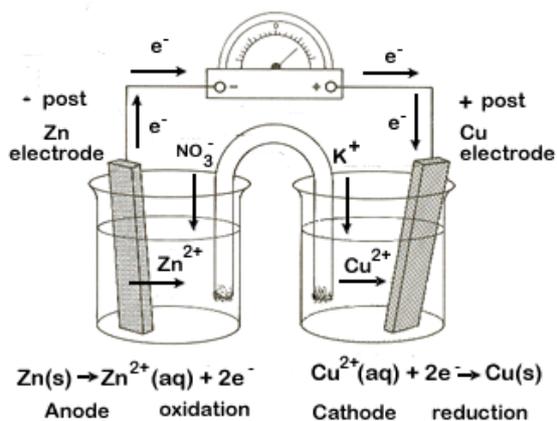
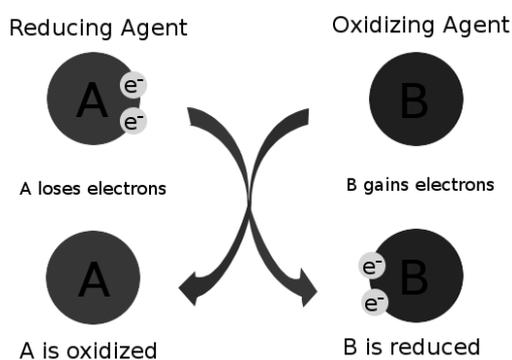


UNIT 6

REDOX REACTIONS

Teacher Version



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Contents

- (a) Oxidation and Reduction
- (b) Redox Reactions
- (c) Examples of common redox reactions
- (d) Qualitative Analysis Part 2 – redox reactions
- (e) Galvanic Cells
- (f) Electrolysis
- (g) The Rusting of Iron

Key words: oxidation, reduction, oxidation number, oxoanion, oxidising agent, reducing agent, half-equation, redox reaction, rusting, galvanisation, electrode potential, electromotive force (emf), potential difference, standard hydrogen electrode, primary electrochemical cell, secondary electrochemical cell, Daniell cell, dry cell, fuel cell, sacrificial cathodic protection, electrolysis, electrolytic cell, anode, cathode, electrolyte, Faraday, electroplating

Units which must be completed before this unit can be attempted:

Unit 1 – Atoms and the Periodic Table

Unit 2 – Particles, Structure and Bonding

Unit 3 – Amount of Substance

Unit 4 – Introduction to Physical Chemistry

Unit 5 – Acids, Bases and Salts

Estimated Teaching Time: 13 hours

UNIT 6 – REDOX REACTIONS

UNIT 6 SUMMARY AND SYLLABUS REFERENCE

Lesson	Title and Syllabus Reference
1	<p>Oxidation, Reduction and Oxidation Numbers CA10a oxidation and reduction processes (oxidation and reduction in terms of addition and removal of oxygen and hydrogen, loss and gain of electrons, change in oxidation numbers/states; oxidation numbers/states)</p>
2	<p>Naming Inorganic Compounds ISA4.3 ionic and covalent compounds (IUPAC names of common compounds)</p>
3	<p>Half-Equations CA10c redox equations (balancing redox equations by ion, electron or change in oxidation number/state method, half reactions and overall reactions IUPAC system method)</p>
4	<p>Redox Reactions; Oxidising and Reducing Agents CA10b oxidizing and reducing agents (definition of oxidising and reducing agents in terms of addition and removal of oxygen and hydrogen, loss and gain of electrons, change in oxidation number/state); CA10c redox equations (balancing redox equations by ion, electron or change in oxidation number/state method, half reactions and overall reactions IUPAC system method)</p>
5	<p>Common Redox Reactions CA7a definitions of acids and bases (effects of acids and bases on metals); CA7b chemical properties of acids and bases (balanced chemical equations of all reactions); CA13aiii General Skills and Principles – Filtration; CC4a methods of preparation of simple salts; ISA7.4 methods of preparation of salts (preparation of salts using the following method: acid + metal)</p>
6	<p>Qualitative Analysis – Redox Reactions CA5bii gases – properties of gases (chemical properties of SO₂); CA10b oxidising and reducing agents (tests for oxidants and reductants); CA13cii Qualitative Analysis - confirmatory test for NO₃⁻ and SO₃²⁻ anions, CA13civ Qualitative Analysis - characteristic test for SO₂ gas (no formal scheme of analysis is required)</p>
7	<p>Galvanic Cells CA10di electrochemical cells - drawing of cell diagrams (only metal/metal ion systems should be used); CA10dii electrochemical cells - emf of cells (electrochemical cells as a combination of two half-cells, the meaning of the magnitude and sign of the emf)</p>
8	<p>Standard Electrode Potentials; Conventional Representation of Cells CA10di electrochemical cells - standard electrode potential, drawing and writing of cell diagrams (standard hydrogen electrode: meaning of standard electrode potential and its measurement, only metal/metal ion systems should be used)</p>
9	<p>Galvanic Cells in Practice CA10diiii electrochemical cells - application of electrochemical cells (distinction between primary and secondary cells, Daniel cell, lead battery cell, dry cells, fuel cells and their use as generators of electrical energy from chemical reactions)</p>
10	<p>Electrolysis – General Principles CA10eii electrolysis - principles of electrolysis (mechanism of electrolysis: compare with electrochemical cells); CA10eii electrolysis - factors influencing discharge of species (limit electrolytes to molten PbBr₂/NaCl, dilute NaCl solution, concentrated NaCl solution, CuSO₄(aq); dilute H₂SO₄ (using platinum or graphite and copper electrodes)); CA10eiii electrolysis – practical applications (smelting of aluminium etc); CA12bi extraction of metals – Al; CC5 electrolysis of molten/fused salts and solutions (electrolysis of the following solutions should also be carried out: NaOH(aq) KI(aq) and CuCl₂(aq)); CC8di copper – purification</p>

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Lesson	Title and Syllabus Reference
11	<p>Electrolysis - Faraday's Laws, Applications CA4bi amount of substance (mole of electrons); CA10eii electrolysis – factors influencing discharge of species (Faraday's Laws: simple calculations based on the relation $F = Le = 96,500 \text{ C}$ and mole ratios to determine mass, volume of gases, number of entities, charges etc using half reactions and overall reactions); CA10eiii electrolysis – practical applications (electroplating etc); CC7bi water and solution - composition of water (Reference should be made to the electrolysis of acidulated water)</p>
12	<p>Rusting and Rust Prevention CA10f corrosion of metals (corrosion treated as redox process, rusting of iron and its economic cost, prevention based on relative magnitude of electrode potentials and preventive methods like galvanising, sacrificial cathodic protection and non-redox methods); ISA12.1 process of rusting (conditions necessary for rusting, experiments to show that air and water are necessary for rusting, experiments to show that salt, dilute acid, dilute base and heat affect the rate of rusting in iron); ISA12.2 prevention of rusting (methods of preventing rusting: oiling/greasing, painting, galvanizing, tin-coating, electroplating, cathode protection and keeping the metal dry, effectiveness of the various methods of preventing rusting, items in the home that undergo rusting)</p>
13	Unit 6 Revision and Summary

The Periodic Table of the Elements

1	2	3	4	5	6	7	0										
(1) 6.9 Li lithium 3	(2) 9.0 Be beryllium 4	(3) 45.0 Sc scandium 21	(4) 47.9 Ti titanium 22	(5) 50.9 V vanadium 23	(6) 52.0 Cr chromium 24	(7) 54.9 Mn manganese 25	(8) 55.8 Fe iron 26	(9) 58.9 Co cobalt 27	(10) 58.7 Ni nickel 28	(11) 63.5 Cu copper 29	(12) 65.4 Zn zinc 30	(13) 10.8 B boron 5	(14) 12.0 C carbon 6	(15) 14.0 N nitrogen 7	(16) 16.0 O oxygen 8	(17) 19.0 F fluorine 9	(18) 4.0 He helium 2
23.0 Na sodium 11	24.3 Mg magnesium 12	39.1 K potassium 19	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	96.0 Mo molybdenum 42	98 Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	209 Po polonium 84	210 At astatine 85	222 Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac † actinium 89	[267] Rf rutherfordium 104	[268] Db dubnium 105	[271] Sg seaborgium 106	[272] Bh bohrium 107	[270] Hs hassium 108	[276] Mt meitnerium 109	[281] Ds darmstadtium 110	[280] Rg roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						
* 58 – 71 Lanthanides																	
† 90 – 103 Actinides																	

Lesson 1 – What is oxidation, what is reduction and what are oxidation numbers?

a) Oxidation and Reduction

(i) Definitions of Oxidation and Reduction

- Oxidation and reduction can be defined in terms of electron transfer:
 - Oxidation is the loss of electrons**; when a species loses electrons it is said to be oxidised
Eg $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ (each sodium atom loses one electron)
 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ (each iodide ion loses one electron, so two in total)
 - Reduction is the gain of electrons**; when a species gains electrons it is said to be reduced
Eg $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ (each chlorine atom gains one electron, so two in total)
 $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$ (each aluminium ion gains three electrons)
- Equations which show the gain or loss of electrons by a species are known as **half-reactions** or **half-equations**; they show simple oxidation or reduction processes (eg $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$, $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$)
- In organic chemistry, it is sometimes more convenient to consider oxidation and reduction in terms of the gain and loss of oxygen and hydrogen:
 - Oxidation is the gain of oxygen or the loss of hydrogen**; when a species gains oxygen or loses hydrogen, it is said to be oxidised
Eg $\text{C}_2\text{H}_6\text{O} + \text{O} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$ (ethanol loses two hydrogen atoms when it is oxidised to ethanal)
ethanol ethanal
Eg $\text{C}_2\text{H}_4\text{O} + \text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2$ (ethanal gains one oxygen atom when it is oxidised to ethanoic acid)
ethanal ethanal
 - Reduction is the gain of hydrogen or the loss of oxygen**; when species loses oxygen or gains hydrogen, it is said to be reduced
Eg $\text{C}_2\text{H}_3\text{N} + 2\text{H} \rightarrow \text{C}_2\text{H}_5\text{N}$ (ethanenitrile gains two hydrogen atoms when it is reduced to ethylamine)
ethanol ethanal
(ethanenitrile gains two hydrogen atoms when it is reduced to ethylamine)
Eg $\text{C}_6\text{H}_5\text{NO}_2 + 6\text{H} \rightarrow \text{C}_6\text{H}_7\text{N} + 2\text{H}_2\text{O}$
nitrobenzene phenylamine
(nitrobenzene loses two oxygen atoms and gains two hydrogen atoms when it is reduced to phenylamine)
- Gaining oxygen and losing hydrogen are just special cases of losing electrons; losing hydrogen and gaining oxygen are just special cases of gaining electrons; defining oxidation and reduction in terms of gain and loss of electrons is therefore a more general (and useful) way of defining oxidation and reduction

**Thinkabout Activity 1.1: What is oxidation and what is reduction?**

- Write an equation for the reaction of Mg with O_2
- When Mg reacts with O_2 , what happens to its valence electrons?
- Give two ways in which the magnesium can be said to be “oxidised” in this reaction
- Write equations for the two half-reactions taking place

- $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$
- Mg loses its two valence electrons
- Mg is oxidised because it “gains oxygen”; it is also oxidised because it “loses electrons”
- $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$; $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$

UNIT 6 – REDOX REACTIONS

(ii) Oxidation numbers

- The concept of oxidation and reduction can be extended to covalent compounds using **oxidation numbers**
- **The oxidation number of an atom is the charge that would exist on an individual atom if the bonding were completely ionic**
- In simple ions, the oxidation number of the atom is the charge on the ion:
 - Na^+ , K^+ , H^+ all have an oxidation number of +1
 - Mg^{2+} , Ca^{2+} , Pb^{2+} all have an oxidation number of +2
 - Cl^- , Br^- , I^- all have an oxidation number of -1
 - O^{2-} , S^{2-} all have an oxidation number of -2
- In molecules or compounds, the sum of the oxidation numbers on the atoms is zero
 - In SO_3 ; oxidation number of S = +6, oxidation number of each O = -2 $+6 + 3(-2) = 0$
 - H_2O_2 ; oxidation number of each H = +1, oxidation number of each O = -1 $2(+1) + 2(-1) = 0$
 - SCl_2 ; oxidation number of S = +2, oxidation number of each Cl = -1 $+2 + 2(-1) = 0$
- In polyatomic ions, the sum of the oxidation numbers on the atoms is equal to the overall charge on the ion.
 - In SO_4^{2-} ; oxidation number of S = +6, oxidation number of O = -2 $+6 + 4(-2) = -2$
 - In PO_4^{3-} ; oxidation number of P = +5, oxidation number of O = -2 $+5 + 4(-2) = -3$
 - In ClO^- ; oxidation number of Cl = +1, oxidation number of O = -2 $+1 + (-2) = -1$
- In elements, the oxidation number of each atom is zero
 - In Cl_2 , S, Na and O_2 all atoms have an oxidation number of zero
- Many atoms, such as S, N and Cl, can exist in a variety of oxidation states; the oxidation number of these atoms can be calculated by assuming that the oxidation number of the other atom is fixed
 - All group I atoms always adopt the +1 oxidation state in their compounds
 - All group II atoms adopt the +2 oxidation state in their compounds
 - Aluminium always adopts the +3 oxidation state in its compounds
 - Fluorine always adopts the -1 oxidation state in its compounds
 - Hydrogen adopts the +1 oxidation state in its compounds unless it is bonded to a metal, silicon or boron in which case it adopts the -1 oxidation state
 - Oxygen adopts the -2 oxidation state in its compounds unless it is bonded to a group I or group II metal or hydrogen (with which it sometimes adopts the -1 oxidation state), or with fluorine (with which it adopts the +2 oxidation state)
 - The oxidation numbers of all other atoms in their compounds can vary



Test your knowledge 1.2: Deducing Oxidation Numbers

Deduce the oxidation numbers of the following atoms:

(a) Si in SiF_4

(b) S in H_2S

(c) Pb in PbO_2

(d) S in H_2SO_4

(e) N in NO_3^-

(f) N in NO_2^-

(g) I in I_2

(h) S in $\text{S}_2\text{O}_3^{2-}$

(i) Cl in ClO^-

(j) Cl in ClO_3^-

(k) Tl in TlCl

(l) C in CaC_2

(m) H in AlH_3

(n) C in $\text{C}_2\text{O}_4^{2-}$

(o) I in IO_3^-

(p) Cl in Cl_2O_7

(q) O in OF_2

(r) Fe in Fe_3O_4

(s) S in $\text{S}_4\text{O}_6^{2-}$

(t) C in HCN

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(a) +4	(h) +2	(o) +5
(b) -2	(i) +1	(p) +7
(c) +4	(j) +5	(q) +2
(d) +6	(k) +1	(r) +8/3
(e) +5	(l) -1	(s) +2.5
(f) +3	(m) -1	(t) +2
(g) 0	(n) +3	

- During oxidation and reduction, the oxidation numbers of atoms change.
 - If an atom is oxidized, its oxidation number increases (ie it becomes more +ve or less -ve)
 - If an atom is reduced, its oxidation number decreases (ie it becomes less +ve or more -ve)

Oxidation	Loss of electrons	Increase in oxidation number
Reduction	Gain of electrons	Decrease in oxidation number



Test your knowledge 1.3: Using oxidation numbers to identify oxidation and reduction

In each of the following changes, use oxidation numbers to deduce whether the named atom has been oxidised and reduced:

- (a) Pb when PbO_2 is converted into PbO
- (b) O when H_2O_2 is converted into O_2
- (c) Cl when ClO^- is converted into Cl^-
- (d) S when $\text{S}_2\text{O}_3^{2-}$ is converted into $\text{S}_4\text{O}_6^{2-}$
- (e) N when NO_3^- is converted into NO

- (a) +4 to +2, so reduction
- (b) -1 to 0, so oxidation
- (c) +1 to -1, so reduction
- (d) +2 to +2.5, so oxidation
- (e) +5 to +2, so reduction

Lesson 2 – How can I use oxidation numbers to name inorganic compounds?

(iii) Naming inorganic ions and compounds

- Oxidation numbers are used when naming compounds according to the internationally agreed IUPAC rules:
- Ionic compounds are named by stating the cation followed by the anion (eg sodium chloride)
- Binary covalent compounds are named by stating the atom with a positive oxidation number followed by the atom with a negative oxidation number (eg hydrogen chloride)

UNIT 6 – REDOX REACTIONS

- Simple cations (and atoms in a positive oxidation state in binary covalent compounds) are named using the name of the atom followed by its oxidation number in brackets and Roman numerals:

K ⁺ is potassium (I) and Cu ⁺ is copper (I)	+1 = I
Mg ²⁺ is magnesium (II) and Cu ²⁺ is copper (II)	+2 = II
Al ³⁺ is aluminium (III) and Fe ³⁺ is iron (III)	+3 = III
C in CO ₂ is carbon (IV)	+4 = IV
P in P ₄ O ₁₀ is phosphorus (V)	+5 = V
W in WO ₃ is tungsten (VI)	+6 = VI
Mn in Mn ₂ O ₇ is manganese (VII)	+7 = VII

- Simple anions (and atoms in a negative oxidation state in binary covalent compounds) are named by changing the final one or two syllables of the atom to -ide
 - Eg Cl⁻ is chloride, H⁻ is hydride, O²⁻ is oxide, S²⁻ is sulphide, N³⁻ is nitride, P³⁻ is phosphide
 - CO₂ is carbon (IV) oxide (although it is usually known as carbon dioxide)
 - H₂O is hydrogen (I) oxide (although it is usually known as water)
 - CuCl is copper (I) chloride
 - CuO is copper (II) chloride



Test your knowledge 2.1: Naming binary inorganic compounds

Give the IUPAC name of the following compounds:

- (a) CuO
(b) Cu₂O
(c) PbO₂
(d) Ca₃N₂
(e) CO
(f) NO₂
(g) NCl₃

- (h) PbS
(i) NH₃
(j) OF₂
(k) H₂Te
(l) UF₆
(m) AlH₃
(n) FeO

- (o) Fe₂O₃
(p) MnO₂
(q) CCl₄
(r) Cl₂O₇
(s) SnCl₄
(t) SnCl₂
(u) SO₂

- (a) copper (II) oxide
(b) copper (I) oxide
(c) lead (IV) oxide
(d) calcium (II) nitride
(e) carbon (II) oxide
(f) nitrogen (IV) oxide
(g) nitrogen (III) chloride

- (h) lead (II) sulphide
(i) hydrogen (I) nitride
(j) oxygen (II) fluoride
(k) hydrogen (I) telluride
(l) uranium (VI) fluoride
(m) aluminium (III) hydride
(n) iron (II) oxide

- (o) iron (III) oxide
(p) manganese (IV) oxide
(q) carbon (IV) chloride
(r) chlorine (VII) oxide
(s) tin (IV) chloride
(t) tin (II) chloride
(u) sulphur (IV) oxide

- Note: many of these compounds have commonly used names which are not their IUPAC names (eg ammonia, water)
- Note: it is common to leave out the Roman numeral if the atom has only one known oxidation number (such as sodium or magnesium); eg sodium (I) chloride is the IUPAC name for NaCl but sodium chloride is also correct; magnesium (II) chloride is the IUPAC name for MgCl₂ but magnesium chloride and magnesium dichloride are also correct

UNIT 6 – REDOX REACTIONS

- In polyatomic anions and non-binary compounds, ie anions containing more than one atom, such as CO_3^{2-} , NO_3^- and SO_4^{2-} , one of the atoms has a positive oxidation number and the other, usually oxygen, has a negative oxidation number
 - these anions are named by changing the last one or two syllables of the atom with a positive oxidation number to -ate, and then adding the oxidation state of that atom in brackets and Roman numerals:
 - sometimes the presence of oxygen is indicated by using the prefix oxo-, preceded by the number of oxygen atoms if more than one (two = di, three = tri, four = tetra, five = penta, six = hexa)
 - eg CO_3^{2-} is called carbonate (IV) or trioxocarbonate (IV)
 - eg NO_3^- is called nitrate (V) or trioxonitrate (V)
 - SO_4^{2-} is called sulphate (VI) or tetraoxosulphate (VI)
 - Note: the oxo prefix is usually omitted in common usage
 - If the atom with a negative oxidation number is not oxygen, it must be mentioned in the prefix, with its final one or two syllables replaced with -o: eg CoCl_4^{2-} is called tetrachlorocobaltate (II)



Test your knowledge 2.2: Naming non-binary inorganic compounds

Give the IUPAC name of the following compounds:

- (a) Na_2SO_3
- (b) KClO_3
- (c) NaClO
- (d) CuCO_3
- (e) $\text{Mg}(\text{NO}_3)_2$

- (f) NaNO_2
- (g) $(\text{NH}_4)_2\text{SO}_4$
- (h) KMnO_4
- (i) K_2CrO_4
- (j) K_2PtF_6

(a) sodium sulphate (IV)

(b) potassium chlorate (V)

(c) sodium chlorate (I)

(d) copper (II) carbonate

(e) magnesium nitrate

(a) sodium nitrate (III)

(b) ammonium sulphate

(c) potassium manganate (VIII)

(d) potassium chromate (VI)

(e) potassium hexafluoroplatinate (IV)

Note: the oxidation number not been used with the cation unless it is a d-block metal and has a number of stable oxidation numbers

Note: the oxidation number has been omitted with very common anions (eg sulphate, nitrate, carbonate) but is always used with less common anions or if the oxidation number is not the most common one (eg sulphate (IV) and nitrate (III))

Lesson 3 – What are half-equations and how can we construct them?

(iv) Half-equations

- Oxidation and reduction half-equations involving simple ions and elements only can be written simply by writing the number of electrons gained (on the left-hand side) or lost (on the right-hand side):

Eg Na to Na^+ : Na becomes Na^+ by losing an electron, so $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$

Eg O_2 to O^{2-} : O_2 becomes 2O^{2-} when both O atoms gain two electrons each, so $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$

Eg Sn^{2+} to Sn^{4+} : Sn^{2+} becomes Sn^{4+} by losing two electrons, so $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$

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- Oxidation and reduction processes involving polyatomic ions or molecules and the half-equations for these processes are more complex (eg PbO_2 to Pb^{2+} , or SO_3^{2-} to SO_4^{2-}); there are two ways to deduce these half-equations:

Method 1: (this shows you straight away whether oxidation or reduction is taking place)

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)
- insert the number of electrons being gained or lost (on the left if reduction, on the right if oxidation)
No of electrons gained/lost = change in oxidation number x number of atoms changing oxidation number
- balance O atoms by adding H_2O
- balance H atoms by adding H^+

Example: Write a balanced half-equation for the process $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$

- the oxidation number of S is increasing from +4 to +6, so S is being oxidised
- there is one S on each side, so the S is already balanced
- the S is losing two electrons, so two electrons are required on the right:

$$\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2\text{e}^-$$
- there are three O atoms on the left and four on the right, so one water is needed on the left:

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{e}^-$$
- there are two H atoms on the left and none on the right, so two H ions are needed on the right:

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$$

Method 2: (this does not use oxidation numbers and is easier in more complex processes)

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)
- balance O atoms by adding water
- balance H atoms by adding H^+
- add the necessary number of electrons to ensure the charge on both sides is the same

Example: Write a balanced half-equation for the process $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}$

- S is being reduced; there is one sulphur on each side, so the S is already balanced
- there are four O atoms on the left and none on the right, so four waters are needed on the right:

$$\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$$
- there are two H atoms on the left and ten on the right, so eight H ions are needed on the left:

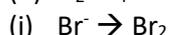
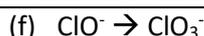
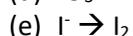
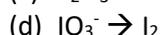
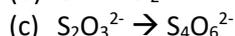
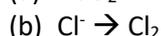
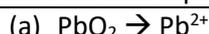
$$\text{H}_2\text{SO}_4 + 8\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$$
- the total charge on the left is +8 and on the right is 0, so eight electrons must be added to the left to balance the charge:

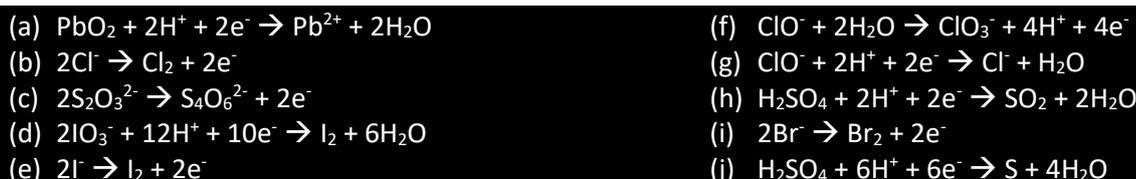
$$\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$$



Test your knowledge 3.1: Writing half-equations

Deduce the half-equations for the following processes, and state whether oxidation or reduction is taking place:





Lesson 4 – What are redox reactions, and what are oxidising and reducing agents?

b) Redox reactions

- Half-equations consider gain and loss of electrons, but in fact electrons cannot be created or destroyed; they can only be transferred from species to species; the gain of electrons by one species necessarily involves loss of electrons by another; oxidation and reduction thus always occur simultaneously; an oxidation is always accompanied by a reduction and vice versa; any reaction consisting of the oxidation of one species and the reduction of another is known as a **redox** reaction
- A redox reaction can be described as a reaction which involves the **transfer of electrons from one species to another**

(i) Deriving equations for redox reactions

- A redox reaction can be derived by combining an oxidation half-equation with a reduction half-equation in such a way that the total number of electrons gained is equal to the total number of electrons lost; in some cases, H_2O and H^+ may appear on both sides of the reaction, which must then be simplified

Eg $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$ (reduction) and $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ (oxidation)

- the oxidation half-equation must be multiplied by 4 to equate the electrons: $8\text{I}^- \rightarrow 4\text{I}_2 + 8\text{e}^-$
- the two half-equations can then be added together:
- $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{I}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} + 4\text{I}_2$ - redox**

Eg $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$ (reduction) and $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$ (oxidation)

- the number of electrons is the same in both half-equations so multiplying one of them is not required
- adding the two half-equations together gives $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+$
- removing 2H^+ and H_2O from both sides gives:
- $\text{PbO}_2 + 2\text{H}^+ + \text{SO}_3^{2-} \rightarrow \text{Pb}^{2+} + \text{H}_2\text{O} + \text{SO}_4^{2-}$**



Test your knowledge 4.1: Writing equations for redox reactions

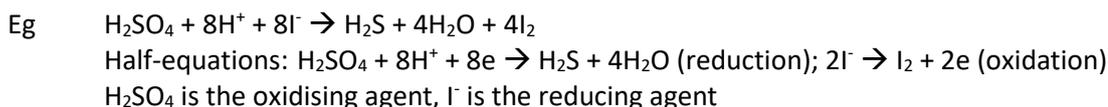
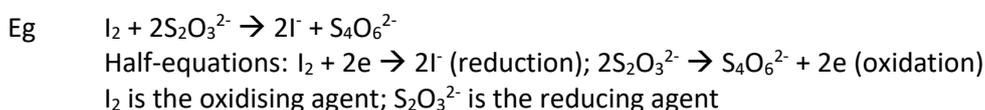
Use your half-equations from test your knowledge 3.1 to write balanced equations for the following reactions:

- | | |
|--|--|
| (a) PbO_2 with Cl^- to make Pb^{2+} and Cl_2 | (e) ClO^- to make ClO_3^- and Cl^- |
| (b) Al^{3+} and 2O^{2-} to make O_2 and Al | (f) H_2SO_4 with Br^- to make SO_2 and Br_2 |
| (c) $\text{S}_2\text{O}_3^{2-}$ with I_2 to make $\text{S}_4\text{O}_6^{2-}$ and I^- | (g) ClO^- with I^- to make Cl^- and I_2 |
| (d) IO_3^- with I^- to make I_2 | (h) H_2SO_4 with I^- to make S and I_2 |
-
- | | |
|--|--|
| (a) $\text{PbO}_2 + 4\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Pb}^{2+} + \text{Cl}_2 + 2\text{H}_2\text{O}$ | (e) $3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$ |
| (b) $4\text{Al}^{3+} + 6\text{O}^{2-} \rightarrow 3\text{O}_2 + 4\text{Al}$ | (f) $\text{H}_2\text{SO}_4 + 2\text{Br}^- + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}$ |
| (c) $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ | (g) $\text{H}_2\text{SO}_4 + 6\text{H}^+ + 6\text{I}^- \rightarrow 3\text{I}_2 + \text{S} + 4\text{H}_2\text{O}$ |
| (d) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ | (h) $\text{ClO}^- + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}$ |

UNIT 6 – REDOX REACTIONS

(ii) Oxidising agents and reducing agents

- The species which is reduced is accepting electrons from the other species and thus causing it to be oxidised; the reduced species is therefore an **oxidising agent**; an oxidising agent is an **electron acceptor**; it causes the oxidation number of the other species to increase
 - H_2SO_4 , Al^{3+} and Cl_2 are all oxidising agents
- The species which is oxidised is donating electrons to another species and thus causing it to be reduced; it is therefore a **reducing agent**; a reducing agent is an electron donor; it causes the oxidation number of the other species to decrease
 - Na , O^{2-} , I^- and $\text{S}_2\text{O}_3^{2-}$ are all reducing agents
- Using the addition/removal of hydrogen/oxygen definition of oxidation and reduction, an oxidising agent can be described as a species which adds oxygen or removes hydrogen from another species; a reducing agent can be described as a species which adds hydrogen to or removes oxygen from another species
- A redox reaction can thus be described as a transfer of electrons from a reducing agent to an oxidising agent



Test your knowledge 4.2: Identifying oxidising and reducing agents in redox reactions

Identify the reducing agents and the oxidising agents in the equations in Test your knowledge 4.1

- | | |
|---|--|
| (a) oxidising agent is PbO_2 ; reducing agent is Cl^- | (e) oxidising agent is ClO^- ; reducing agent is ClO^- |
| (b) oxidising agent is Al^{3+} ; reducing agent is O^{2-} | (f) oxidising agent is H_2SO_4 ; reducing agent is Br^- |
| (c) oxidising agent is I_2 ; reducing agent is $\text{S}_2\text{O}_3^{2-}$ | (g) oxidising agent is H_2SO_4 ; reducing agent is I^- |
| (d) oxidising agent is IO_3^- ; reducing agent is I^- | (h) oxidising agent is ClO^- ; reducing agent is I^- |

Lesson 5 – What are the some common examples of redox reactions?

c) Examples of Common Redox Reactions

(i) Reaction of Metals with Acids

- Most metals react with acids to make a salt and hydrogen
Eg $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$ (salt = magnesium chloride)
 $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$ (salt = zinc sulphate)

UNIT 6 – REDOX REACTIONS

- This reaction is an example of a **redox** reaction:
The metal is oxidised from 0 to +2 (in the above reactions): $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ or $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
The H^+ ion in the acid is reduced from +1 to 0 (in hydrogen): $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
The overall equation can therefore be written: $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$ or $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$
The chloride and sulphate ions are not part of the reaction and can be omitted from the equation
- Salts are often prepared using neutralisations (see Unit 5 – Acids, Bases and Salts), but metal-acid reactions can also be a useful way of preparing salts:



Practical 5.1: Prepare a sample of zinc sulphate from zinc and sulphuric acid

- Measure out 20 cm³ of 0.5 moldm⁻³ sulphuric acid into a 100 cm³ beaker.
- Warm the beaker gently on a tripod until the temperature reaches 50 °C.
- Add 1 g of zinc granules gradually to the beaker over a period of 2 minutes, stirring gently.
- Heat gently for a few minutes.
- Allow the mixture to cool.
- Place a folded piece of filter paper inside a filter funnel, and then place the funnel into the neck of a 250 cm³ conical flask.
- Pour the warm mixture into the filter funnel and allow the solution to filter through. A colourless solution should collect in the conical flask.
- Rinse the beaker and then pour the colourless solution back into it.
- Heat the mixture gently until 80% of the water has evaporated.
- Label the beaker with your name and leave it for a week.
- Use a spatula to remove any crystals in the beaker and dry them with a piece of filter paper.

How many moles of sulphuric acid (H₂SO₄) are used in the reaction?

How many moles of zinc (Zn) are used in the reaction?

Why is it important that the Zn is in excess?

Cannot do this practical: watch it at <https://www.youtube.com/watch?v=uwbJcDO3vCM>

Equipment needed per group: 100 cm³ beaker, tripod, gauze, Bunsen burner, thermometer, 20 cm³ of 0.5 moldm⁻³ H₂SO₄, 1 g zinc granules, 2 pieces filter paper, funnel, spatula, 100 cm³ conical flask, label, access to of 0.5 moldm⁻³ H₂SO₄ (20 cm³ per group), access to zinc granules (1 g per group), weighing boat, mass balance

Make sure students do not overheat the mixture

- Moles of H₂SO₄ = 20/1000 x 0.5 = 0.01
- Moles of Zn = 1/65.4 = 0.015
- Excess zinc can be easily removed by filtration; excess H₂SO₄ cannot easily be removed

(ii) Reaction of Metals with Water and Bases

- Water also contains H⁺, although in smaller concentrations than acids; some very reactive metals can react with the H⁺ in water:
Eg $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$
- In the above reaction the Na is oxidised from 0 to +1 and the H is reduced from +1 to 0
- Bases contain even lower concentrations of H⁺ than water, but if the metal forms an amphoteric oxide (such as Al, Zn or Pb), the OH⁻ can form a stable oxoanion:
Eg $\text{Al} + 3\text{NaOH} \rightarrow \text{Na}_3\text{AlO}_3 + 1.5\text{H}_2$
- Just as with acids and water, the metal is oxidised from 0 to (in this case) +3 and the H is reduced from +1 to 0; this is therefore another example of a redox reaction

UNIT 6 – REDOX REACTIONS

(iii) Metal Displacement Reactions

- Metals will displace any less reactive metal from a solution of its salt:
Eg $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$
 - the more reactive metal (eg Zn) is oxidised from 0 to (in this case) +2 ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$)
 - the less reactive metal (eg Cu) is reduced from (in this case) +2 to 0 ($\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$)
 - the sulphate ion is not directly involved in the reaction
 - the simplified chemical equation can therefore be written: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
 - this is therefore another example of a redox reaction

(iv) Formation and Reduction of Metallic Oxides

- Most metals react directly with oxygen to produce oxides:
Eg $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$
 $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$
 - during these reactions, the metal is oxidised from 0 to its typical oxidation state:
eg $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$, or $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$
 - the oxygen is reduced from 0 to -2
 - the reaction of metals with oxygen to form oxides is an example of a redox reaction
- Many metals are found in nature (ie in their ores) as metallic oxides; during their extraction from their ores, they have to be converted from the metal oxide to the metal, usually by reacting them with a more reactive element:
Eg $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
 $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$
 $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$
 - in all of these reactions, the metal in the oxide is reduced from +2 or +3 to 0
 - the more reactive element is oxidised (H from 0 to +1, C from 0 to +2 or +4, Al from 0 to +3)
 - the reduction of metal oxides is therefore an example of a redox reaction



Test your knowledge 5.2: Analysing common redox reactions

Write balanced symbol equations (with or without spectator ions) for the following redox reactions; in each case, state which atom is oxidised and which atom is reduced by writing r (for reduced) or o (for oxidised) under the atom in the equation:

- Zinc with hydrochloric acid to form zinc (II) chloride
- Aluminium with nitric acid
- Zinc (II) sulphate with magnesium
- Copper with silver (I) nitrate to form copper (II) nitrate
- Silver with oxygen to form silver (I) oxide
- Iron (III) oxide with carbon monoxide to form iron and carbon dioxide
- Titanium (IV) chloride with magnesium to form titanium and magnesium chloride

- $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$ or $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$ (o = Zn; r = H)
- $2\text{Al} + 6\text{HNO}_3 \rightarrow 2\text{Al}(\text{NO}_3)_3 + 3\text{H}_2$ or $2\text{Al} + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2$ (o = Al; r = H)
- $\text{ZnSO}_4 + \text{Mg} \rightarrow \text{MgSO}_4 + \text{Zn}$ or $\text{Zn}^{2+} + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{Zn}$ (o = Mg; r = Zn)
- $2\text{AgNO}_3 + \text{Cu} \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$ or $2\text{Ag}^+ + \text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{Ag}$ (o = Cu; r = Ag)
- $4\text{Ag} + \text{O}_2 \rightarrow 2\text{Ag}_2\text{O}$ (o = Ag; r = O)
- $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ (o = C; r = Fe)
- $\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2$ (o = Mg; r = Ti)

Lesson 6 – How can we identify oxidising and reducing agents?

d) Qualitative Analysis Part 2 – redox reactions

**Summary Activity 6.1: What can you remember about qualitative analysis?**

- What is meant by the term “qualitative analysis”?
 - How can you test for carbonate ions (CO_3^{2-}) and sulphate (IV) ions (SO_3^{2-}) in a solid sample?
 - How can you test for ammonium ions in aqueous solution?
 - How can you test for hydrogen ions (H^+) and hydroxide ions (OH^-) in aqueous solution?
 - How can you test for the gases CO_2 , SO_2 , NH_3 and HCl ?
- Identification of ions or molecules by simple tests
 - CO_3^{2-} : add HCl (aq) and observe fizzing, or add CaCl_2 (aq) and observe white precipitate, then add HCl (aq) and observe fizzing as the precipitate dissolves; gas should be odourless
 - SO_3^{2-} : add HCl (aq) and observe fizzing, or add CaCl_2 (aq) and observe white precipitate, then add HCl (aq) and observe fizzing as the precipitate dissolves; gas should smell like burning matches
 - NH_4^+ : add NaOH (aq) and warm; pungent gas should be given off
 - H^+ : add CaCO_3 (s) and observe fizzing, or add blue litmus paper – it will turn red
 - OH^- : add NH_4Cl (aq) and warm; pungent gas should be given off or add red litmus paper – it will turn blue
 - CO_2 : turns limewater milky and then colourless; no smell
 - SO_2 : turns limewater milky and then colourless; smell of burning matches; will turn damp blue litmus paper red
 - NH_3 : pungent smell, will turn damp red litmus paper blue, will give white smoke with filter paper soaked in concentrated HCl
 - HCl : will turn damp blue litmus paper red, will give white smoke with filter paper soaked in concentrated NH_3

- Qualitative analysis is the experimental identification of a substance or of a particular species present in a substance; this can include cations, anions, gases or organic molecules
- Some cations, anions and gases can be identified using simple acid-base reactions (see Unit 5 – Acids, Bases and Salts); others can be identified using redox reactions:

(i) test for oxidising agents

- To determine whether something is an oxidising agent, you need to add a reducing agent and observe whether a reaction takes place; the easiest reducing agent to use is **potassium iodide (KI)**
 - the iodide ions are readily oxidised to iodine
 - the oxidation number of the I increases from -1 to 0 ($2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$)
 - Iodine (I_2) is a brown colour in solution
 - If a brown colour forms when KI is added to a solution, then that solution must contain an oxidising agent (something in that solution is oxidised); the presence of iodine can be confirmed by adding a small quantity of starch and observing an intense blue/black solution
 - Eg Fe^{3+} is an oxidising agent; it is readily reduced to Fe^{2+} by iodide ions: $2\text{Fe}^{2+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$; on addition of KI to a solution containing Fe^{3+} ions, a brown colour of iodine will appear; this brown colour will turn blue/black if starch is added

UNIT 6 – REDOX REACTIONS

- The **nitrate ion (NO₃⁻)** is a mild oxidising agent in aqueous solution; in dilute form it does not readily react with potassium iodide, but when heated with aluminium powder in alkaline conditions, it can be reduced to ammonia gas (NH₃) which has a pungent smell and turns red litmus paper blue:



- this is the test for nitrate ions

(ii) test for reducing agents

- To determine whether something is a reducing agent, you need to add an oxidising agent and observe whether a reaction takes place; the easiest oxidising agents to use are **acidified potassium dichromate (VI) (K₂Cr₂O₇)** or **acidified potassium manganate (VII) (KMnO₄)**
 - K₂Cr₂O₇ is an orange colour, but when it reacts with reducing agents in acidic conditions the Cr is reduced from +6 to +3 and the resulting solution is green; reducing agents will therefore turn an acidified solution of potassium dichromate from orange to green
 - KMnO₄ is a dark purple colour, but when it reacts with reducing agents in acidic conditions the Mn is reduced from +7 to +2 and the resulting solution is colourless; reducing agents will therefore decolorise an acidified solution of potassium manganate (VII)
 - Eg The sulphate (IV) ion (SO₃²⁻) in aqueous solution is a reducing agent; SO₃²⁻ can be oxidised to SO₄²⁻ (the S is oxidised from +4 to +6); SO₃²⁻ ions will turn acidified potassium dichromate from orange to green and will decolorise potassium manganate (VII)
- Acidified potassium dichromate (VI) paper is used as a confirmatory test for **sulphur dioxide** gas (SO₂):
 - SO₂ turns blue litmus red because it is acidic (but so does HCl)
 - SO₂ turns limewater milky and then colourless again (but so does CO₂)
 - SO₂ also turns dichromate paper green because it is a reducing agent (HCl and CO₂ do not do this because they are not reducing agents)

UNIT 6 – REDOX REACTIONS



Practical 6.2: Test for oxidising and reducing agents in solution

You are given four solutions: A, B, C and D; one of them contains nitrate ions (KNO_3), one of them contains SO_3^{2-} ions (Na_2SO_3), one contains Fe^{2+} ions (FeSO_4) and one contains Fe^{3+} ions ($\text{Fe}_2(\text{SO}_4)_3$); you are also given a solid sample of sodium sulphate (IV) (Na_2SO_3)

- 1) Measure out approximately 1 cm^3 of solution A into three different test tubes
- 2) Add approximately 1 cm^3 of acidified potassium dichromate (VI) to the first test tube; record your observations
- 3) Add approximately 1 cm^3 of acidified potassium manganate (VII) to the second test tube; record your observations
- 4) Add approximately 1 cm^3 of potassium iodide to the third test tube; record your observations
- 5) Repeat steps 1 – 4 using solutions B, C and D
- 6) Identify the solution which did not give a positive test for oxidising or reducing agents, and measure out approximately 2 cm^3 of the solution into a test tube
- 7) Add 3 cm^3 of 1 mol dm^{-3} NaOH and then add one spatula of aluminium powder
- 8) Heat the mixture gently; when a gas is given off, test it with damp red litmus paper
- 9) Place one spatula measure of Na_2SO_3 in a test tube and add approximately 1 cm^3 of HCl; test the gas evolved with dichromate paper

Which solution contains an oxidising agent (Fe^{3+})?

Which solutions contain a reducing agent (SO_3^{2-} or Fe^{2+})?

Which solution contains nitrate ions? How did you confirm this?

How can you confirm whether a gas is SO_2 ?

How can you confirm the presence of sulphate (IV) ions in a solid sample?

Can't do this experiment: watch these videos:

www.youtube.com/watch?v=fpG6XRg2gSU

www.youtube.com/watch?v=nRlabYLKvsQ

www.youtube.com/watch?v=r9iexLFfedY

Chemicals required per group: access to bottles of 0.05 mol dm^{-3} $\text{Fe}_2(\text{SO}_4)_3$ (labelled A), 0.1 mol dm^{-3} FeSO_4 (labelled B), 0.1 mol dm^{-3} KNO_3 (labelled C), 0.1 mol dm^{-3} Na_2SO_3 (labelled D), 1 mol dm^{-3} NaOH, 1 mol dm^{-3} HCl, 0.02 mol dm^{-3} $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 mol dm^{-3} H_2SO_4 , 0.02 mol dm^{-3} KMnO_4 in 1 mol dm^{-3} H_2SO_4 , each with its own dropping pipette (approx 3 cm^3 of each needed per group), access to pots of Na_2SO_3 and Al powder, each with a spatula (approx 1 g per group), access to red litmus paper, access to dichromate paper

Apparatus required per group: 12 test tubes, 1 test tube rack, Bunsen burner, tongs

- Solution A should give a brown colour with KI
- Solutions B and D should decolorise KMnO_4 and turn $\text{K}_2\text{Cr}_2\text{O}_7$ green
- Solution C should not give a positive test for the above but will give off a pungent gas when warmed with NaOH and Al; the gas should turn red litmus blue
- Na_2SO_3 should fizz on addition of HCl and the gas evolved should turn dichromate paper green



Test your knowledge 6.3: Describing qualitative analysis using redox reactions

- (a) Describe a test for nitrate ions in aqueous solution
- (b) State how you would distinguish between SO_3^{2-} and CO_3^{2-} in aqueous solution
- (c) State how you would distinguish between solid samples containing SO_3^{2-} and CO_3^{2-}
- (d) State how you would distinguish between SO_2 and CO_2
- (e) State how you would distinguish between Fe^{2+} and Fe^{3+} in aqueous solution

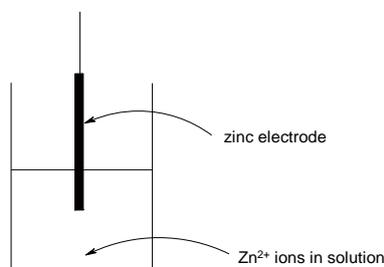
- (a) Warm with NaOH and Al powder; pungent-smelling gas should be evolved which turns red litmus blue
- (b) Add acidified KMnO_4 ; SO_3^{2-} will decolorise it but CO_3^{2-} will not OR add acidified $\text{K}_2\text{Cr}_2\text{O}_7$; SO_3^{2-} will turn it green it but CO_3^{2-} will not
- (c) Add HCl; SO_3^{2-} sample will evolve gas with burning-match smell which turns dichromate paper green; CO_3^{2-} sample will evolve odourless gas which has no effect on dichromate paper
- (d) SO_2 has burning-match smell and turns dichromate paper green; CO_2 is odourless and has no effect on dichromate paper
- (e) Fe^{2+} decolorises acidified KMnO_4 but does not react with KI; Fe^{3+} turns KI brown but has no effect on acidified KMnO_4

Lesson 7 – What is a Galvanic cell?

e) Galvanic Cells

(i) Electrode potentials

- Consider a zinc rod immersed in a solution containing Zn^{2+} ions (eg ZnSO_4):



- the Zn atoms on the rod can deposit two electrons on the rod and move into solution as Zn^{2+} ions:

$$\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \text{ (oxidation)}$$
- this process would result in an accumulation of negative charge on the zinc rod
- alternatively, the Zn^{2+} ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms:

$$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)} \text{ (reduction)}$$
- this process would result in an accumulation of positive charge on the zinc rod
- in both cases, a potential difference is set up between the rod and the solution; this is known as an **electrode potential**
- a similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg CuSO_4), due to the following processes:

$$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)} \text{ (reduction - rod becomes positively charged)}$$

$$\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \text{ (oxidation - rod becomes negatively charged)}$$
- no chemical reaction is actually taking place in these situations – there is nowhere for the electrons to go and as soon as the potential difference is established, equilibrium is reached
- the potential difference will depend on the nature of the ions in solution, the concentration of the ions in solution, the type of electrode used and the temperature

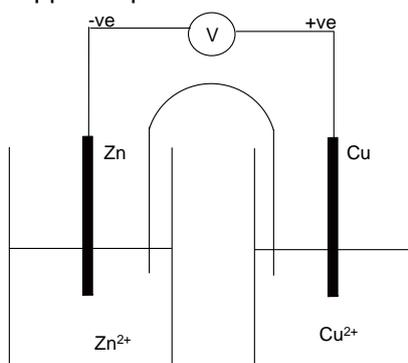
UNIT 6 – REDOX REACTIONS

(ii) Creating an Electromotive Force (emf)

- If two different electrodes are connected, the potential difference between the two electrodes will cause a current to flow between them; thus an **electromotive force (emf)** is established and the system can generate electrical energy
- The circuit must be completed by allowing ions to flow from one solution to the other; this is achieved by means of a **salt bridge** - often a piece of filter paper saturated with a solution of an inert electrolyte such as $\text{KNO}_3(\text{aq})$
- The combination of two electrodes in this way is known as a **Galvanic cell**; this is how chemical reactions can be used to generate electricity; the two components which make up the cell are known as half-cells
- The emf can be measured using a **voltmeter**; voltmeters have a high resistance so that they do not divert much current from the main circuit; voltmeters measure potential on the right-hand side of the cell and subtract the potential on the left-hand side of the cell to give the reading:

$$\text{potential difference} = E_{\text{RHS}} - E_{\text{LHS}}$$

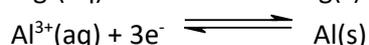
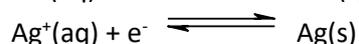
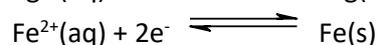
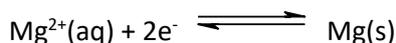
- A typical electrochemical cell can be made by combining a zinc electrode in a solution of zinc sulphate with a copper electrode in a solution of copper sulphate.



- at the positive electrode, a reduction half-reaction will take place; in this case it is the copper electrode:
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$
 - at the negative electrode an oxidation half-reaction will take place; in this case it is the zinc electrode:
 $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
 - the overall cell reaction is as follows:
 $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 - the sulphate ions flow through the salt bridge from the $\text{Cu}^{2+}(\text{aq})$ solution to the $\text{Zn}^{2+}(\text{aq})$ solution, to complete the circuit and compensate for the reduced Cu^{2+} concentration and increased Zn^{2+} concentration
 - the cell reaction including spectator ions can thus be written as follows:
 $\text{CuSO}_4(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{ZnSO}_4(\text{aq})$
 - the external connection must be made of a metallic wire in order to allow electrons to flow
 - the salt bridge must be made of an aqueous electrolyte to allow ions to flow
- By allowing two chemical reagents to be connected electrically, but not chemically, a reaction can only take place if the electrons flow externally; the chemical energy is thus converted into electrical energy

UNIT 6 – REDOX REACTIONS

- The **magnitude** of the potential difference (or emf) is a measure of how much energy can be obtained from the cell; in the above case, 1 mol dm⁻³ solutions of both CuSO₄(aq) and ZnSO₄(aq) will generate an emf of 1.10 V at 25 °C
- The **sign** of the potential difference (or emf) shows the direction of the reaction:
 - reduction takes place at the more positive electrode and oxidation takes place at the more negative electrode
 - if the voltmeter reading is positive, it means that the more positive electrode is on the right-hand side and reduction is therefore taking place on the right, with oxidation taking place on the left
 - if the voltmeter reading is negative, it means that the more positive electrode is on the right-hand side and reduction is therefore taking place on the right, with oxidation taking place on the left
 - In the above cell, oxidation is taking place on the left, so the emf of the cell will be positive
- Other possible metal-ion half reactions which could be used to set up electrochemical cells might include:



Practical 7.1: Build a simple electrochemical cell

- 1) Pour around 50 cm³ of 1 mol dm⁻³ CuSO₄ into a 100 cm³ beaker
- 2) Place a strip of copper in the beaker; the top of the strip should be out of the solution
- 3) Pour around 50 cm³ of 1 mol dm⁻³ ZnSO₄ into another 100 cm³ beaker
- 4) Place a strip of zinc in the beaker; the top of the strip should be out of the solution
- 5) Take a strip of filter paper, approximately 1 cm wide and 15 cm long; soak it in a saturated solution of potassium nitrate (wear disposable gloves when dealing with the KNO₃)
- 6) Place the strip of filter paper soaked in potassium nitrate, into both solutions simultaneously, so that one end of the strip is in one solution and the other end is in the other solution
- 7) Attach crocodile clips to the two electrodes
- 8) Use two wires to connect each set of crocodile clips to different sides of a voltmeter
- 9) Note the reading on the voltmeter

From the voltmeter reading, which is the positive electrode and which is the negative electrode?

What are the half-reactions taking place at each electrode?

Cannot do this practical?: watch this video: www.youtube.com/watch?v=afEX2FD4Ado

Equipment needed per group: 2 x 100 cm³ beakers, 1 copper strip, 1 zinc strip, 1 strip filter paper (1 x 15 cm), 2 crocodile clips, 2 electrical wires, 1 voltmeter, access to 1 mol dm⁻³ CuSO₄, 1 mol dm⁻³ ZnSO₄ (50 cm³ per group), saturated KNO₃ (10 cm³ per group), disposable gloves

The voltmeter should read around 1.1 V; either +1.1 V (if the Cu electrode is on the RHS) or -1.1 V (if the Cu electrode is on the left hand side; the Cu is the positive electrode

$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$; $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$


Test your knowledge 7.2: Understanding how Galvanic cells work

When a piece of magnesium is inserted into a 1 mol dm^{-3} solution of MgSO_4 , and a piece of zinc inserted into a 1 mol dm^{-3} solution of ZnSO_4 , and the two solutions are connected with a salt bridge, and the two electrodes connected to a voltmeter with the zinc electrode on the left-hand side, the voltmeter reading is -1.62 V .

- Identify the positive and the negative electrodes
- Deduce the half-reactions taking place at each electrode
- Deduce an equation for the overall cell reaction
- Deduce the direction in which electrons are moving through the wire
- Deduce the direction in which sulphate ions are moving through the salt bridge

- Voltmeter reading $-ve$ so positive electrode is on LHS, and is therefore the zinc electrode, so magnesium electrode is negative
- Zn electrode $+ve$ so reduction: $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$; Mg electrode $-ve$ so oxidation: $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$
- $\text{Zn}^{2+} + \text{Mg} \rightarrow \text{Zn} + \text{Mg}^{2+}$
- Electrons move from Mg (oxidised) to Zn (reduced)
- Sulphate ions move from Zn^{2+} (which is decreasing in concentration) to Mg^{2+} (which is increasing in concentration)

Lesson 8 – What are electrode potentials and how can we measure them?
(iii) Conventional Representation of Cells

- As it is cumbersome and time-consuming to draw out every electrochemical cell in full, a system of notation is used which describes the cell in full, but does not require it to be drawn
- Half-cells are written as follows:
 - the metal electrode is placed on one side of a vertical line.
 - the species in solution are placed together on the other side of the vertical line
 - Eg the $\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$ half-cell is represented as: $\text{Fe}^{2+} | \text{Fe}$
 - Eg the $\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$ half-cell is represented as: $\text{Zn}^{2+} | \text{Zn}$
- When two half-cells are connected to form a full electrochemical cell, the two half-cells are placed on either side of two vertical broken lines (which represent the salt bridge); the electrodes are placed on the far left and far right, and the metal ions are placed adjacent to the vertical broken lines in the centre:
 - Eg For a cell made from a $\text{Fe}^{2+} | \text{Fe}$ electrode and a $\text{Zn}^{2+} | \text{Zn}$ electrode, the representation would be:
 $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$
 - Eg For a cell made from a $\text{Cu}^{2+} | \text{Cu}$ electrode and a $\text{Ag}^+ | \text{Ag}$ electrode, the representation would be:
 $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$
- If the direction of the reaction is known, it is conventional to place the half-cell undergoing oxidation on the left and the half-cell undergoing reduction on the right


Test your knowledge 8.1: Using the Conventional Representation of Cells

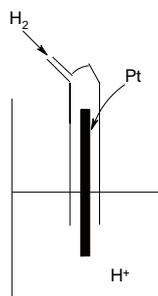
Draw the conventional representation of the Galvanic cells in which the following reactions are taking place:

- (a) $\text{Zn}^{2+} + \text{Mg} \rightarrow \text{Zn} + \text{Mg}^{2+}$
- (b) $\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Zn}^{2+} + \text{Fe}$
- (c) $2\text{Ag}^+ + \text{Zn} \rightarrow 2\text{Ag} + \text{Zn}^{2+}$
- (d) $2\text{Al} + 3\text{Pb}^{2+} \rightarrow 2\text{Al}^{3+} + 3\text{Pb}$
- (e) $3\text{Mg} + 2\text{Al}^{3+} \rightarrow 3\text{Mg}^{2+} + 2\text{Al}$

- (a) $\text{Mg} | \text{Mg}^{2+} || \text{Zn}^{2+} | \text{Zn}$
- (b) $\text{Zn} | \text{Zn}^{2+} || \text{Fe}^{2+} | \text{Fe}$
- (c) $\text{Zn} | \text{Zn}^{2+} || \text{Ag}^+ | \text{Ag}$
- (d) $\text{Al} | \text{Al}^{3+} || \text{Pb}^{2+} | \text{Pb}$
- (e) $\text{Mg} | \text{Mg}^{2+} || \text{Al}^{3+} | \text{Al}$

(iv) Measuring electrode potentials

- The emf of a Galvanic cell is easy to measure, but the individual electrode potentials themselves cannot actually be measured at all; it is only possible to measure the potential difference between two electrodes
- It is therefore only possible to assign an electrode potential value to a half-cell if one half-cell is arbitrarily allocated a value and all other electrodes are measured relative to it
- The electrode conventionally used for this purpose is the standard hydrogen electrode; it involves the half-reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$; because the half-reaction does not contain a metal, an inert platinum electrode is used:



- the gas pressure is fixed at 100 Kpa, the temperature is 25°C and the H^+ ions have a concentration of 1.0 mol dm^{-3} ; this electrode is arbitrarily assigned a value of 0.00 V and is represented as $\text{Pt} | \text{H}_2, 2\text{H}^+$
- Using this electrode, it is possible to assign an electrode potential to all other half-cells by connecting each half-cell to the standard hydrogen electrode and measuring the potential difference between the two electrodes; **potential difference = $E_{\text{RHS}} - E_{\text{LHS}}$**
- If the standard hydrogen electrode is placed on the left-hand side of the voltmeter, therefore, the E_{LHS} will be zero and the voltmeter reading will be the electrode potential of the right-hand electrode
 - Eg if the $\text{Zn} | \text{Zn}^{2+}$ half-cell is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the voltmeter reading is -0.76V; the $\text{Zn} | \text{Zn}^{2+}$ half-cell thus has an electrode potential of -0.76V
 - Eg if the $\text{Cu} | \text{Cu}^{2+}$ electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the voltmeter reading is +0.34V; the $\text{Cu} | \text{Cu}^{2+}$ half-cell thus has an electrode potential of +0.34V

UNIT 6 – REDOX REACTIONS

- The electrode potential of a half-reaction can be defined as follows: "**the electrode potential of a half-reaction is the voltmeter reading of a cell in which the left-hand electrode is the standard hydrogen electrode and the right-hand electrode is the electrode in question**".

(v) Standard electrode potentials

- The electrode potential depends on the conditions used, including temperature, pressure and concentration of reactants; it is therefore necessary to specify the conditions used when measuring electrode potentials; these conditions are normally set at a temperature of 298 K, a pressure of 100 kPa and with all species in solution having a concentration of 1.0 mol dm⁻³; electrode potentials measured under these conditions are known as **standard electrode potentials**; they are denoted by the symbol E^o
- Here are the standard electrode potentials of the most common metal-ion half-reactions:

Half-reaction	Conventional representation	E ^o /V
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Mg}(\text{s})$	Mg Mg ²⁺	-2.37
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Al}(\text{s})$	Al Al ³⁺	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$	Zn Zn ²⁺	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Fe}(\text{s})$	Fe Fe ²⁺	-0.44
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Pb}(\text{s})$	Pb Pb ²⁺	-0.13
$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$	Pt H ₂ , 2H ⁺	0.00 (by definition)
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	Cu Cu ²⁺	+0.34
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$	Ag Ag ⁺	+0.80

The standard electrode potential of a metal-ion half reaction is a very good indicator of the reactivity of a metal (ie its tendency to get oxidised); the more negative the electrode potential, the greater the tendency for oxidation to take place; the more positive the electrode potential, the greater the tendency for reduction to take place



Test your knowledge 8.2: Using standard electrode potentials

- Use the data on standard electrode potentials in the table above to deduce: (i) the conventional representation of the cell; (ii) the emf of the cell; (iii) the cell reaction, which takes place when each of the following half-cells are combined:
 - Cu|Cu²⁺ and Ag|Ag⁺
 - Pb|Pb²⁺ and Zn|Zn²⁺
 - Al|Al³⁺ and Fe|Fe²⁺
 - Mg|Mg²⁺ and Al|Al³⁺
 - Ag|Ag⁺ and Pb|Pb²⁺
- When an electrochemical cell is made using the Cu²⁺|Cu half-cell on the left-hand side and a V²⁺|V half-cell on the right-hand side, the reading on the voltmeter is -1.46 V
 - Deduce the chemical reaction taking place
 - Use the standard electrode potential of Cu²⁺|Cu given in the table above to deduce the standard electrode potential of the V²⁺|V half-cell

UNIT 6 – REDOX REACTIONS

- a) (i) $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$; $\text{emf} = +0.46 \text{ V}$; $2\text{Ag}^+ + \text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{Ag}$
(ii) $\text{Zn}|\text{Zn}^{2+}||\text{Pb}^{2+}|\text{Pb}$; $\text{emf} = +0.63 \text{ V}$; $\text{Pb}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Pb}$
(iii) $\text{Al}|\text{Al}^{3+}||\text{Fe}^{2+}|\text{Fe}$; $\text{emf} = +1.22 \text{ V}$; $3\text{Fe}^{2+} + 2\text{Al} \rightarrow 2\text{Al}^{3+} + 3\text{Fe}$
(iv) $\text{Mg}|\text{Mg}^{2+}||\text{Al}^{3+}|\text{Al}$; $\text{emf} = +0.71 \text{ V}$; $2\text{Al}^{3+} + 2\text{Mg} \rightarrow 2\text{Mg}^{2+} + 2\text{Al}$
(v) $\text{Pb}|\text{Pb}^{2+}||\text{Ag}^+|\text{Ag}$; $\text{emf} = +0.93 \text{ V}$; $2\text{Ag}^+ + \text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{Ag}$
- b) (i) emf -ve so oxidation on RHS so $\text{V} \rightarrow \text{V}^{2+} + 2\text{e}^-$, so $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$: $\text{Cu}^{2+} + \text{V} \rightarrow \text{V}^{2+} + \text{Cu}$
(ii) $\text{emf} = E_r - E_i$ so $-1.46 = \text{V}^{2+}|\text{V} - 0.34$ so $\text{V}^{2+}|\text{V} = -1.46 + 0.34 = -1.12 \text{ V}$

Lesson 9 – What are the different types of Galvanic cell?

(v) Primary and Secondary Cells

- Electrochemical cells are the basis for all batteries; most batteries contain one or cells in series; the sum of the emf values of the cells is the total emf of the battery
- Batteries only contain a fixed amount of energy, dependent on the quantity of reactants in each cell and the enthalpy change of the reaction; as the reaction takes place, the concentrations of reactants decrease, the emf of the cell decreases until eventually the emf of the cell falls to zero when the reaction is complete; when this happens, the battery is flat
- In some cells, the reactions taking place are irreversible, and once the reaction is complete the cell cannot be used again; these cells cannot be re-charged and are known as **primary** electrochemical cells; simple batteries for use in domestic appliances contain primary cells
- If the reaction in the cell is reversible, and the cell is connected to another power supply with a larger emf than the cell, electrons and ions can be forced around the circuit in the opposite direction; this reverses the spontaneous chemical reaction and hence recharges the cell, allowing it to be used again; re-chargeable cells are known as **secondary** electrochemical cells; car batteries contain secondary cells, which means that they can be re-charged

(vi) Examples of Electrochemical Cells

- The purpose of electrochemical cells is to generate electrical energy from chemical reactions
- Most redox reactions can be converted into an electrochemical cell, provided that a half-cell can be constructed for each half-reaction; the two half-cells must be kept chemically separate and connected internally only by a salt bridge; the electrodes are the terminals of the cell
- **The Daniell cell** was one of the first useful electrochemical cells to be invented
 - it consists of a $\text{Cu}|\text{Cu}^{2+}$ half-cell and a $\text{Zn}|\text{Zn}^{2+}$ half-cell
 - at the positive electrode, copper ions are reduced to copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
 - at the negative electrode, zinc is oxidised to zinc ions: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 - The overall cell reaction is as follows: $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 - this reaction is reversible in theory but its design at the time could not keep the Cu^{2+} and Zn^{2+} ions completely separated and so the original designs of the cell were primary (non-rechargeable)
 - the cell provides an emf of approximately 1 volt and was used in the development of the volt as a unit of energy per unit charge.

UNIT 6 – REDOX REACTIONS

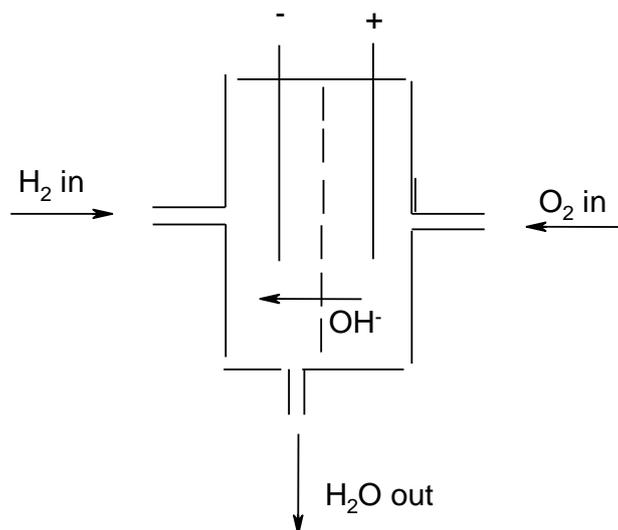
- The **Lead-Acid Battery** was the first type of secondary (rechargeable) cell to be invented
 - it is still used in cars and has several other applications, because it is able to withstand a high current flow for a short time
 - at the positive electrode, lead (IV) oxide is reduced to lead (II) sulphate:

$$\text{PbO}_2 + 2\text{H}^+ + \text{H}_2\text{SO}_4 + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$$
 - at the negative electrode, lead is oxidised to lead (II) sulphate:

$$\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^-$$
 - the overall cell reaction is: $\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$
 - when the cell is recharged, the reverse half-reactions take place at the two electrodes and so the overall reaction is also reversed

- **Dry cells** are cells in which the electrolyte is a paste, rather than a liquid; there is enough moisture to allow a current to flow but no more
 - the advantage of dry cells is that they can be used in any orientation without spilling
 - most modern batteries used in standard electrical appliances contain dry cells

- A **fuel cell** is a cell in which a chemical reaction between a fuel and oxygen is used to create an emf
 - the fuel and oxygen flow into the cell continuously and the products flow out of the cell
 - therefore the cell requires a continuous supply of fuel and oxygen, but does not need to be recharged
 - a fuel cell, like a regular electrochemical cell, consists of two half-cells connected by a semi-permeable membrane
 - an aqueous solution of sodium hydroxide is used as the electrolyte
 - oxygen is pumped into one of the half-cells: $\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$; this is the positive electrode (reduction is taking place)
 - fuel is pumped into the other half-cell
 - the most widely used fuel cell is the **hydrogen-oxygen fuel cell** in which hydrogen is the fuel: $\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$; this is the negative electrode (oxidation is taking place); the overall cell reaction is $\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$; hydroxide ions are generated in the oxygen half-cell and travel through the membrane into the hydrogen half-cell, where they are used up; water is the product of the reaction and it is allowed to run off:



- any fuel could be used as an alternative to hydrogen
- fuel cells are more efficient (typically around 50%) than combustion engines (typically around 20%)



Test your knowledge 9.1: Understanding Applications of Galvanic Cells

- (a) Explain the difference between a primary and a secondary Galvanic cell and give one example of each
- (b) Give two reasons why the lead-acid battery is useful
- (c) Explain what is meant by a dry cell and explain the advantage of dry cells
- (d) Explain what is meant by a fuel cell and explain their main advantage over combustion engines

- (a) A primary cell is non-rechargeable (eg most typical batteries); a secondary cell is rechargeable (eg a lead-acid battery)
- (b) It is rechargeable and can withstand a large current for a short time
- (c) The electrolyte is in the form of a paste rather than a liquid or solution; they can be turned around and used in any orientation
- (d) Reaction between fuel and oxygen; fuel is constantly entering the cell at one electrode and oxygen at the other; the products leave the electrode as they are made; they are more efficient than combustion engines

Lesson 10 – What is electrolysis?

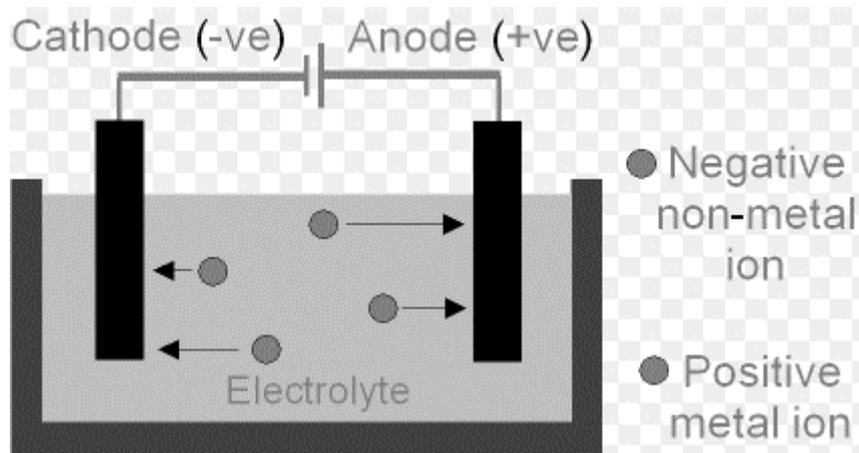
f) Electrolysis

(i) Principles of Electrolysis

- Electrolysis is the use of an electric current to force a chemical reaction to take place which would not otherwise happen spontaneously
- If two electrodes are dipped into an electrolyte and a potential difference is applied across the electrodes, the anions in the solution will move towards the positively charged electrode (known as the anode) and the cations in the solution will move towards the negatively charged electrode (known as the cathode)
- Electrolysis can be used to separate the components of any liquid provided it contains electrolytes; it is most commonly used to separate ionic compounds into their elements
- Once the anions reach the anode, they are oxidised, usually to a non-metallic element (O^{2-} and OH^- ions are oxidised to O_2 , Cl^- ions are oxidised to Cl_2)
- Once the cations reach the cathode, they are reduced, usually to an element (Cu^{2+} ions are reduced to Cu and H^+ ions are reduced to H_2)
- In most cases graphite electrodes are used, as they are cheap and relatively inert; if it is likely that graphite will cause a reaction of its own, platinum electrodes are used (these are more expensive)

UNIT 6 – REDOX REACTIONS

- The apparatus in which electrolysis takes place is called an **electrolytic cell**; electrolytic cells are used to convert electrical energy into chemical energy; this is the opposite of a Galvanic cell, in which chemical energy is converted into electrical energy; an example of an electrolytic cell is shown below:



- If an electrolyte contains more than one type of cation, and/or more than one type of anion, then the electrode reactions will take place one at a time:
 - if there is more than one anion, then whichever anion is more easily oxidised will be oxidised first; this will be the anion in the half-reaction with the more negative electrode potential; consider, for example, a mixture of chloride and iodide ions:
$$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^- \quad E = +0.54 \text{ V}$$
$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad E = +1.36 \text{ V}$$
In this case, the iodide ion would be oxidised before the chloride ion and iodine would be produced at the anode before chlorine
 - If there is more than one cation, then whichever cation is more easily reduced will be reduced first. This will be the cation in the half-reaction with the more positive electrode potential; consider, for example, a mixture of copper (II) ions and hydrogen ions:
$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E = +0.00 \text{ V}$$
$$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad E = +0.34 \text{ V}$$
In this case, the copper ion would be reduced before the hydrogen ion and copper would be produced at the cathode before hydrogen

(ii) Examples of electrolysis

- Molten lead (II) bromide** contains Pb^{2+} and Br^- ions
 - during electrolysis, the Pb^{2+} ions move to the cathode where they are reduced, and Br^- ions move to the anode where they are oxidised
 - Lead is produced at the cathode: $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$
 - Bromine is produced at the anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
 - Lead (II) bromide has a low melting point, making this reaction easy to demonstrate
- Molten sodium chloride** contains Na^+ and Cl^- ions
 - During **electrolysis**, the Na^+ ions move to the cathode where they are reduced, and the Cl^- ions move to the anode where they are oxidised
 - Sodium is produced at the cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
 - chlorine is produced at the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - this is the reaction used in the industrial preparation of sodium

UNIT 6 – REDOX REACTIONS

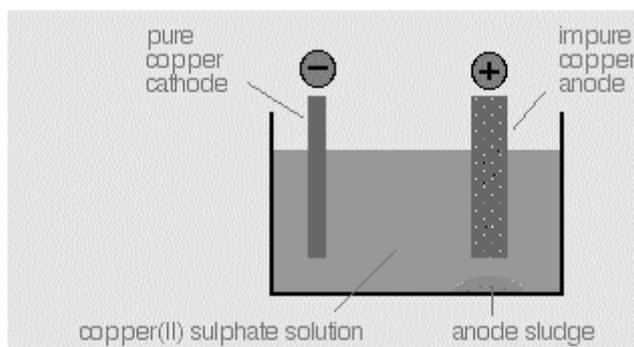
- **Molten aluminium oxide** contains Al^{3+} and O^{2-} ions
 - During electrolysis, the Al^{3+} ions move to the cathode where they are reduced, and the O^{2-} ions move to the anode where they are oxidised
 - aluminium is produced at the cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
 - oxygen is produced at the anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$
 - this is the reaction used in the industrial preparation of aluminium and is often known as the **smelting of aluminium**
- **Aqueous sodium chloride (dilute)** contains Na^+ and Cl^- ions, but it also contains water, which contains H^+ and OH^- ions
 - the $\text{Pt}|\text{H}_2, 2\text{H}^+$ electrode potential is much more positive than the $\text{Na}|\text{Na}^+$ electrode potential, so H^+ ions in H_2O are reduced at the cathode and hydrogen gas is produced: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
 - the $\text{Pt}|\text{O}_2, 2\text{OH}^-$ electrode potential is more negative than the $\text{Pt}|\text{Cl}_2, 2\text{Cl}^-$ electrode potential, so OH^- ions are oxidised at the anode and oxygen gas is produced: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$
 - the overall reaction is: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, so effectively water is separated into H_2 and O_2 during this electrolysis; the sodium and chloride ions remain in the solution, which becomes gradually more concentrated
- **Aqueous sodium chloride (concentrated)** contains Na^+ and Cl^- ions, but it also contains water, which contains H^+ and OH^- ions
 - As with dilute sodium chloride, the $\text{Pt}|\text{H}_2, 2\text{H}^+$ electrode potential is much more positive than the $\text{Na}|\text{Na}^+$ electrode potential, so H^+ ions in H_2O are reduced at the cathode and hydrogen gas is produced: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
 - although the $\text{Pt}|\text{O}_2, 2\text{OH}^-$ standard electrode potential is more negative than the $\text{Pt}|\text{Cl}_2, 2\text{Cl}^-$ standard electrode potential, the very high concentration of Cl^- ions make the $\text{Pt}|\text{Cl}_2, 2\text{Cl}^-$ electrode potential more positive than in dilute sodium chloride in this solution, and as a result Cl^- , and not OH^- ions, are oxidised and chlorine gas and not oxygen gas is produced: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - the overall reaction is therefore: $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{NaOH}$, so the solution gradually turns into sodium hydroxide
 - this is the method used in the industrial preparation of sodium hydroxide
- **Aqueous potassium iodide** contains K^+ and I^- ions, but it also contains water, which contains H^+ and OH^- ions
 - As with concentrated sodium chloride, the $\text{Pt}|\text{H}_2, 2\text{H}^+$ electrode potential is much more positive than the $\text{K}|\text{K}^+$ electrode potential, so H^+ ions in H_2O are reduced at the cathode and hydrogen gas is produced: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
 - although the $\text{Pt}|\text{I}_2, 2\text{I}^-$ standard electrode potential is more negative than the $\text{Pt}|\text{O}_2, 2\text{OH}^-$ standard electrode potential, so I^- ions are oxidised and iodine is produced: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
 - the overall reaction is therefore: $2\text{KI} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{I}_2 + 2\text{KOH}$, so the solution gradually turns into potassium hydroxide
- **Dilute sulphuric acid** contains H^+ and SO_4^{2-} ions, but it also contains water, which contains H^+ and OH^- ions
 - H^+ is the only cation in the solution; it is reduced at the cathode and hydrogen gas is formed:
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 - SO_4^{2-} ions are very difficult to oxidise at the anode, so OH^- ions in H_2O are oxidised at the anode and oxygen gas is formed: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - the overall reaction is: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, so just as with dilute sodium chloride, this reaction is effectively the electrolysis of water; the sulphuric acid solution becomes gradually more concentrated

UNIT 6 – REDOX REACTIONS

- **Dilute sodium hydroxide** contains Na^+ and OH^- ions, but it also contains water, which contains H^+ and OH^- ions
 - H^+ ions are easier to reduce than Na^+ ions, so H^+ is reduced at the cathode and hydrogen gas is formed:
$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$
 - OH^- ions are the only anions present, so OH^- ions are oxidised at the anode and oxygen gas is formed: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - the overall reaction is: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, so just as with dilute sodium chloride and dilute sulphuric acid, this reaction is effectively the electrolysis of water; the sodium hydroxide solution becomes gradually more concentrated
- **Copper chloride solution** contains Cu^{2+} and Cl^- ions, but it also contains water, which contains H^+ and OH^- ions
 - The $\text{Cu}|\text{Cu}^{2+}$ electrode potential is more positive than the $\text{Pt}|\text{H}_2, 2\text{H}^+$ electrode potential, so Cu^{2+} ions are reduced at the cathode and copper is produced: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - although the $\text{Pt}|\text{O}_2, 2\text{OH}^-$ standard electrode potential is more negative than the $\text{Pt}|\text{Cl}_2, 2\text{Cl}^-$ standard electrode potential, the very high concentration of Cl^- ions make the $\text{Pt}|\text{Cl}_2, 2\text{Cl}^-$ electrode potential more positive than in dilute sodium chloride in this solution, and as a result Cl^- , and not OH^- ions, are oxidised and chlorine gas and not oxygen gas is produced: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - the overall reaction is $\text{CuCl}_2 \rightarrow \text{Cu} + \text{Cl}_2$
- **Copper sulphate solution** contains Cu^{2+} and SO_4^{2-} ions, but it also contains water, which contains H^+ and OH^- ions
 - The $\text{Cu}|\text{Cu}^{2+}$ electrode potential is more positive than the $\text{Pt}|\text{H}_2, 2\text{H}^+$ electrode potential, so Cu^{2+} ions are reduced at the cathode and copper is produced: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - SO_4^{2-} ions are difficult to oxidise, so OH^- ions are oxidised at the anode and oxygen gas is produced: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$
 - the overall reaction is $2\text{CuSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + \text{O}_2 + 2\text{H}_2\text{SO}_4$, so the solution gradually turns into sulphuric acid

Copper sulphate solution can also be electrolysed **using copper electrodes** instead of graphite electrodes

- in this case, a different reaction takes place at the anode; the $\text{Cu}|\text{Cu}^{2+}$ electrode potential is more negative than the $\text{Pt}|\text{O}_2, 2\text{OH}^-$ electrode potential, so copper is oxidised at the anode and copper ions are produced: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
- the cathode reaction is not affected: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- this reaction is used in the purification of copper; the anode is made of impure copper, and it gradually dissolves during the reaction; pure copper is collected at the cathode:



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Test your knowledge 10.1: Describing electrolysis

- (a) Write half-equations for the reactions taking place at the cathode and anode, and write the overall equation for the reaction occurring, during the electrolysis of:
- molten sodium chloride
 - molten aluminium oxide
 - concentrated aqueous sodium chloride
 - dilute sulphuric acid
 - aqueous copper sulphate using graphite electrodes
- (b) Write half-equations for the reactions taking place at the cathode and anode during the electrolysis of aqueous copper sulphate using copper electrodes, and explain why this reaction is useful

- (a) (i) cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$; anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$; overall: $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$
 (ii) cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$; anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$; overall: $2\text{Al}_2\text{O}_3 \rightarrow 4\text{Al} + 3\text{O}_2$
 (iii) cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$; anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$; overall: $2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{OH}^-$
 (iv) cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$; anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$; overall: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$
 (v) cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$; anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$; overall: $2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + \text{O}_2 + 4\text{H}^+$
 (b) cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$; anode: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$; used in purification of copper


Demonstration 10.2: Electrolyse aqueous solutions

- Pour 50 cm^3 of 1 mol dm^{-3} NaOH into a 100 cm^3 beaker
- Place two graphite electrodes into the beaker
- Using wires and crocodile clips, connect both electrodes to opposite terminals of a 12V power supply
- Turn on the power; set it initially at around 6 V
- Observe what happens at the two electrodes
- Repeat steps 1 – 5 using 1 mol dm^{-3} CuCl_2 instead of NaOH
- Repeat steps 1 – 5 using 1 mol dm^{-3} KI instead of NaOH

What do you observe at each electrode during the electrolysis?

What is being produced at each electrode?

Can you write equations for the three reactions taking place?

Equipment needed: one power pack able to produce a variable power supply up to 12 V, two electrical wires, two crocodile clips, two graphite electrodes, preferably with a support to keep them parallel, three 100 cm^3 beakers, access to 1 mol dm^{-3} solutions of NaOH, CuCl_2 and KI

- Electrolysis of NaOH: bubbles at both electrodes, more concentrated at cathode; gases could be collected and confirmed as H_2 at cathode (burns with a squeaky pop) and O_2 at anode (relights glowing splint); $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$
- Electrolysis of CuCl_2 : bubbles at anode, layer of copper at cathode; gas at anode should bleach litmus paper; $\text{CuCl}_2 \rightarrow \text{Cu} + \text{Cl}_2$
- Electrolysis of KI: bubbles at cathode, brown solution of I_2 at anode; gas at cathode could be collected and confirmed as H_2 (burns with a squeaky pop); solution should turn red litmus blue as NaOH is being formed; $2\text{KI} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{I}_2 + 2\text{KOH}$

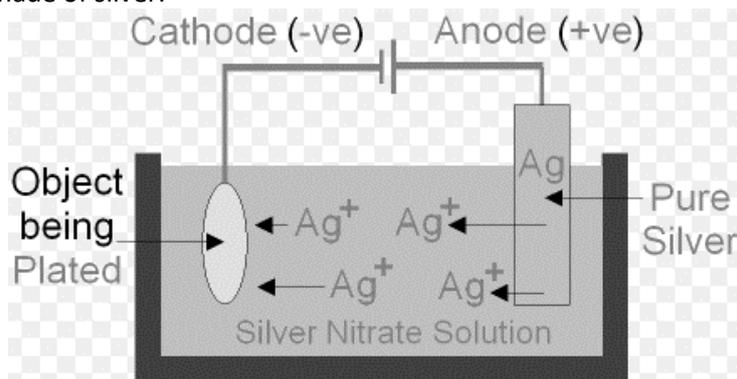
Note: the tests for hydrogen, oxygen and chlorine gases are covered in Unit 12 – Non-metals and their compounds

Cannot do this demonstration? Watch it here: www.youtube.com/watch?v=vFR9zUGt2C4, www.youtube.com/watch?v=cV35DHVeNm8, www.youtube.com/watch?v=mIT-nghOB4

UNIT 6 – REDOX REACTIONS

Lesson 11 – How can we predict the quantity of each substance produced during electrolysis?

- **Electroplating** is the use of electrolysis to cover the surface of one metal with a thin layer of another metal
 - it can be used either to protect or to decorate the metal
 - the metal to be plated is used as the cathode in an electrolytic cell
 - the electrolyte should contain the cations of a metal it is to be plated with
 - if a large quantity of electroplating is needed, the anode should also be made of this metal
 - for example, to electroplate a copper vessel with a thin layer of silver, the vessel should be used as the cathode in the electrolytic cell, the electrolyte should be silver nitrate (AgNO_3) and the anode should be made of silver:



the Ag^+ ions move to the cathode and are reduced to Ag, covering the vessel with a thin layer of silver ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$); at the anode, the Ag will be oxidised to Ag^+ ($\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$)

- electroplating with silver is commonly used to improve the appearance of cutlery, crockery and jewellery



Summary Activity 11.1: Units of charge and amount of substance

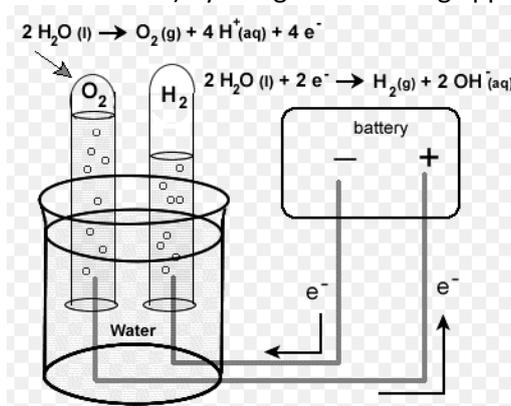
- What is the SI unit of electrical charge?
- What is the charge on an electron? What is the total charge on one mole of electrons?
- What is the mass of 0.1 mole of copper?
- How many moles of oxygen are present in a 1 dm^3 sample at 298 K and 100 kPa?

- Pipette: very accurate but can only deliver one volume
- Volumetric flask: very accurate but can only store one volume
- Burette: slightly less accurate than a pipette but can deliver any volume up to 50 cm^3
- Measuring cylinder: not accurate
- Pipettes and burettes are most useful for carrying out titrations

UNIT 6 – REDOX REACTIONS

(iii) Using electrolysis to prove the composition of water

- it is possible to measure the volume of hydrogen and oxygen produced during the electrolysis of acidified or alkaline water (dilute H_2SO_4 or dilute NaOH) by using the following apparatus:



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- The hydrogen and oxygen can be collected using test tubes, inverted burettes or inverted measuring cylinders
- Because the two gases are produced in a 2:1 mole ratio, their volumes will also be in a 2:1 ratio; this proves that water must contain hydrogen and oxygen in a 2:1 ratio and provides proof of the composition of water

(iv) Faraday's Constant

- It is often important to know how much electricity is required to achieve a particular electrolysis, or how much product can be obtained from a certain amount of electricity
- The unit of charge is the Coulomb and one electron has a charge of $1.6 \times 10^{-19} \text{ C}$
- One mole of electrons therefore has a total charge of $6 \times 10^{23} \times 1.6 \times 10^{-19} \text{ C} = 96000 \text{ Cmol}^{-1}$; more accurately, this value, to 3 significant figures, can be shown to 96500 Cmol^{-1} ; this is known as the **Faraday constant**; $1 \text{ Faraday} = 96500 \text{ Cmol}^{-1}$
- Half-equations can be used to calculate how much electrical charge is needed to achieve a particular oxidation or reduction:
 - Eg $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$; 2 Faradays of charge are required to reduce one mole of Cu^{2+} ions to Cu
 - Eg $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$; 4 Faradays of charge are required to oxidise 4 moles of OH^- ions and produce 1 mole of O_2

Worked example: What mass of copper can be produced by electrolysis of $\text{CuSO}_4(\text{aq})$ from 19300 C of charge?

Answer:

- $19300/96500 = 0.2 \text{ F}$
- $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ so 2 F of charge is needed per mole of copper produced
- So moles of Cu = $0.2/2 = 0.1$
- So mass of Cu = $0.1 \times 63.5 = 6.35 \text{ g}$

UNIT 6 – REDOX REACTIONS

Worked example: How much charge, in coulombs, is needed to produce 1 dm³ of O₂ gas during the electrolysis of dilute sulphuric acid at 100 kPa and 298 K?

Answer:

- moles of O₂ = PV/RT = (100,000 x 0.001)/(8.31 x 298) = 0.040 moles
- 4OH⁻ → O₂ + 2H₂O + 4e⁻ so moles of electrons needed = 0.04 x 4 = 0.16
- So total charge needed: 96500 x 0.16 = 15400 C



Test your knowledge 11.2: Calculating the quantities produced during electrolysis

- Describe a simple experiment you could perform to show that water contains hydrogen and oxygen in a 2:1 ratio
- How much charge will be required for the complete electrolysis of 20 g of molten NaCl?
- What volume of hydrogen and oxygen (at 100 kPa and 298 K) can be obtained if 2000 C are used to electrolyse dilute sulphuric acid?
- How much charge is needed to produce 1 kg of aluminium from its ore (Al₂O₃)?
- What mass of copper can be purified (ie transferred from anode to cathode) if 1000 C of charge is used to electrolyse copper sulphate solution using copper electrodes?
- How much charge is needed to produce 100 cm³ of hydrogen (at 298 K and 100 kPa) during the electrolysis of aqueous sodium chloride?
- How much charge is needed to electroplate a knife with 2 g of silver?

- Electrolyse dilute NaCl or dilute H₂SO₄ using electrodes fully submerged; place inverted measuring cylinders filled with water above the electrodes and collect the gases produced at each electrode; the gas at the cathode will have twice the volume of the gas at the anode
- 20/58.5 = 0.34 moles of NaCl; each NaCl needs 1 electron for separation so 0.34 F needed = 33,000 C
- 2000/96500 = 0.02 moles; which will produce 0.01 moles of H₂ and 0.05 moles of O₂; V = nRT/P = 2.6 x 10⁻⁴ m³ = 0.26 dm³ of hydrogen and 0.13 dm³ of oxygen
- 1000 g of Al₂O₃ = 0.98 moles; each Al₂O₃ requires 6e for electrolysis so 0.98 x 6 = 5.88 F = 568,000 C
- 1000/96500 = 0.0104 F; each Cu requires 2e so moles of Cu = 0.00518 so mass = 0.00518 x 63.5 = 0.33 g
- n = PV/RT = (100000 x 100 x 10⁻⁶)/(8.31 x 298) = 0.00403; 2e required per H₂ so 0.00808 F required; 0.00808 x 96500 = 779 C
- 2/107.9 = 0.0185 moles Ag; each Ag needs 1 e so 0.0185 C required = 1790 C

Lesson 12 – What is rusting and how can we prevent it?

g) The Rusting of Iron

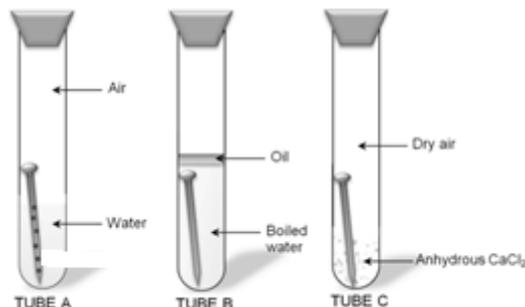
- Rusting is a redox reaction between iron, oxygen and water; it involves a number of different chemical reactions but can be summarised as: $4\text{Fe} + 6\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4\text{Fe}(\text{OH})_3$
 - the Fe is oxidised from 0 to +3; the O is reduced from 0 to -2
- Most metals react with oxygen and water in the environment, but usually the oxides or hydroxides formed stick to the surface of the metal and protect it from further corrosion; most metals are therefore protected naturally by their oxide layer; the oxides and hydroxides of iron, however, flake off the surface and so provide the iron metal with no protection; hence the oxidation process continues indefinitely
- It can be shown experimentally that both air and water are necessary for rusting to happen:

UNIT 6 – REDOX REACTIONS



Practical 12.1: Demonstrate that oxygen and water are both required for rusting

- 1) Place three iron nails in three different test tubes (see below)
- 2) Add water to the first test tube until it is covering half of the nail
- 3) Add recently boiled water (no oxygen) to the second test tube until it completely covers the nail, and then add a thin layer of vegetable oil
- 4) Add no water to the third test tube; instead add one spatula measure of a drying agent such as CaCl_2
- 5) Leave for a week and then observe the condition of all three nails



Equipment needed per group: 3 test tubes, 3 bungs which fit the test tubes, 1 test tube rack, three small nails (2 - 4 cm), access to anhydrous CaCl_2 and a spatula (1 g per group), access to vegetable oil with dropping pipette (1 cm^3 per group), 5 cm^3 of recently boiled water, access to distilled water

- The nail in tubes B and C should show no signs of rusting after one week, but the nail in tube A should show clear signs of rusting



Practical 12.2: Demonstrate that acids, bases, salts and heating increase the rate of rusting

- 1) Place five iron nails in five different test tubes
- 2) Add water to the first test tube until it is covering half of the nail
- 3) Add 1 mol dm^{-3} HCl to the second test tube until it is covering half of the nail
- 4) Add 1 mol dm^{-3} NaOH to the third test tube until it is covering half of the nail
- 5) Add 1 mol dm^{-3} NaCl to the fourth test tube until it is covering half of the nail
- 6) Add 1 mol dm^{-3} NaCl to the fifth test tube until it is covering half of the nail
- 7) Leave the first four test tubes in a warm place for a week; leave the fifth test tube in a fridge for a week
- 8) Observe the degree of rusting on each nail after one week

Equipment needed per group: 5 test tubes, one test tube rack, 5 small nails (2 – 4 cm), access to distilled water, access to 0.1 mol dm^{-3} solutions of HCl and NaOH, each with dropping pipette (2 cm^3 per group) and NaCl with dropping pipette (4 cm^3 per group), access to a fridge

- The test tubes containing HCl, NaOH and NaCl should all have rusted significantly more than the test tube containing water only; the acid test tube may not appear rusty as rust dissolves in acid; the solution may appear green/orange; the test tube containing NaCl in the fridge should rust less than the test tube containing NaCl in a warm place

- Any solutions containing electrolytes such as acids, bases or salts will increase the rate of rusting; acids will actually also dissolve the rust (by neutralising it) and it may appear not to be causing rusting, but the metal is still corroding

UNIT 6 – REDOX REACTIONS

- Iron is a very widely used metal and the rusting of iron is a major economic problem; there are many items in the home which are prone to rusting, including fridges, freezers, food containers - any metallic object made of iron
- It is important to prevent iron from rusting as much as possible and there are a number of methods available for doing this:
 - the simplest methods involve oiling, greasing and painting; this provides limited protection to the iron by preventing water and oxygen from coming into contact with the surface of the iron; titanium nitride (TiN) is another inert protective layer which can be applied to an iron surface to prevent rusting; again, the protection will only last until it is scratched or damaged
 - if the iron is not under water, maintaining a dry environment through the presence of drying agents in the room will also prevent rusting
 - iron can also be protected by adding a thin layer of another metal to the surface of the iron; tin and zinc are the metals most commonly used for this purpose; the coating of iron with a thin layer of zinc is known as **galvanisation**; zinc and tin both get oxidised by air, but the oxide formed sticks to the surface of the metal, providing protection; the thin layer of tin or zinc can be applied either by dipping the iron into the molten metal (known as hot-dipping) or by **electroplating**
- It is possible to provide more sustainable long-term protection of iron using a technique called **sacrificial cathodic protection**:
 - if another metal is attached to a piece of iron under water, an electrochemical cell will be set up, because the two metals have different electrode potentials
 - if a metal is used which has a more negative electrode potential than iron ($\text{Fe}|\text{Fe}^{2+}$ has a standard electrode potential of -0.44 V), then iron will become the positive electrode (this is the cathode in an electrochemical cell) and the other metal will become the negative electrode (the anode); this will mean that the other metal, and not iron, will be oxidised
 - Zinc is the most commonly used metal for this purpose ($\text{Zn}|\text{Zn}^{2+}$ has a standard electrode potential of -0.76 V); this means that zinc will act as the negative electrode and get oxidised, protecting the iron
 - magnesium and aluminium are also used
 - if small pieces of zinc, magnesium or aluminium are placed at regular intervals along an underwater iron pipe or an iron jetty, rusting can be prevented because the more reactive metal (with the more negative electrode potential) is oxidised preferentially
 - metals such as tin, copper or lead, which have metal-ion electrode potentials more positive than $\text{Fe}|\text{Fe}^{2+}$ cannot provide sacrificial cathodic protection
 - galvanisation of iron (covering it with a layer of zinc) is a particularly effective anti-rusting technique because even if the zinc coating is damaged, the zinc provides sacrificial cathodic protection
 - tin-coating is less effective because tin cannot provide sacrificial cathodic protection if the tin coating is damaged



Test your knowledge 12.3: Understanding Rusting

- Write an equation to show how iron rusts, and use oxidation numbers to show that it is a redox reaction
- State the two conditions necessary for the rusting of iron
- State two conditions which increase the rate of rusting of iron
- Suggest two simple methods by which rusting can be prevented
- Explain the meaning of the term “sacrificial cathodic protection”; give one example of a metal which can provide sacrificial protection to iron and one which cannot

UNIT 6 – REDOX REACTIONS

- (a) $4\text{Fe} + 6\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4\text{Fe}(\text{OH})_3$; Fe oxidised from 0 to 3; O reduced from 0 to -2
- (b) Oxygen (air) and water
- (c) Salt, acids, alkalis (ie electrolytes), heat
- (d) Oiling, painting, galvanisation
- (e) Attaching pieces of a more reactive metal to the iron surface; the more reactive metal is oxidised preferentially; zinc can provide sacrificial protection but tin cannot

Lesson 13 – What have I learned and understood about redox reactions?

13.1 END-OF-TOPIC QUIZ

UNIT 6 – ACIDS, BASES AND SALTS



1. Deduce the oxidation numbers of the following atoms and name the resulting compound:
(a) Cl in NaClO; (b) S in K_2SO_3 ; (c) Mn in KMnO_4
2. Identify the following changes as oxidation or reduction and write a balanced half-equation for each change: (a) ClO^- to Cl^- ; (b) SO_3^{2-} to SO_4^{2-} ; (c) MnO_4^- to Mn^{2+} ; (d) Fe^{2+} to Fe^{3+} ; (e) H_2SO_4 to H_2S ; (f) I^- to I_2
3. Use your answers to Q2 to write balanced equations for the following redox reactions:
(a) H_2SO_4 with I^- to make H_2S and I_2
(b) MnO_4^- with Fe^{2+} to make Mn^{2+} and Fe^{3+}
(c) ClO^- with SO_3^{2-} to make Cl^- and SO_4^{2-}
4. Describe how a solid sample of magnesium nitrate could be made by reacting a metal with an acid; use oxidation numbers to show that a redox reaction is taking place.
5. Explain how you could use redox reactions to confirm the presence of:
(a) Nitrate ions in an aqueous sample
(b) Sulphate (IV) ions in a solid sample
6. Given the following electrode potentials: $\text{Zn}^{2+}|\text{Zn} -0.76 \text{ V}$; $\text{Ni}^{2+}|\text{Ni} -0.14 \text{ V}$
(a) Write the conventional representation for a cell which could be set up using these two half-reactions
(b) Deduce the emf of the cell and write an equation for the reaction taking place
7. When concentrated aqueous NaCl is electrolysed,
(a) Write half-equations for the reactions taking place at each electrode
(b) Write an equation for the overall reaction
(c) Calculate the volume of hydrogen produced at 298 K and 100 kPa after 2000 C of charge have passed through the cell
8. Describe how you could coat a copper coin with a thin layer of silver.
9. (a) Write an equation to show the rusting of iron
(b) State two conditions which increase the rate of rusting of iron
(c) Explain the meaning of the term “sacrificial cathodic protection” of iron
(d) Name two other ways to prevent the rusting of iron

UNIT 6 – REDOX REACTIONS

1. (a) +1, sodium chlorate (I); (b) +4, potassium sulphate (IV); (c) +7, potassium manganate (VII)
2. (a) reduction: $\text{ClO}^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$; (b) oxidation: $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$; (c) reduction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$; (d) oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$; (e) reduction: $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$; (f) oxidation: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
3. (a) $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{I}^- \rightarrow \text{H}_2\text{S} + 4\text{I}_2 + 4\text{H}_2\text{O}$; (b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$; (c) $\text{ClO}^- + \text{SO}_3^{2-} \rightarrow \text{Cl}^- + \text{SO}_4^{2-}$
4. Add excess Mg to dilute HNO_3 ; filter off excess magnesium; heat solution until 75% evaporated; then leave until crystals form; dry crystals in filter paper; $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$; Mg oxidised from 0 to +2; H reduced from +1 to 0
5. (a) Warm with dilute NaOH and Al powder; a pungent gas will be given off which turns red litmus blue and/or gives a white smoke when in contact with HCl; (b) Add dilute HCl; a gas will be given off which smells like burning matches and which turns dichromate paper from orange to green
6. (a) $\text{Zn}|\text{Zn}^{2+}||\text{Ni}^{2+}|\text{Ni}$; (b) +0.62 V, $\text{Zn} + \text{Ni}^{2+} \rightarrow \text{Zn}^{2+} + \text{Ni}$
7. (a) cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$; anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$; (b) $2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{OH}^-$; $2000/96500 = 0.0207 \text{ F}$; 1 H_2 needs 2e so 0.0104 mol H_2 produced; $V = nRT/P = 0.0104 \times 8.31 \times 298 / 100000 = 2.57 \times 10^{-4} \text{ m}^3 = 0.257 \text{ dm}^3$
8. Make it the cathode of an electrolytic cell containing AgNO_3 as the electrolyte and with an anode made of silver, and pass a current through
9. (a) $4\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3$; (b) dissolved electrolytes and heat; (c) attaching the iron to a piece of a more reactive metal; (d) oiling, greasing, painting