CHEMISTRY LEVEL 4C
(CHM415115)

ELECTROLYTIC CELLS

THEORY SUMMARY
&
REVISION QUESTIONS

(CRITERION 5)

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INTRODUCTION:

In our recent investigation of electrochemical cells, we encountered spontaneous redox reactions that *release* electrical energy such as takes place in the familiar situations of "batteries".

When a car battery is 'flat' and needs to be recharged, a power supply ('battery charger') is connected to the flat battery and chemical changes take place and it is subsequently able to operate again as a power supply.

The 'recharging' process is non-spontaneous and requires an ***input of energy*** to occur. When a cell is such that an energy input is required to make a non-spontaneous redox reaction take place, we describe the cell as an **ELECTROLYTIC CELL.**

The redox process occurring in an **ELECTROLYTIC CELL** is referred to as **ELECTROLYSIS.**

For example, consider the ***spontaneous redox reaction*** associated with an electrochemical (fuel) cell;

i.e. $\quad\quad\quad 2H_{2(g)} \;+\; O_{2(g)} \;\rightarrow\; 2H_2O_{(l)} \;+\;$ **ELECTRICAL ENERGY**
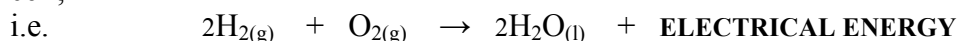
This chemical reaction **RELEASES** energy which can be used to power an electric motor, to drive a machine, appliance or car.

The reverse reaction will **NOT** occur spontaneously but can be made to occur if an adequate **ENERGY INPUT** occurs.

i.e. $\quad\quad\quad 2H_2O_{(l)} \;+\;$ **ELECTRICAL ENERGY** $\;\rightarrow\; 2H_{2(g)} \;+\; O_{2(g)}$

This is the exact reverse process and requires the same amount of energy as was released in the spontaneous electrochemical cell process.

This can be more easily understood if we consider a ball rolling down a ramp spontaneously releasing energy whereas the ball needs an input of energy to be pushed back up the ramp.

SUMMARY:

ELECTROCHEMICAL CELLS	ELECTROLYTIC CELLS
Involve a spontaneous redox reaction	Involve a non-spontaneous redox reaction
Releases electrical energy as it operates	Requires electrical energy input to operate
Chemical reactions releasing electrical energy	Chemical reactions driven by electrical energy
Can be used to power an appliance	Needs an external power supply to work
Like an object rolling DOWN a hill	Like an object being pushed UP the hill
Net redox reaction has net $E^o > 0$	Net redox reaction has net $E^o < 0$

ENERGY CONVERSIONS:

In an electrochemical cell, the reactants have high chemical potential energy and this is converted into electrical energy, leaving the products with a lower chemical potential energy. In an electrolytic cell, the reactants have low chemical potential energy and by the input of electrical energy, the products will now have a higher chemical potential energy.
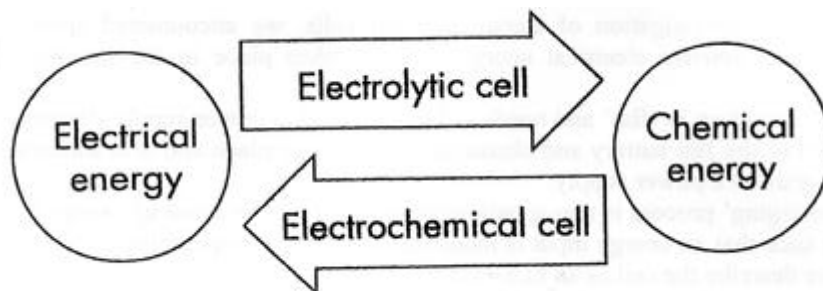
APPLICATIONS OF ELECTROLYSIS:

As already mentioned, the chemical reactions occurring in electrolytic cells would not normally happen without the input of electrical energy i.e. they are ***non-spontaneous***.
The chemical products of electrolytic cells are often difficult and in some cases, impossible to obtain unless formed by electrolysis. Some important products of electrolysis include:

- Metal electroplating – a thin layer of metal is plated onto the surface of other metals to protect them from corrosion or to enhance their appearance. e.g. Cr, Au, Ag, Cd,...........

- Extraction of reactive metals such as aluminium, sodium, potassium, calcium, magnesium,.......... from compounds of the metals.

    This occurs at Rio Tinto's Bell Bay smelter for extracting aluminium and also at Nyrstar's Risdon smelter for the extraction of zinc metal.

- Industrial production of chlorine, hydrogen oxygen, sodium hydroxide and fluorine.

- Anodising aluminium to increase the protective oxide layer's thickness.

- Recharging car batteries and other rechargeable cells such as NiCad's and Lithium ion cells.

- Electro-refining of metals such as copper. Impure Cu metal is oxidised at the anode and then Cu^{2+} ions are reduced back to pure copper at the cathode.

ELECTROPLATING:

There are many instances where a thin layer of metal is deposited onto the surface of another metal. This is especially important in jewellery where silver, gold and other precious metals are deposited onto cheaper metals such as nickel and copper.

Suppose we wish to electroplate a teapot with a thin silver (Ag) coating; i.e. silverplate the teapot.
The procedure used would involve:
1. Ensuring that the surface to be plated is perfectly clean and free from greasy marks where the silver metal may not adhere properly.
2. Prepare an electrolyte containing silver ions ($Ag^+_{(aq)}$) such as aqueous silver nitrate.
3. Obtain a D.C. electrical power supply and ammeter.
4. Connect the teapot to the negative terminal **(ANODE)** of the power supply and immerse the teapot into the electrolyte. The teapot becomes a **CATHODE**.
5. Connect the positive terminal of the power supply **(CATHODE)** to a silver metal rod and immerse the rod into the electrolyte. The $Ag_{(s)}$ rod becomes an **ANODE**.
6. Turn on the power supply and operate the electrolytic cell with a low current of less than 250 milliamps.
7. Rotate the teapot very slowly to ensure an even coating of silver plate.
8. Allow the electroplating process to take place very slowly over a long period of time. This ensures a smooth and even coating of silver.

The diagram shown to the right reveals that the circuit has an upper power supply (e.g. an electrochemical cell) which has anode and cathode labelled with polarity as discussed in the section on *electrochemical cells*.
i.e.   **CATHODE = (+) & ANODE = (−)**

The lower section of the diagram shows the *electrolytic cell*, in which the electrode polarities are reversed.
i.e.   **CATHODE = (−) & ANODE = (+)**

The reactions occurring at the electrodes are:

ELECTROLYTIC CELL

CATHODE = (−)
$Ag^+_{(aq)}$ + e^- → $Ag_{(s)}$
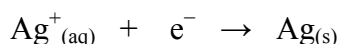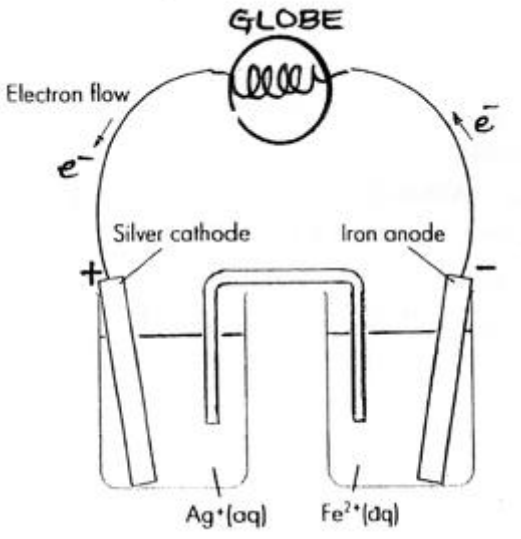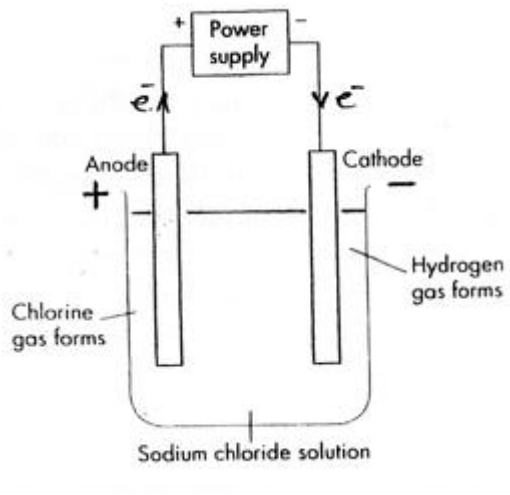
ANODE = (+)
$Ag_{(s)}$ → $Ag^+_{(aq)}$ + e^-

Note that the electrons flow in *both* branches
From: **ANODE → CATHODE**

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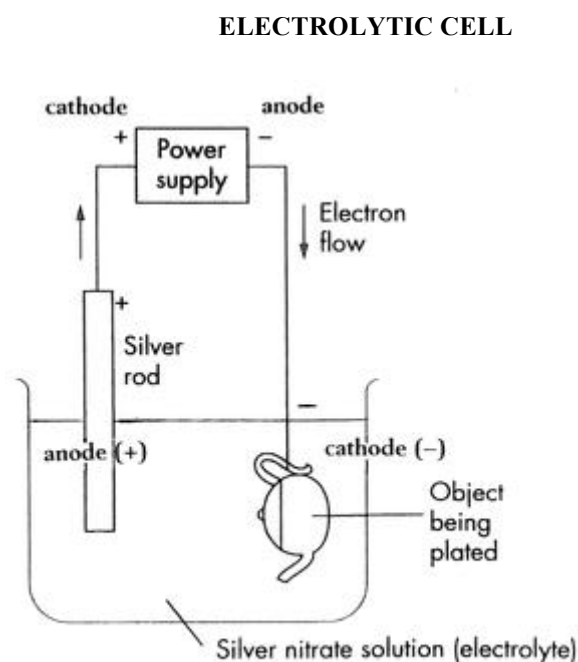
COMPARING CELLS:

There are several points of similarity between electrochemical cells and electrolytic cells but there are some key differences such as the labelling of the electrode polarities.

ELECTROCHEMICAL CELL	ELECTROLYTIC CELL
Typical electrochemical cell	Typical electrolytic cell
Involves a spontaneous redox reaction $(E^o > 0)$	Involves a non-spontaneous redox reaction $(E^o < 0)$
Releases electrical energy which can be used to power radios, cameras, phones,…	Requires an input of electrical energy from an external power supply
Has two different electrolytes usually separated by a salt-bridge	Usually has only one electrolyte and thus no salt-bridge is required
Has two electrodes; an anode and a cathode	Has two electrodes; an anode and a cathode
Oxidation occurs at the anode	Oxidation occurs at the anode
Reduction occurs at the cathode	Reduction occurs at the cathode
Electrons flow from anode → cathode	Electrons flow from anode → cathode
Anode is labelled (−)	Anode is labelled (+)
Cathode is labelled (+)	Cathode is labelled (−)
Anions migrate towards the anode	Anions migrate towards the anode
Cations migrate towards the cathode	Cations migrate towards the cathode

THE ELECTROCHEMICAL SERIES:

AQUEOUS IONS (1.00 mol L⁻¹ and 25°C)

REDUCTION HALF EQUATIONS →

VERY STRONG OXIDISERS ↑ (left side)

VERY WEAK REDUCERS (right side)

Reduction Half Equation	E°(volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.78
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.49
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.28
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	+0.78
$NO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$	+0.78
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.17
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.41
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

INCREASING STRENGTH AS OXIDISERS ↑ (left side, lower)

INCREASING STRENGTH AS REDUCERS ↓ (right side)

VERY WEAK OXIDISERS (bottom left)

VERY STRONG REDUCERS (bottom right)

← **OXIDATION HALF EQUATIONS**

PREDICTING ELECTROLYSIS PRODUCTS:

The accurate prediction of the products of electrolysis is reliant upon knowledge of some key determining factors; namely
- The nature of the electrolyte
- The oxidising and reducing agents present
- The concentrations of the ions present
- The type of electrodes used; specifically the anode

1. THE NATURE OF THE ELECTROLYTE:

There are two types of electrolyte that will concern us in this course.
(i) Aqueous electrolytes where an ionic compound has been dissolved in water. These solutions are shown by the subscript "(aq)".

e.g. **AQUEOUS SOLUTIONS** e.g. $NaCl_{(aq)}$, $H_2SO_{4(aq)}$, $Al(NO_3)_{3(aq)}$, ...

(ii) The other type of electrolyte occurs when an ionic compound has been melted
These electrolytes are shown by the subscript "(l)" for liquid.
Molten electrolytes are usually at very high temperatures (e.g. the melting point of $NaCl_{(l)}$ = $801^{o}C$) and thus, these electrolytes need special heat resistant equipment for electrolysing.
e.g. **MOLTEN ELECTROLYTES** e.g. $NaCl_{(l)}$, $Al_2O_{3(l)}$, $PbCl_{2(l)}$, ...
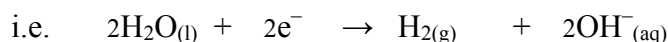
2. OXIDISING AND REDUCING AGENTS PRESENT:

By referring to the Electrochemical Series (ECS) we note that water can be both an oxidising agent and a reducing agent. When electrolysing *aqueous* solutions, this factor is often an important consideration.

If there are two (or more) oxidising agents present in an electrolyte, then the general rule is that whichever is the **STRONGER** oxidising agent will undergo reduction at the cathode.
e.g.1 in aqueous silver nitrate solution, there are two oxidising agents present (see ECS). These are $Ag^+_{(aq)}$ and $H_2O_{(l)}$. As silver ions are stronger oxidising agents than water, silver ions will be reduced at the cathode and not water.
i.e. $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$
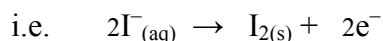
e.g.2 in aqueous aluminium chloride solution, there are two oxidising agents present (see ECS). These are $Al^{3+}_{(aq)}$ and $H_2O_{(l)}$. As water is a stronger oxidising agent than aluminium ions, water will be reduced at the cathode and not aluminium ions.
i.e. $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Similarly, if there are two (or more) reducing agents present in an electrolyte, then the general rule is that whichever is the **STRONGER** reducing agent will undergo oxidation at the anode.

e.g. 1 In aqueous sodium iodide solution there are two reducing agents present (see E.C.S.). These are $I^-_{(aq)}$ and $H_2O_{(l)}$.

As iodide ions are stronger reducing agents than water, iodide ions will be oxidised at the anode and not water.

$$\text{i.e.} \quad 2I^-_{(aq)} \rightarrow I_{2(s)} + 2e^-$$

e.g. 2 In aqueous sodium fluoride solution there are two reducing agents present (see E.C.S.). These are $F^-_{(aq)}$ and $H_2O_{(l)}$.

As water is a stronger reducing agent than fluoride ions, water will be oxidised at the anode and not fluoride ions.

$$\text{i.e.} \quad 2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$
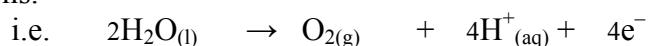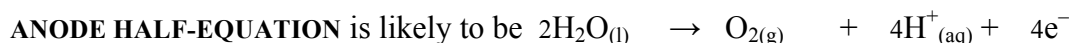
3. CONCENTRATIONS OF THE IONS PRESENT:

The molarity of the ions present has a significant influence on the outcome of some electrolytic processes.

e.g. In aqueous solutions with a high chloride ion concentration, $Cl_{2(g)}$ is a likely anode product but when the chloride ion concentration is low, then $O_{2(g)}$ is the likely anode product.

i.e. If $[Cl^-_{(aq)}]$ is high concentration then:

      ANODE HALF-EQUATION is likely to be $2Cl^-_{(aq)} \rightarrow Cl_{2(s)} + 2e^-$

If $[Cl^-_{(aq)}]$ is low concentration (dilute) then:

      ANODE HALF-EQUATION is likely to be $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

A similar situation occurs with solutions involving bromide ions.
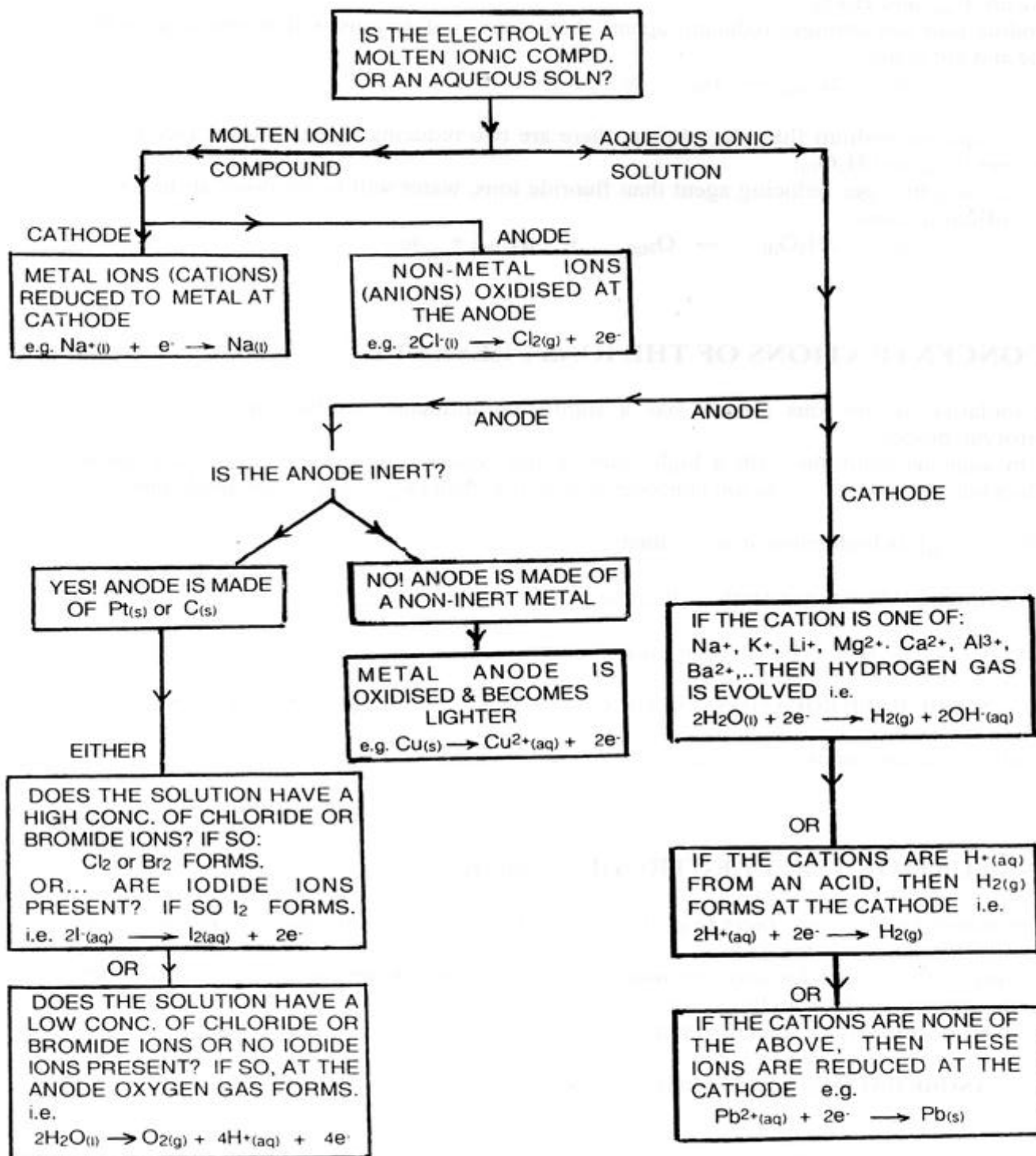
4. NATURE OF THE ELECTRODES USED:

If the electrodes used are *inert* (e.g. they are platinum or graphite) they do not affect the products of electrolysis formed.

However, if the electrodes used are ***non-inert*** metals (e.g. copper, lead, tin,....... electrodes) then the **ANODE** made from this metal is likely to be oxidised.

e.g. when electrolysing aqueous sodium iodide with nickel metal electrodes, the

      ANODE HALF-EQUATION is likely to be $Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

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ELECTROLYSIS PREDICTION FLOWCHART:

IS THE ELECTROLYTE A MOLTEN IONIC COMPD. OR AN AQUEOUS SOLN?

MOLTEN IONIC COMPOUND

AQUEOUS IONIC SOLUTION

CATHODE

METAL IONS (CATIONS) REDUCED TO METAL AT CATHODE

e.g. $Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$

ANODE

NON-METAL IONS (ANIONS) OXIDISED AT THE ANODE

e.g. $2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e^-$

ANODE

ANODE

IS THE ANODE INERT?

YES! ANODE IS MADE OF $Pt_{(s)}$ or $C_{(s)}$

NO! ANODE IS MADE OF A NON-INERT METAL

METAL ANODE IS OXIDISED & BECOMES LIGHTER

e.g. $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$

EITHER

DOES THE SOLUTION HAVE A HIGH CONC. OF CHLORIDE OR BROMIDE IONS? IF SO:
Cl_2 or Br_2 FORMS.
OR... ARE IODIDE IONS PRESENT? IF SO I_2 FORMS.
i.e. $2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$

OR

DOES THE SOLUTION HAVE A LOW CONC. OF CHLORIDE OR BROMIDE IONS OR NO IODIDE IONS PRESENT? IF SO, AT THE ANODE OXYGEN GAS FORMS.
i.e.
$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

CATHODE

IF THE CATION IS ONE OF:
Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ba^{2+},...THEN HYDROGEN GAS IS EVOLVED i.e.
$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$

OR

IF THE CATIONS ARE $H^+_{(aq)}$ FROM AN ACID, THEN $H_{2(g)}$ FORMS AT THE CATHODE i.e.
$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

OR

IF THE CATIONS ARE NONE OF THE ABOVE, THEN THESE IONS ARE REDUCED AT THE CATHODE e.g.
$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$

ELECTROLYSIS PREDICTION EXAMPLES

Predict the anode and cathode products in each of the following cases by giving the appropriate half equations.

Q1.　**ELECTROLYTE USED** = aqueous copper(II) nitrate
　　　ELECTRODES USED = platinum (Pt)

ANS.

The *only* reducing agent present is water and so the anode half-equation must involve the oxidation of water. (The prediction flowchart confirms this outcome) i.e.

　　　ANODE HALF-EQUATION:　　　$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
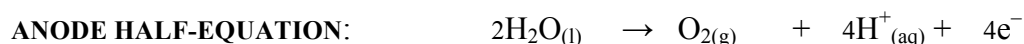
The oxidising agents present are Cu^{2+} ions and water and Cu^{2+} ions are the stronger so these ions are reduced at the cathode. (The prediction flowchart confirms this outcome) i.e.

　　　CATHODE HALF-EQUATION:　　　$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

Q2.　**ELECTROLYTE USED** = aqueous sodium iodide
　　　ELECTRODES USED = platinum (Pt)

ANS.

The reducing agents present are $I^-_{(aq)}$ ions and water and $I^-_{(aq)}$ ions are the stronger so these ions are oxidised at the anode. (The prediction flowchart confirms this outcome) i.e.

　　　ANODE HALF-EQUATION:　　　$2I^-_{(aq)} \rightarrow I_{2(aq)} + 2e^-$

The oxidising agents present are Na^+ ions and water and water is the stronger so water is reduced at the cathode. (The prediction flowchart confirms this outcome) i.e.

　　　CATHODE HALF-EQUATION:　　　$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

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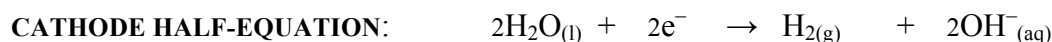
Q3.　**ELECTROLYTE USED** = molten potassium oxide ($K_2O_{(l)}$)
　　　ELECTRODES USED = graphite (C)

ANS.

Using the prediction flowchart gives:

　　　ANODE HALF-EQUATION:　　　$2O^{2-}_{(l)} \rightarrow O_{2(g)} + 4e^-$

　　　CATHODE HALF-EQUATION:　　　$K^+_{(l)} + e^- \rightarrow K_{(l)}$

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QUESTIONS ON ELECTROLYSIS PREDICTION

Predict the anode and cathode products in each of the following cases by giving the likely half-equations at the anode and cathode respectively. The electrodes used are shown in brackets.

ELECTROLYTE & ELECTRODES USED IN BRACKETS	ANODE HALF-EQUATION	CATHODE HALF-EQUATION
(i) dilute $Cu(NO_3)_{2(aq)}$ (Pt)		
(ii) dilute $NaCl_{(aq)}$ (Pt)		
(iii) conc. $KBr_{(aq)}$ (C)		
(iv) molten $Al_2O_{3(l)}$ (C)		
(v) $Pb(NO_3)_{2(aq)}$ (Pb)		
(vi) $CuSO_{4(aq)}$ (Cu)		
(vii) $KI_{(aq)}$ (Pt)		
(viii) molten $KBr_{(l)}$ (Pt)		
(ix) dilute $H_2SO_{4(aq)}$ (Pt)		
(x) conc. $NaCl_{(aq)}$ (Pt)		
(xi) dilute $CaBr_{2(aq)}$ (Pt)		

FIVE INDUSTRIAL ELECTROLYTIC PROCESSES

1. DOWN'S CELL FOR THE PRODUCTION OF SODIUM
- ELECTROLYTE: molten NaCl with a small trace of calcium chloride added to lower the melting point.
- ELECTRODES: ANODE = carbon (inert graphite), CATHODE = iron

Q1. What will be the anode half-equation? ....

Q2. What will be the cathode half-equation? ....

Q3. What will be the overall equation? ....

2. HALL-HEROULT CELL FOR THE PRODUCTION OF ALUMINIUM
- ELECTROLYTE: molten Al_2O_3 with a small trace of cryolite (Na_3AlF_6) added to lower the melting point.
- ELECTRODES: ANODE = carbon (inert graphite), CATHODE = carbon (inert graphite)

Q4. What will be the anode half-equation? ....

Q5. What will be the cathode half-equation? ....

Q6. What will be the overall equation? ....

3. DIAPHRAGM CELL FOR THE PRODUCTION OF NaOH
- ELECTROLYTE: concentrated $NaCl_{(aq)}$ solution (called brine)
- ELECTRODES: ANODE = carbon (inert graphite), CATHODE = steel

Q7. What will be the anode half-equation? ....

Q8. What will be the cathode half-equation? ....

Q9. What will be the overall equation? ....

4. ELECTROLYSIS FOR THE INDUSTRIAL PRODUCTION OF ZINC METAL
- ELECTROLYTE: $ZnSO_{4(aq)}$ solution
- ELECTRODES: ANODE = inert metal, CATHODE = aluminium

Q10. What will be the anode half-equation? ....

Q11. What will be the cathode half-equation? ....

Q12. What will be the overall equation? ....
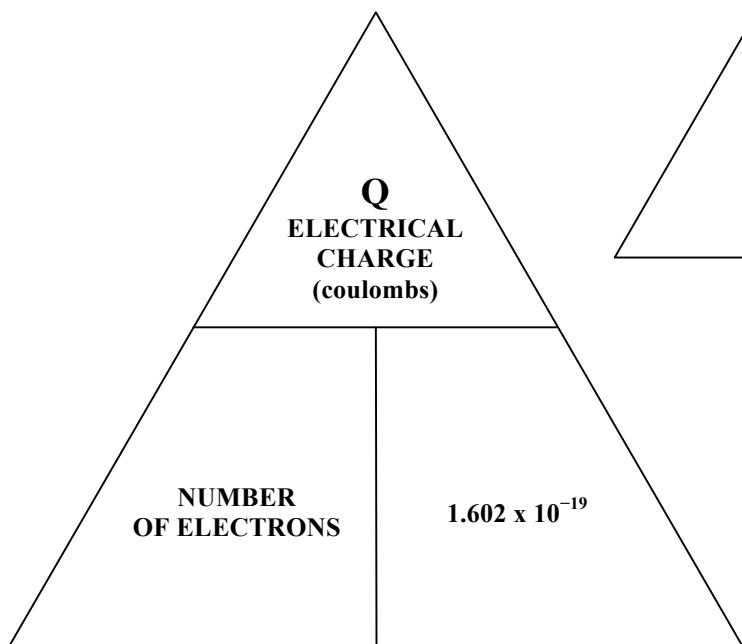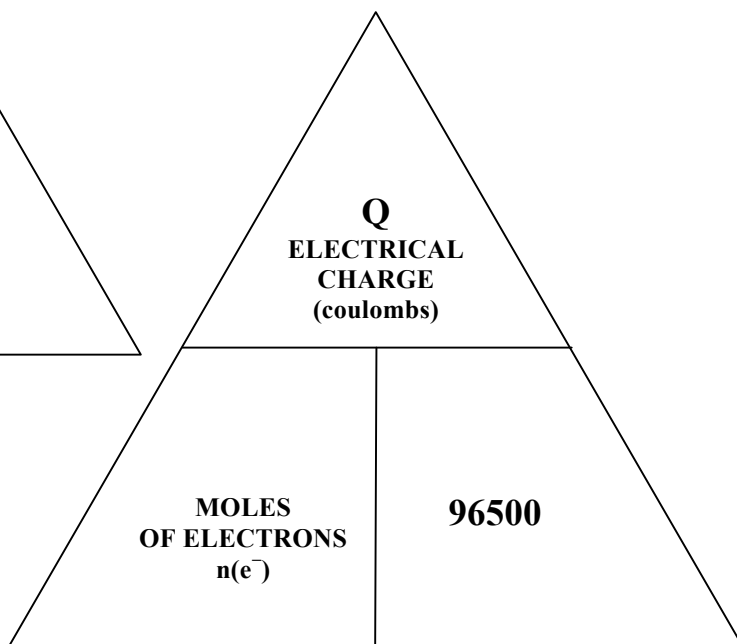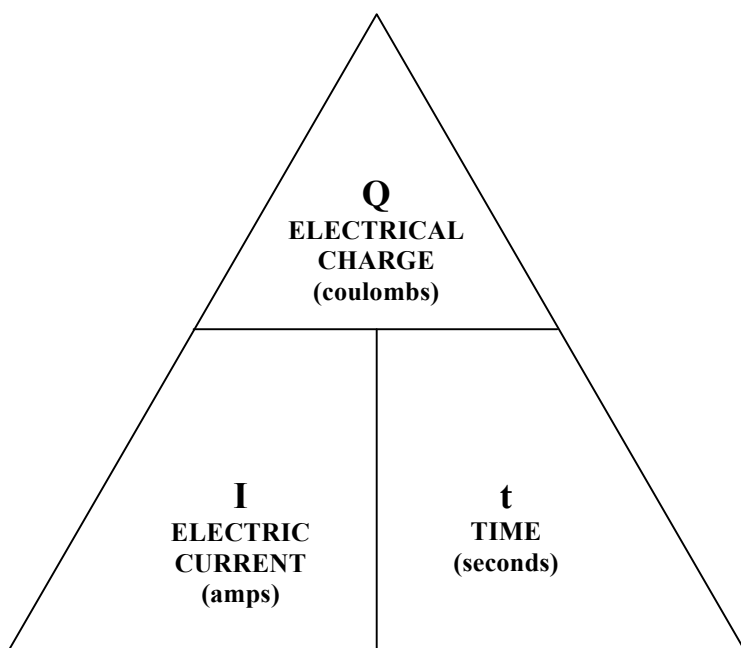
5. ELECTROLYSIS FOR THE ELECTROREFINING OF COPPER
- ELECTROLYTE: $CuSO_{4(aq)}$ solution
- ANODE: impure copper metal including both more reactive metals such as Pb, Fe, Zn as well as less reactive metals such as Ag and Au.
- CATHODE: pure copper
- The voltage is adjusted so that at the anode, copper and the more reactive metals are oxidised but only Cu^{2+} ions are reduced at the cathode. The less reactive metals are not oxidised at the anode and fall underneath the anode as the valuable 'anode-sludge'.

Q13. What will be the anode half-equation? ....

Q14. What will be the cathode half-equation? ....

ELECTROLYSIS: IMPORTANT ELECTRICAL THEORY

1. ELECTRICAL CHARGE (Q) is measured in coulombs (C)
2. ELECTRIC CURRENT (I) is measured in amperes (A)
3. TIME (t) is measured in seconds (s)
4. $Q = I \times t$
5. $Q = (\text{no. of electrons}) \times (1.602 \times 10^{-19})$ C
6. $Q = n(e^-) \times 96500$ C

Q
ELECTRICAL CHARGE
(coulombs)

I
ELECTRIC CURRENT
(amps)

t
TIME
(seconds)

Q
ELECTRICAL CHARGE
(coulombs)

MOLES OF ELECTRONS
$n(e^-)$

96500

Q
ELECTRICAL CHARGE
(coulombs)

NUMBER OF ELECTRONS

1.602×10^{-19}

FARADAY'S LAWS OF ELECTROLYSIS

INTRODUCTORY THEORY:

1.   The unit for electrical charge (Q) is the coulomb (C)

2.   The charge on 1electron = 1.602×10^{-19} coulombs (negative)

3.   The charge on 1 mole of electrons   = $(1.602 \times 10^{-19} \times 6.022 \times 10^{23})$ C

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 96470 C or 96500 C (to 3 sig. figs.)

4.   When a current of I amps flows for t seconds, the charge passing is given by:

$$\boxed{Q \;=\; I \times t}$$

FARADAY'S EQUATION:

Consider the electrolysis process involving the reduction of ions M^{z+} where M is a metal having ions with a charge of z+

$\quad$ i.e. $\qquad\qquad$ at the cathode: M^{z+} + ze^- $\rightarrow$ M

Thus if z mole of electrons pass through the cell, 1 mole of metal M will be reduced;

$\quad$ i.e. $\qquad\qquad$ (z x 96500) coulombs reduces 1 mole of M

$\quad$ or: $\qquad\qquad$ (z x 96500) coulombs reduces {A_r(M)} grams of metal M

$\quad$ so: $\qquad\qquad$ 1 coulomb reduces $\dfrac{A_r(M)}{z \times 96500}$ g of M

$\quad$ Thus $\qquad\qquad$ Q coulombs reduces $\dfrac{Q \times A_r(M)}{z \times 96500}$ g of M

$$\boxed{\text{i.e. mass of element electrolysed}\; =\; \dfrac{A_r \times Q}{z \times 96500}\quad \text{g}}$$

$$\boxed{\text{i.e. mass of element electrolysed}\; =\; \dfrac{A_r \times I \times t}{z \times 96500}\quad \text{g}}$$

$\quad$ m $\;=\;$ mass in grams of element being electrolysed
$\quad$ A_r $=$ relative atomic mass of the element undergoing electrolysis
$\quad$ I $\;\;=\;$ electric current measured in amperes (A)
$\quad$ t $\;\;=\;$ time of electrolysis operation in seconds
$\quad$ z $\;\;=\;$ charge on the ions being electrolysed

This equation is equally applicable to non-metallic elements such as oxygen, chlorine,….

$$\text{mass of element electrolysed} = \frac{A_r \times I \times t}{z \times 96500} \text{ g}$$

This equation represents the combination of the two Faraday Laws of Electrolysis.

LAW 1: The mass of element electrolysed is proportional to the electric charge passing (mass ∞ Q)

LAW 2: The mass of element electrolysed is proportional to the A_r of the element and inversely proportional to the ionic charge

QUANTITATIVE ELECTROLYSIS PROBLEMS

Q1. What mass of cadmium metal plates onto the cathode during a 3.00 hour period of electrolysing aqueous cadmium(II) sulfate using a current of 755 mA?

ANS.   Mass of cadmium = ? g
                A_r(Cd) =112.4
                Current I = 0.755 A
        Electrolysis time t = (3.00 x 60 x 60) = 10800 seconds
            Ionic charge z   = 2   (because the compound involves Cd^{2+} ions)

Thus, mass of cadmium metal plated = $\frac{(112.4 \times 0.755 \times 10800)}{2 \times 96500}$ g

                = 4.75 g

Q2. For what period of time must a current of 2.68 A pass through gold(I) cyanide in order to plate out 5.00 g of gold?

ANS.   Mass of gold = 5.00 g A_r(Au) = 197
            Current I = 2.68 A   Electrolysis time t =   ? seconds
        Ionic charge z = 1   (because the compound involves Au^+ ions)

Now mass of gold electrolysed   = $\frac{A_r \times I \times t}{z \times 96500}$ g

Thus, time t = $\frac{\text{mass} \times z \times 96500}{A_r(Au) \times I}$ seconds

                = (5.00 $\times$ 1 $\times$ 96500)/(197 $\times$ 2.68) seconds

                = 914 seconds (or 15 min 14 seconds)

CELLS IN SERIES:

When two or more electrolytic cells are connected in series (see diagram below) then the same electric current and operating time apply to all the cells.
i.e. "I" and "t" are identical for cells connected in series and as $Q = I \times t$, this means that cells in series have the same Q (electric charge) value

i.e. For electrolytic cells 1, 2, 3 and 4 in series above,

$$Q_1 \text{ (for cell 1)} = Q_2 \text{ (for cell 2)} = Q_3 \text{ (for cell 3)} = Q_4 \text{ (for cell 4)}$$

Q. Two electrolytic cells are connected in series. Descriptions of the two cells are:
   CELL 1: electrolyte is silver nitrate ($AgNO_{3(aq)}$) electrodes are inert.
   CELL 2: electrolyte is chromium(III) nitrate ($Cr(NO_3)_{3(aq)}$) electrodes are inert.
If 0.785 g of silver metal ($Ag_{(s)}$) plates onto the cathode in cell 1 during electrolysis, what corresponding mass of chromium metal plates onto the cathode of cell 2?
ANS.
For Cell 1,   mass of silver electrolysed $= \dfrac{(A_r \times I \times t)}{(z \times 96500)}$ g $= \dfrac{(A_r \times Q)}{(z \times 96500)}$ g

$$\text{Thus } Q = (\text{mass of silver} \times z \times 96500)/A_r$$
$$(Ag^+ \qquad z = 1)$$

$$= (0.785 \times 1 \times 96500)/ 108$$
$$= 701 \text{ coulombs   (which will be the same Q value for cell 2)}$$

For Cell 2,   mass of chromium electrolysed $= \dfrac{(A_r \times Q)}{(z \times 96500)}$ g $(Cr^{3+} \quad z = 3)$

$$= (52.0 \times 701)/3 \times 96500 \text{ g}$$

$$= 0.126 \text{ g.}$$

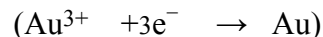Thus 0.126 g of chromium plates out onto the cathode of cell 2.

ELECTROLYSIS QUESTIONS:

1. What mass of chromium metal $Cr_{(s)}$ is theoretically plated out at the cathode of an electrolytic cell when a current of 349 mA passes through $Cr(CN)_{3(aq)}$ electrolyte for 200.0 minutes? The $A_r(Cr) = 52.0$ (0.752 g)

2. A chemist wishes to electroplate an object with silver metal. She makes the object the cathode of an electrolytic cell in which the electrolyte is $AgNO_{3(aq)}$ and she passes an unknown current for 3 hours 25 minutes. The mass increase of the object is found to be 2.760g. Find the current used in this electroplating experiment.   (0.201 A)

3(a) Two electrolytic cells are connected in **series**. In cell #1 aqueous $CuSO_4$ is electrolysed and during electrolysis 0.965 g of copper metal is plated onto the cathode. What mass of gold metal is plated onto the cathode of cell #2 simultaneously if the electrolyte used is aqueous gold(III) sulfate?   (2.00 g)

(b) What is the cathode half-reaction occurring in **cell #2**?

$$(Au^{3+} \quad +3e^- \quad \rightarrow \quad Au)$$

4. Predict the anode(A) and cathode(C) products resulting from the electrolysis of:

(a) molten LiBr (Pt electrodes)	$A = Br_2$ $C = Li$
(b) aqueous *dilute* LiBr (Pt electrodes)	$A = O_2/H^+$ $C = H_2/OH^-$
(c) aqueous *conc*. LiBr (Pt electrodes)	$A = Br_2$ $C = H_2/OH^-$
(d) aqueous *conc*. LiBr (Zn electrodes)	$A = Zn^{2+}$ $C = H_2/OH^-$

5. An aqueous solution of cadmium(II) nitrate is electrolysed using cadmium electrodes and a current of 350 mA. On completion of electrolysis the anode is found to have decreased by 0.750g.
Find   (a) the anode half-equation $(Cd \rightarrow Cd^{2+} + 2e^-)$
              (b) the cell operating time.   (61.3 minutes)

6(a) What mass of chlorine gas $Cl_{2(g)}$ is theoretically produced per day in an industrial plant when a concentrated aqueous solution of sodium chloride (brine) is electrolysed using Pt electrodes and a current of 125 A?   (3.97 kg)

(b) The mass of chlorine gas $Cl_{2(g)}$ produced per day in the industrial plant discussed above is found to be 3.200 kg. What is the efficiency of the electrolytic cell as a chlorine producing unit?   (80.6%)

(c) Give **two** plausible reasons for the electrolytic cell being less than 100% efficient.

7. An unknown aqueous solution of an ionic compound "XSO_4 " is electrolysed using a current of 260 mA for 30.0 minutes. The metal plated onto the cathode has a mass of 0.1429 g.
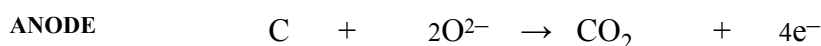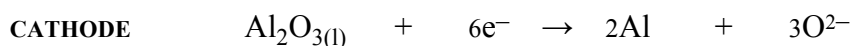What is the likely identity of unknown metal X?   ($A_r(X) = 58.9$ X = cobalt)

8. When electrolysing dilute sulfuric acid, what mass of hydrogen is produced at the cathode per megacoulomb (MC) of electrical charge that passes?   (10.4 g)

9. Give the anode and cathode products for the electrolysis of dilute sulfuric acid.
$$(A = O_2/H^+ \quad C = H_2/OH^-)$$

10. How is the Faraday constant (96500 C) derived?
(it is the electrical charge on 1.00 mol of electrons)

11. Aluminium metal is obtained industrially by the electrolysis of molten aluminium oxide $Al_2O_{3(l)}$ using graphite electrodes. The reactions at the electrodes are:

    CATHODE $Al_2O_{3(l)}$ + $6e^-$ $\rightarrow$ $2Al$ + $3O^{2-}$

    ANODE C + $2O^{2-}$ $\rightarrow$ CO_2 + $4e^-$

Establish the net cell reaction and hence find the ratio of aluminium atoms formed to molecules of carbon dioxide formed.

$$(4 : 3)$$

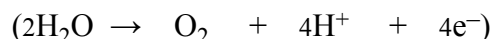12. Consider two hypothetical metals A and B that form ions A^+ and B^{2+} respectively. The $A_r(A) = 20$ and the $A_r(B) = 40$. Two electrolytic cells are connected in series and metal A plates onto the cathode of cell #1 whereas metal B plates onto the cathode of cell #2. Compare the masses of metal A plating out with the mass of metal B plating out.
(the same in each cell)

13. Electrolysis of aqueous sodium nitrate ($NaNO_{3(aq)}$) produces hydrogen at the cathode and *not* sodium metal. Offer an explanation for this.
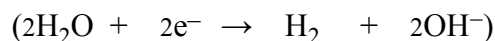
(ANS. water being a more powerful oxidising agent than sodium ions is therefore more easily reduced than sodium ions Na^+)

14. During the electrolysis of water using dilute sulfuric acid ($H_2SO_{4(aq)}$) as the electrolyte and using inert electrodes;
    (i) what is the half-equation for the **anode** reaction?
$$(2H_2O \rightarrow O_2 + 4H^+ + 4e^-)$$
    (ii) what is the half-equation for the **cathode** reaction?
$$(2H_2O + 2e^- \rightarrow H_2 + 2OH^-)$$

15. Four electrolytic cells are operated in **series**. The electrolytes used are: $Cd(NO_3)_{2(aq)}$, $Pb(NO_3)_{2(aq)}$, $Cu(NO_3)_{2(aq)}$ and $Sn(NO_3)_{2(aq)}$. In each case, metal plates onto the cathode of the respective cell.
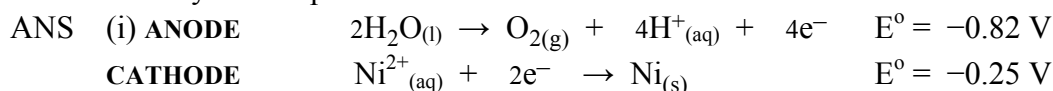
(i) With which cathode will the *greatest* mass increase occur?   (Pb)
(ii) With which cathode will the *least* mass increase occur?   (Cu)

*16. An aqueous solution contains a mixture of copper(II) sulfate, silver nitrate and aluminium sulfate. If the mixture is used as an electrolyte and electrolysis is carried out using platinum electrodes, explain the likely products and specifically their ***order of formation*** at the cathode.

(Ag metal forms first, Cu metal forms next)
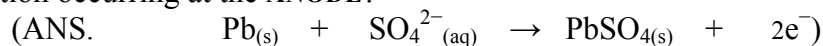(H_2 gas forms next but ***no*** Al metal forms!)

*17. A 1.0 mol L^{-1} aqueous solution of nickel(II) sulfate is to be used in an electrolysis experiment. (Assume the electrolyte is originally neutral i.e. $[H^+_{(aq)}] = 10^{-7}$ mol L^{-1})
(i) What will be the half-reactions occurring at the anode and cathode respectively.
(ii) What minimum voltage will need to be applied across the electrolytic cell in order   to make electrolysis take place?
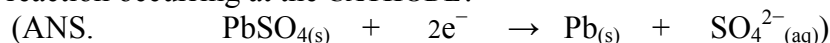
ANS (i) **ANODE** $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ $E^o = -0.82$ V

CATHODE $Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ $E^o = -0.25$ V

(ii) **NET**: $E^o = -1.07$ V, thus minimum voltage needed to commence electrolysis is $> +1.07$ V

18(i) During the ***discharge*** of a standard lead-acid car battery, what is the oxidation half-reaction occurring at the **ANODE**?
(ANS. $Pb_{(s)} + SO_4^{2-}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$)

(ii) During the ***recharging*** of a "flat" standard lead-acid car battery, what is the reduction half-reaction occurring at the **CATHODE**?
(ANS. $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}_{(aq)}$)

19. A student attempts to electroplate magnesium metal onto an iron cathode in an electrolytic cell involving a magnesium anode and having magnesium nitrate as the electrolyte.
The student is disappointed to discover that no Mg metal plated out onto the iron cathode despite the electrical circuit being connected correctly.
Why did no Mg plate onto the cathode?
(ANS. water being a more powerful oxidising agent than magnesium ions is therefore more easily reduced than magnesium ions Mg^{2+})

20. Consider the half-reaction: $Al^{3+}_{(l)} + 3e^- \rightarrow Al_{(l)}$
(i) How many mole of aluminium is in 1.00 tonne of Al?   (3.70×10^4 mol)
(ii) How many mole of electrons are needed to produce 1.00 tonne of Al?
(1.11×10^5 mol)
(iii) How many coulombs of electric charge are needed to produce 1.00 tonne of Al?
(1.07×10^{10} C)

ELECTROLYSIS TEST QUESTIONS
CRITERION 5   **TOTAL = 25 marks**

Q1. What mass of manganese metal $Mn_{(s)}$ is theoretically plated out at the cathode of an electrolytic cell when a current of 235 mA passes through $MnSO_{4(aq)}$ electrolyte for 250.0 minutes?   (4 marks)

Q2. Two electrolytic cells are connected in **series**. In cell #1 aqueous $CuSO_4$ is electrolysed and during electrolysis **1.325**g of copper metal is plated onto the cathode. What mass of lead metal is plated onto the cathode of cell #2 simultaneously if the electrolyte used is aqueous lead(II)nitrate?   (4 marks)

Q3. Predict the anode and cathode products for the following electrolytic cells by giving the relevant half-cell equations.
(i) molten KBr (Pt electrodes)
     ANODE   ....

     CATHODE   ....

(ii) aqueous *dilute* KBr (Pt electrodes)
     ANODE   ....

     CATHODE   ....

Q3. (continued)

(iii) aqueous *conc*. KBr   (Pt electrodes)
ANODE   ....

CATHODE   ....

(iv) aqueous *conc*. KBr   (Cu electrodes)
ANODE   ....

CATHODE   ....

(8 marks)

Q4. When a current of 255 mA passes through $X_2(SO_4)_{3(aq)}$ electrolyte for 3.00 hours, the mass of metal $X_{(s)}$ plated out at the cathode is found to be 0.428 g.
Use these data to establish the likely identity of metallic element X.   (4 marks)

Q5. Explain why the industrial electrolysis for aluminium metal (e.g. Comalco at Bell Bay) has to use an electrolyte of molten Al_2O_3 whereas the industrial electrolysis for zinc metal (e.g. Zinifex at Risdon) uses an electrolyte of aqueous zinc sulfate.

(5 marks)

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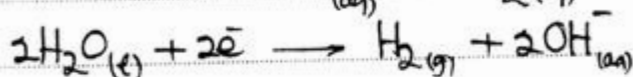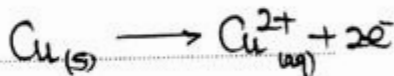
ELECTROLYSIS TEST (CRITERION 5)
ANSWERS

Q1. What mass of manganese metal $Mn_{(s)}$ is theoretically plated out at the cathode of an electrolytic cell when a current of 235 mA passes through $MnSO_{4(aq)}$ electrolyte for 250.0 minutes? (4 marks)

$$mass = ?\, g$$
$$A_r(Mn) = 54.9\, g$$
$$I = 0.235\, A$$
$$t = (250 \times 60)\, sec$$
$$z = 2\ (Mn^{2+})$$

$$\therefore mass\ of\ Mn = \left(\frac{A_r \times I \times t}{z \times 96500}\right) g$$

$$= \left(\frac{54.9 \times 0.235 \times 250 \times 60}{2 \times 96500}\right) g$$

$$= 1.00\, g$$

Q2. Two electrolytic cells are connected in **series**. In cell #1 aqueous $CuSO_4$ is electrolysed and during electrolysis **1.325g** of copper metal is plated onto the cathode. What mass of lead metal is plated onto the cathode of cell #2 simultaneously if the electrolyte used is aqueous lead(II)nitrate? (4 marks)

CELL 1

$$mass\ of\ Cu = \frac{A_r \times Q}{z \times 96500}\, g$$

$$\therefore Q = \frac{mass \times z \times 96500}{A_r}$$

$$= \left(\frac{1.325 \times 2 \times 96500}{63.5}\right)$$

$$= 4027\ coulombs$$

CELL 2

$$mass\ of\ lead = \left(\frac{A_r \times Q}{z \times 96500}\right) g$$

$$= \left(\frac{207 \times 4027}{2 \times 96500}\right) g$$

$$= 4.32\, g$$

$$\therefore Mass\ of\ lead\ plated\ is\ 4.32\, g$$

Q3. Predict the anode and cathode products for the following electrolytic cells by giving the relevant half-cell equations.

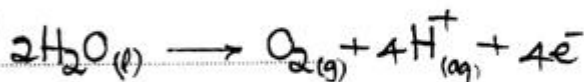(i) molten KBr (Pt electrodes)

ANODE $\quad 2Br^-_{(l)} \longrightarrow Br_{2(g)} + 2e^-$

CATHODE $\quad K^+_{(l)} + e^- \longrightarrow K_{(l)}$

(ii) aqueous *dilute* KBr (Pt electrodes)

ANODE $\quad 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

CATHODE $\quad 2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$

Q3. (continued)
(iii) aqueous *conc.* KBr (Pt electrodes)

ANODE $2Br^-_{(aq)} \longrightarrow Br_{2\,(aq)} + 2e^-$

CATHODE $2H_2O_{(\ell)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(aq)}$

(iv) aqueous *conc.* KBr (Cu electrodes)

ANODE $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$

CATHODE $2H_2O_{(\ell)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(aq)}$

(8 marks)

Q4. When a current of 255 mA passes through $X_2(SO_4)_{3(aq)}$ electrolyte for 3.00 hours, the mass of metal $X_{(s)}$ plated out at the cathode is found to be 0.428 g.
Use these data to establish the likely identity of metallic element X.   (4 marks)

$$mass\ of\ X = \frac{A_r(X) \times I \times t}{Z \times 96500}$$

$t = (3 \times 60 \times 60)\ sec$
$I = 0.255A$
$Z = 3\ \left(from\ X_2(SO_4)_3\right)$

$$\therefore A_r(X) = \frac{\left(mass \times Z \times 96500\right)}{I \times t}$$

$$= \frac{0.428 \times 3 \times 96500}{0.255 \times 3 \times 60 \times 60}$$

$$= 45.0$$

$$\therefore element\ X\ is\ probably\ scandium\ (Sc)$$

Q5. Explain why the industrial electrolysis for aluminium metal (e.g. Comalco at Bell Bay) has to use an electrolyte of molten Al_2O_3 whereas the industrial electrolysis for zinc metal (e.g. Pasminco at Risdon) uses an electrolyte of aqueous zinc sulfate.
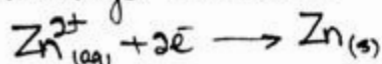(5 marks)

Al^{3+} ions, Zn^{2+} ions and water are all oxidising agents that can be made to undergo reduction.
However, water is a stronger oxidiser than Al^{3+} and thus water is reduced (to give H_2 gas) and $Al^{3+}_{(aq)}$ are not reduced.
The only way to reduce Al^{3+} ions is to have NO water present at all. This necessitates molten Al_2O_3 in which $Al^{3+}_{(\ell)}$ occur.
Zn^{2+} ions are stronger oxidisers than water and thus do undergo reduction even in aqueous solutions.

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