00$

$VO_2^+ + 2H^+ + V^{2+} \rightleftharpoons V^{3+} + VO^{2+} + H_2O$ [1]

(iii) Draw a fully labelled diagram of the apparatus you could use to measure the potential of this cell. Include the necessary chemicals.



[4]

(b) Use data from the *Data Booklet* to predict whether a reaction might take place when the following pairs of aqueous solutions are mixed. If a reaction occurs, write an equation for it and calculate the $E^\ominus_{cell}$.

- V^{2+}(aq) and Sn^{4+}(aq)

			reverse
$2(V^{3+} + e^-$	⇌	$V^{2+})$	-0.26
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	$+0.15$

$E^\ominus = 0.15 - (-0.26) = 0.41$ $(E^\ominus \geq 0.30)$

Does a reaction occur? ....Yes..........

equation ....$Sn^{4+} + 2V^{2+} \rightleftharpoons Sn^{2+} + 2V^{3+}$..........

$E^\ominus_{cell}$ ....0.41V..........

- VO^{2+}(aq) and Fe^{3+}(aq)

$VO_2^+ + 2H^+ + e^-$	⇌	$VO^{2+} + H_2O$	$+1.00$
$Fe^{3+} + e^-$	⇌	Fe^{2+}	$+0.77$
			reverse

$E^\ominus = 1 - 0.77 = 0.23$

Does a reaction occur? ....no..........

equation ....

$E^\ominus_{cell}$ ....

[3]

[Total: 9]

- ions tend to stay in ionic form unless metal electrode is present

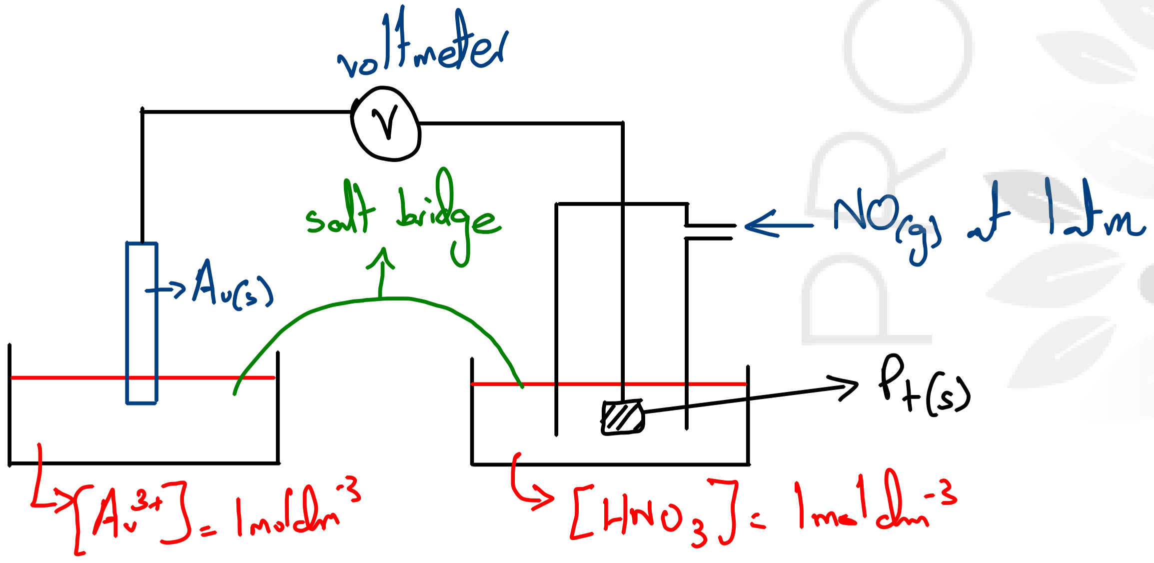
(a) The standard electrode potential, $E^{\ominus}$, of $Au^{3+}(aq)/Au(s)$ is +1.50 V.

(i) Define the term *standard electrode potential*.

The potential difference obtained between a half cell containing $1\,mol\,dm^{-3}$ of its ions in solution in equilibrium and the standard hydrogen electrode at 298 K / standard conditions. [2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard cell potential, $E^{\ominus}_{cell}$, of $Au^{3+}(aq)/Au(s)$ and $HNO_3(aq)/NO(g)$.

Include all necessary chemicals.



[4]

Some relevant half-equations and their standard electrode potentials are given.

	half-equation	$E^{\ominus}$/V
1	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
2	$[AuCl_4]^-(aq) + 3e^- \rightleftharpoons Au(s) + 4Cl^-(aq)$	+1.00
3	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96

reverse

(iii) Write an ionic equation to show the spontaneous reaction that occurs when an electric current is drawn from the cell in **(a)(ii)**.

$Au^{3+}_{(aq)} + NO_{(g)} + 2H_2O_{(l)} \rightleftharpoons Au_{(s)} + 4H^+_{(aq)} + NO_3^-{}_{(aq)}$ [1]

(iv) Calculate the $E^{\ominus}_{cell}$ of the reaction in **(a)(iii)**.

$= 1.50 - 0.96$

$= +0.54$

$E^{\ominus}_{cell}$ = +0.54 V [1]

(v) Gold can be oxidised by a mixture of concentrated hydrochloric acid and concentrated nitric acid, known as *aqua regia*. Concentrated hydrochloric acid is $12\,mol\,dm^{-3}$. Concentrated nitric acid is $16\,mol\,dm^{-3}$.

Explain why *aqua regia* is able to dissolve gold.

In your answer, state and explain what effect the use of concentrated hydrochloric acid and concentrated nitric acid have on the *E* values of half-equations 2 and 3.

Using concentrated HCl shifts the equilibrium towards left hand side in equation 2 so its $E^{\ominus}$ decreases. Using concentrated HNO_3 shifts equilibrium towards right hand side in equation 3 so its $E^{\ominus}$ increases. $E^{\ominus}_3$ increases and becomes greater than $E^{\ominus}_2$ which results in a very positive $E^{\ominus}$cell and so the reaction becomes highly feasible [3]

Nernst Equation :- Used to calculate exact $E^\ominus$ if concentrations are different

$$E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

E → E we want to find out!

$E^\ominus$ → standard E (given in data booklet)

z → electrons transferred in the reaction

[oxidised species] → higher ox. state

[reduced species] → lower ox. state (if reduced species is metal/solid, then its concentration is constant and can be omitted)

1 An electrochemical cell is constructed using two half-cells.

- an Sn^{4+}/Sn^{2+} half-cell
- an Al^{3+}/Al half-cell

(a) State the material used for the electrode in each half-cell.

- Sn^{4+}/Sn^{2+} half-cell ..... platinum
- Al^{3+}/Al half-cell ..... Aluminium

[1]

(b) The cell is operated at 298 K.

The Al^{3+}/Al half-cell has standard concentrations.

The Sn^{4+}/Sn^{2+} half-cell has $[Sn^{4+}] = 0.300\,mol\,dm^{-3}$ and $[Sn^{2+}] = 0.150\,mol\,dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Sn^{4+}/Sn^{2+} half-cell under these conditions.

$$E = 0.15 + \frac{0.059}{2} \log\left(\frac{[0.300]}{[0.150]}\right)$$

$E = 0.159$

E = ... 0.159 ..... V [2]

(ii) Calculate the E_{cell} under these conditions.

$2(Al^{3+} + 3e^-$	$\rightleftharpoons$	$Al)$	$\cancel{-1.66}$ reverse
$3(Sn^{4+} + 2e^-$	$\rightleftharpoons$	$Sn^{2+})$	+0.15

$0.159 + 1.66 = 1.819$

E_{cell} = ... 1.82 ..... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

$3Sn^{4+} + 2Al \rightleftharpoons 3Sn^{2+} + 2Al^{3+}$ ..... [2]

1 An electrochemical cell is constructed using two half-cells.

- a Br_2/Br^- half-cell
- an Mn^{3+}/Mn^{2+} half-cell

(a) State the material used for the electrode in each half-cell.

Br_2/Br^- half-cell ..... Platinum

Mn^{3+}/Mn^{2+} half-cell ..... Platinum

[1]

(b) The cell is operated at 298 K.

The Br_2/Br^- half-cell has standard concentrations.

The Mn^{3+}/Mn^{2+} half-cell has $[Mn^{3+}] = 0.500\,mol\,dm^{-3}$ and $[Mn^{2+}] = 0.100\,mol\,dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Mn^{3+}/Mn^{2+} half-cell under these conditions.

$$E = 1.49 + \frac{0.059}{1}\left(\log \frac{0.5}{0.1}\right)$$

$E = 1.53$

E = ... 1.53 ..... V [2]

(ii) Calculate the E_{cell} under these conditions.

$2(Mn^{3+} + e^-$	$\rightleftharpoons$	$Mn^{2+})$	$\cancel{+1.49}$ 1.53
$Br_2 + 2e^-$	$\rightleftharpoons$	$2Br^-$	+1.07 reverse

$1.53 - 1.07 = 0.46$

E_{cell} = ... +0.46 ..... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

$2Mn^{3+} + 2Br^- \rightleftharpoons Br_2 + 2Mn^{2+}$ ..... [2]

Electrolysis:- Breaking of a compound using electricity.

- Reduction happens at cathode
- Oxidation happens at anode

cathode
Red cat and ox
reduction anode oxidation

Molten Electrolytes:- When pure molten ionic compounds are electrolysed, metal is produced at cathode and non metal at anode
cation goes to ↗ anion goes to ↗

Compound electrolysed	Cathode product	Anode product
Aluminium oxide	Al	O_2
Magnesium oxide	Mg	O_2
NaCl	Na	Cl
ZnI_2	Zn	I_2

Electrolysis of Aqueous solutions:- When aqueous solutions are electrolysed, due to more than 1 cation and anion being present, a vareity of other factors must be considered

- relative electrode potential of the ion
- concentration of ions
- nature of the electrode (some are not inert)

- Between OH^- and halogens, the anion with more concentration is produced at anode
- Anions like SO_4^{2+}, NO_3^- donot produce on anode under aqueous conditions (OH^- goes to anode)
- Cations with lower reactivity will be deposited at cathode

How to remember the Reactivity Series?

Please	Potassium	Most reactive
Stop	Sodium	
Calling	Calcium	
Me	Magnesium	
A	Aluminium	
Careless	(Carbon)	
Zebra	Zinc	
Instead	Iron	
Try	Tin	
Learning	Lead	
How	(Hydrogen)	
Copper	Copper	
Saves	Silver	
Gold	Gold	Least reactive

← or use $E^{\ominus}$ values! →

(b) $E^{\ominus}$ in decreasing order of oxidising power

(a selection only – see also the extended alphabetical list on the previous pages)

Electrode reaction	$E^{\ominus}$/V
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.83
$V^{2+} + 2e^- \rightleftharpoons V$	−1.20
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.87
$K^+ + e^- \rightleftharpoons K$	−2.92

most reactive metal

Q. Identify products at cathode and anode:

	Cathode	Anode
a) KNO_3 (aq)	H_2 (g)	O_2 (g)
b) $CuSO_4$ (aq)	Cu(s)	O_2 (g)
c) molten NaCl	Na(s)	Cl_2 (g)
d) concentrated NaCl(aq)	H_2 (g)	Cl_2 (g)
e) dilute NaCl (aq)	H_2 (g)	O_2 (g)

Equations:-

a) Cathode: $2H^+ + 2e^- \rightarrow H_2(g)$ Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

b) Cathode: $Cu^{2+} + 2e^- \rightarrow Cu(s)$ Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

c) Cathode: $Na^+ + e^- \rightarrow Na(s)$ Anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

d) Cathode: $2H^+ + 2e^- \rightarrow H_2(g)$ Anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

e) Cathode: $2H^+ + 2e^- \rightarrow H_2(g)$ Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Quantitative electrolysis:-

Suppose the reaction $2Cl^- + \overset{3}{2}e^- \longrightarrow Cl_2(g)$ happening at anode.

- To calculate the moles of $Cl_2(g)$ liberated, we can use e^- to Cl_2 ratio
  $3 : 1$

- Calculating moles of electrons:-
  - First find out charge ($Q = It$)
  - Then divide charge by F. Faraday's constant = $9.65 \times 10^4\ C\ mol^{-1}$
    this much charge is carried by 1 mol of electrons
  - $\left(n_e = \dfrac{It}{F}\right)$

- Using e^- to Cl_2 ratio:-

$$\begin{array}{ccc} 3 & : & 1 \\ \dfrac{It}{F} & : & n \end{array} \Rightarrow \boxed{n = \dfrac{It}{3F}}$$

I = current
t = time
3 = moles of electrons transferred
F = $9.65 \times 10^4\ C\ mol^{-1}$ (given)

3 (a) Complete the table, identifying the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
$AgNO_3(aq)$	$O_2(g)$	$Ag(s)$
concentrated $NaCl(aq)$	$Cl_2(g)$	$H_2(g)$
$CuSO_4(aq)$	$O_2(g)$	$Cu(s)$

[3]

(b) Molten calcium iodide, CaI_2, is electrolysed in an inert atmosphere with inert electrodes.

(i) Write ionic equations for the reactions occurring at the electrodes.

- $Ca^{2+} + 2e^- \longrightarrow Ca$: Cathode
- $2I^- \longrightarrow I_2 + 2e^-$: Anode

[2]

(ii) The electrolysis of molten CaI_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced, explaining your answer by reference to oxidation numbers.

Ca^{2+} is reduced as its oxidation number went from +2 to 0 (decreased). I^- is oxidised as its oxidation number went from -1 to zero (increased) [2]

(iii) Describe **two** visual observations that would be made during this electrolysis.

1 silvery substance deposited at cathode

2 purple vapour at anode

[1]

(c) An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 hours using a current of 0.800A. The electrolysis products are iron and oxygen. The mass of iron produced is 1.11 g.

Calculate the oxidation number of Fe in the oxide of iron. Show **all** your working.

$$\text{moles} = \frac{\text{Mass}}{M_r/A_r} = \frac{1.11}{55.8} = \frac{37}{1860} \text{ moles}$$

$$n = \frac{It}{zF} \Rightarrow \frac{37}{1860} = \frac{(0.8)(2\times60\times60)}{z(9.65\times10^4)} \Rightarrow z = 3$$

oxidation number of Fe = +3 [3]

3 (a) Complete the table by predicting the identity of the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
$NaOH(aq)$	$O_2(g)$	$H_2(g)$
dilute $CuCl_2(aq)$	$O_2(g)$	$Cu(s)$
concentrated $MgCl_2(aq)$	$Cl_2(g)$	$H_2(g)$

[3]

(b) (i) The electrolysis of molten $ZnBr_2$ is a redox process.

Identify the ion that is oxidised and the ion that is reduced.

Use ionic half-equations to explain your answer.

$Zn^{2+} + 2e^- \longrightarrow Zn(s)$: Cathode

$2Br^- \longrightarrow Br_2(g) + 2e^-$: Anode

Zn was reduced as its oxidation number decreased from +2 to zero. Br was oxidised as its oxidation number increased from -1 to zero [3]

(ii) Describe **one** visual observation that would be made during this electrolysis.

Brown vapour at anode. [1]

(c) Dilute sulfuric acid is electrolysed for 50.0 minutes using inert electrodes and a current of 1.20A. A different gas is collected above each electrode. The volumes of the two gases are measured under room conditions.

Calculate the maximum volume of gas that could be collected at the **cathode**. (H_2)

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

$$n = \frac{It}{zF} = \frac{(1.2)(50\times60)}{2(9.65\times10^4)} = \frac{18}{965}$$

$$V = \frac{18}{965} \times 24000 = 448\text{cm}^3$$

volume = 448 cm³ [3]

(c) A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

(i) Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

- $Li_{(s)} \rightleftharpoons Li^{+} + e^{-}$: $+3.04$
- $I_2 + 2e^{-} \rightleftharpoons 2I^{-}$: $+0.54$

overall equation $2Li_{(s)} + I_2 \rightleftharpoons 2Li^{+} + 2I^{-}$

[2]

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this cell.

$= +3.04 + 0.54$

$= +3.58$

$E^{\ominus}_{cell} =$ $+3.58$ V [1]

(iii) A current of 2.5×10^{-5} A is drawn from this cell.

Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

$n = \frac{It}{3F}$ moles $= \frac{mass}{M_r/A_r} = \frac{0.1}{6.9} = \frac{1}{69}$ moles

$\frac{1}{69} = \frac{(2.5 \times 10^{-5})(t)}{(1)(9.65 \times 10^{4})} \Rightarrow t = 5.6 \times 10^{7}$

time = 5.6×10^{7} s [3]

[Total: 10]

(c) Aluminium is produced industrially by electrolysis of a melt containing large amounts of Al^{3+} ions.

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

$n = \frac{It}{3F}$ mass $= \frac{It}{3F} \times M_r/A_r$

$= \frac{(300\,000)(24 \times 60 \times 60)}{(3)(9.65 \times 10^{4})} \times 27 = 2417409\,g$

$= 2417.409$

mass = 2.42×10^{3} units = Kg [4]

(d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

$Cr^{2+} + 2e^{-} \rightleftharpoons Cr \quad E^{\ominus} = -0.91 \qquad 2H^{+} + 2e^{-} \rightleftharpoons H_2 \quad E^{\ominus} = 0.00$

The more positive $E^{\ominus}$ value for Hydrogen shows that it is much easier to reduce than Cr^{2+}. Therefore $H_2(g)$ will be liberated at cathode

[2]

[Total: 12]

equilibrium lies in favour of left hand side

$Cr^{2+} + 2e^{-} \rightleftharpoons Cr \qquad -0.91$

$2H^{+} + 2e^{-} \rightleftharpoons H_2 \qquad 0.00$

equilibrium lies in favour of right hand side

Finding Avogadro's (L) and Faraday's (F) constant from electrolysis:-

Electrolysing $CuSO_4$ with copper electrodes

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$ Anode:- $Cu_{(s)} \longrightarrow Cu^{2+} + 2e^-$

- Measure gain in mass of cathode or loss in mass of anode
- Measure current using ammeter
- Measure time using stopwatch
- Find out moles using mol = Mass / Mr / Ar
- Find F using:-

$$n = \frac{It}{zF}$$

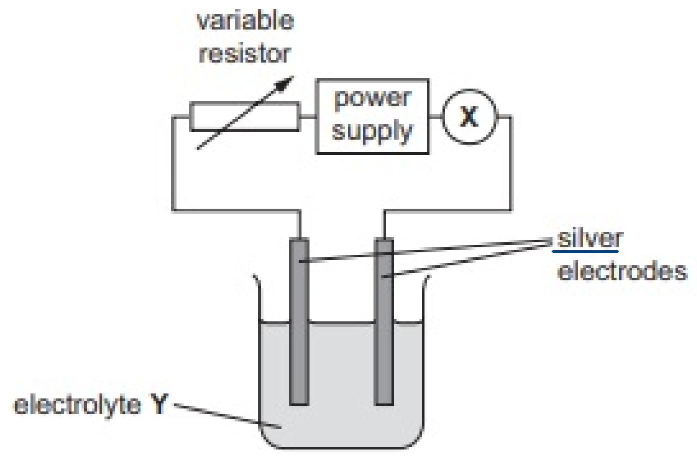
- Find L using:-

$$F = L \times e$$

L ↓ Avagadro's constant (6.02×10^{23})

↳ $e = 1.6 \times 10^{-19}$ C (elementary charge: given)

6 The apparatus shows a cell which can be used to determine a value of the Avogadro constant, L.



(a) (i) Name component **X**.

Ammeter [1]

(ii) Suggest a suitable electrolyte **Y**.

$AgNO_3$ [1]

(b) In an experiment, a current of 0.200A was passed through the cell for 40.0 minutes. The mass of the silver cathode increased by 0.500g.

The charge on the electron is -1.60×10^{-19}C.

Calculate the:

- number of moles of silver deposited on the cathode

$\text{moles} = \frac{0.500}{107.9} = 4.63 \times 10^{-3}$

- number of coulombs of charge passed

$Q = It = (0.2)(40\times60) = 480\text{C}$

- number of electrons passed

$Q = Ne \Rightarrow N = \frac{Q}{e} = \frac{480}{1.6\times10^{-19}} = 3.00\times10^{21}$

- number of electrons needed to deposit 1 mol of silver at the cathode.

$4.63\times10^{-3} : 3.00\times10^{21}$

$1\text{ mol} : x$

$x = 6.48\times10^{23}$

[3]

(c) An aqueous solution of copper(II) sulfate is electrolysed using copper electrodes. A current of 1.50A is passed for 3.00 hours. 5.09g of copper is deposited on the cathode.

The charge on one electron is -1.60×10^{-19}C.

The relative atomic mass of copper is 63.5.

Use these data to calculate an experimentally determined value for the Avogadro constant, *L*. Give your answer to **three** significant figures.

$\text{moles} = \text{mass}/M_r/A_r = 5.09/63.5 = \frac{509}{6350}\text{ mol}$

$n = \frac{It}{zF} \Rightarrow \frac{509}{6350} = \frac{(1.5)(3\times60\times60)}{(2)\ F} \Rightarrow F = 101051 = 1.01\times10^5$

$F = L\times e \Rightarrow 1.01\times10^5 = L \times 1.6\times10^{-19}$

$L = 6.32\times10^{23}$

L = 6.32×10^{23} mol^{-1} [5]

(d) Explain why magnesium metal cannot be obtained by the electrolysis of dilute aqueous magnesium sulfate. Your answer should include data from the *Data Booklet*.

$Mg^{2+} + 2e^- \rightleftharpoons Mg;\ E^\ominus = -2.38$ $\quad 2H^+ + 2e^- \rightleftharpoons H_2;\ E^\ominus = 0.00$

The $E^\ominus$ for hydrogen is more positive than for magnesium and therefore the hydrogen ions are much easier to reduce and are liberated at the cathode as $H_2(g)$ [2]

[Total: 13]

$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	-2.38
$2H^+ + 2e^-$	$\rightleftharpoons$	H_2	0.00