Chapter 7 Redox and electrolysis

LEO = loss of electrons, oxidation

{Oxidation - gain of oxygen}

oxidation # increases

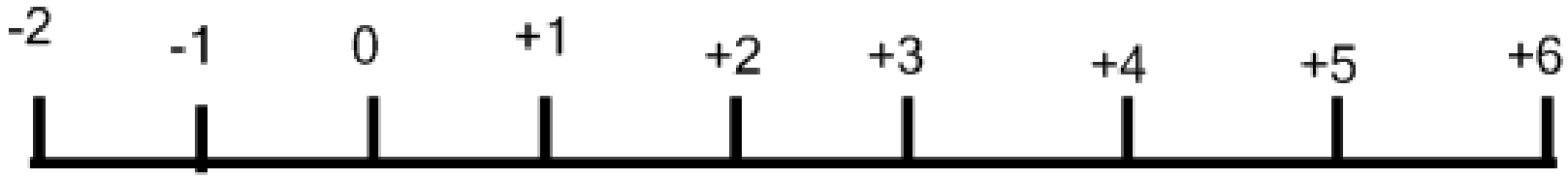
$$\overset{0}{2Mg} + \overset{0}{O_2} \rightarrow \overset{+2}{2Mg}\overset{-2}{O}$$

Reduction - gain of electrons

	Rule	Example
1	The oxidation number of any uncombined element is 0. (An element by itself)	$Na(s) = 0$, $H_2(g) = 0$
2	The oxidation number of a monatomic ion equals the charge on the ion.	$Br^- = -1$, $Ca^{2+} = +2$
3	The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	CN^-; N = -3, C = +2
4	Fluorine always has an oxidation state of -1. (Most electronegative.)	NaF; F = -1, Na = +1
5	Oxygen almost always has an oxidation state of -2. Except with fluorine, then it is +2. Or if it is in a peroxide like H_2O_2, then it is -1.	OF_2; F = -1, O = +2 H_2O_2; H = +1, O = -1
6	Hydrogen has an oxidation state of +1, unless it is with a metal, then it is -1.	LiH; Li = +1, H = -1
7	Elements in Group I, II, and aluminum have oxidation numbers of +1, +2, and +3, respectively.	$Al(OH)_3$; Al = +3, O = -2, H = +1
8	In a neutral compound, the sum of the oxidation numbers is always 0.	$CaCO_3$; Ca = +2, O = -2, C = +4; 2 + (-6) + 4 = 0
9	In a polyatomic ion, the oxidation numbers equal the charge of the ion.	HSO_4^-, S = +6, H = +1, O = -2

*number gets more positive
oxidized, gains oxygen
*number gets more negative
reduced, loses oxygen

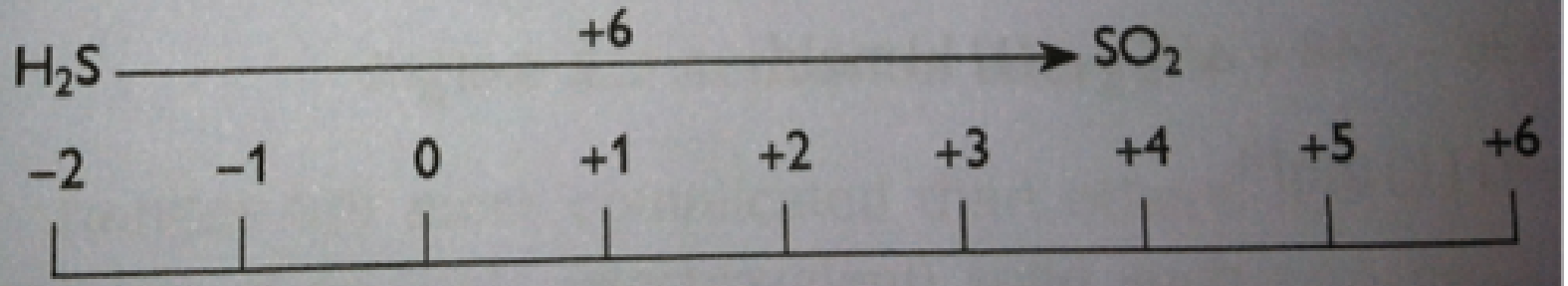
$$\overset{+2\ -2}{CuO} + \overset{0}{H_2} \rightarrow \overset{0}{Cu} + \overset{+1\ -2}{H_2O}$$



Consider the oxidation of hydrogen sulfide to form sulfur dioxide:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

What is the change in oxidation number of sulfur?



Electrolysis – the decomposition of a compound into its elements by an electric current.

Electrolyte- the compound , either molten ionic compound or concentrated aqueous solution of ions, which is broken down.

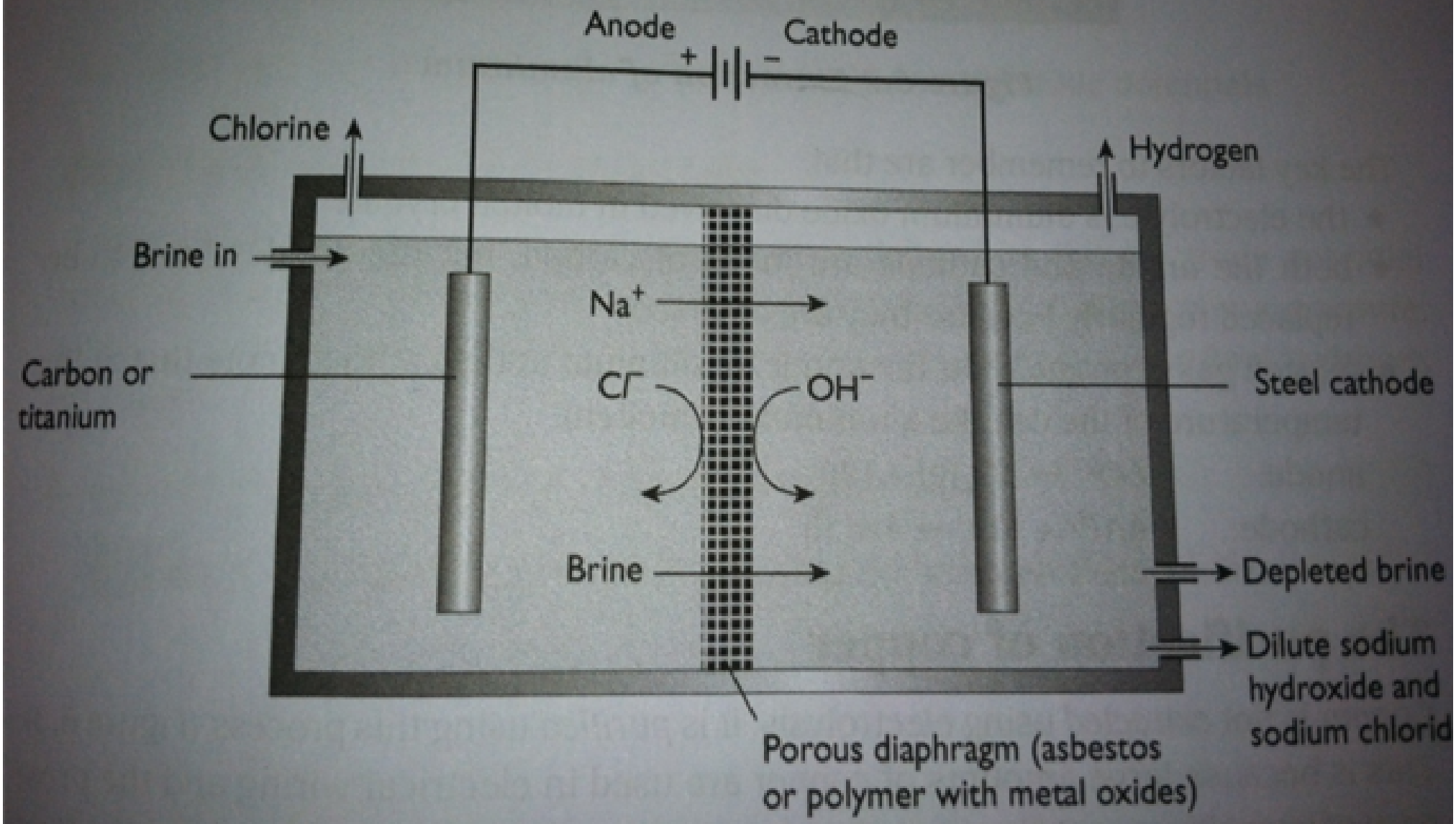
Electrodes – rods made from carbon (graphite) or metal, which conduct electricity to and from the electrolyte.

Anode – positive , attracts anions which loses electrons making it an oxidation (electrons on right of equation)

Cathode - negative , attracts cations which gains electrons making it a reduction (electrons of the left of equation)

The diaphragm cell

Chlorine has been produced by electrolysis for many years, and the most recent method uses the diaphragm cell shown in Figure 6.1.



The key factors to remember are that:

- the electrodes are separated by a diaphragm, usually made of asbestos
- the electrolyte is brine (a solution of sodium chloride)
- the anode is usually made of titanium
- the cathode is usually made of steel
- chlorine gas is produced at the anode, hydrogen gas at the cathode:

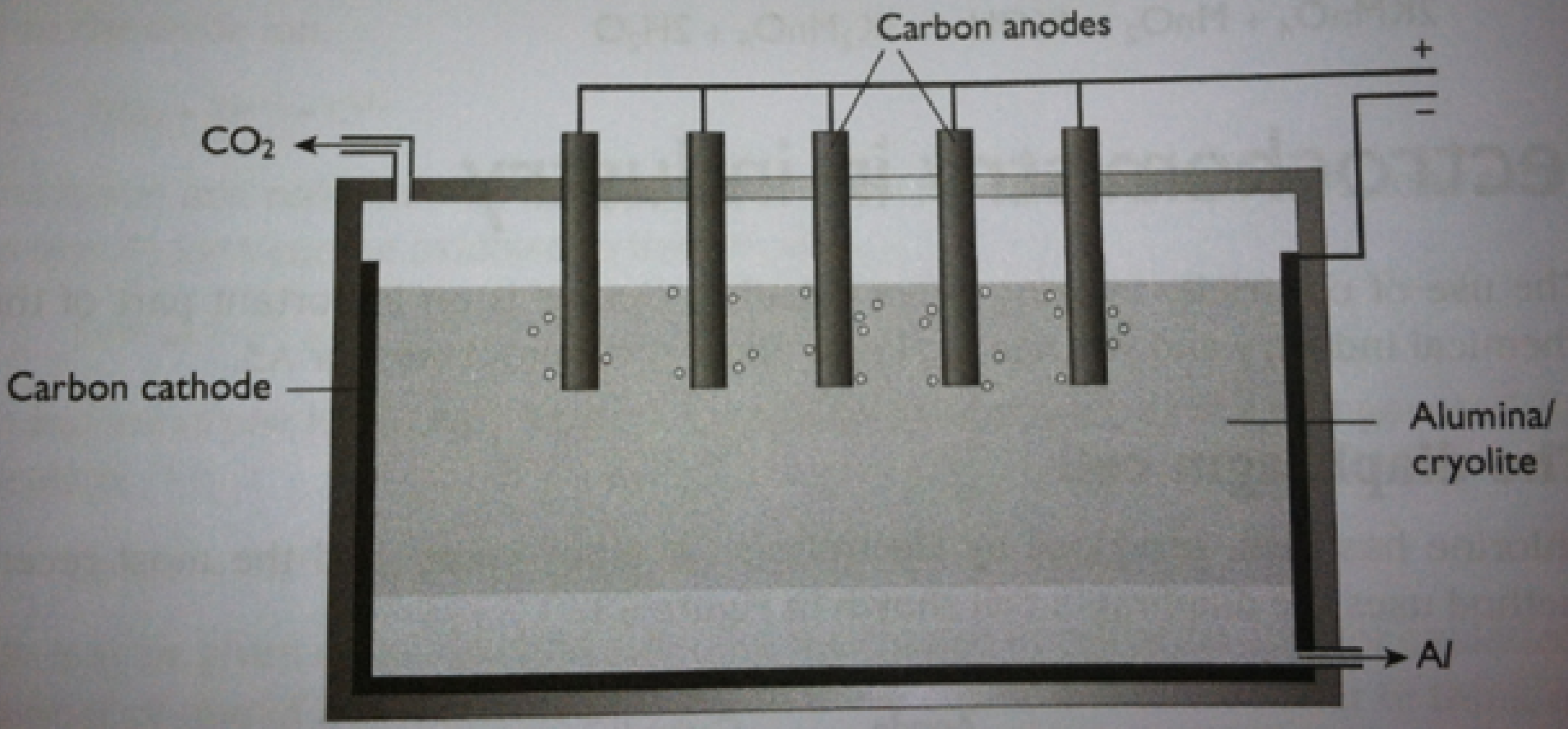
  anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

  cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

- sodium hydroxide is an important by-product

The extraction of aluminium

Aluminium is too reactive a metal to be extracted by heating with coke (carbon), like other metals such as iron. It is extracted by electrolysing aluminium oxide dissolved in molten cryolite, Na_3AlF_6 (Figure 6.2).



The key factors to remember are that:

- the electrolyte is aluminium oxide dissolved in molten cryolite
- both the anode and cathode are made of carbon, but the anodes have to be replaced regularly because they are oxidised
- oxygen gas is produced at the anode, aluminium at the cathode (note that at the temperature of the cell the aluminium is molten):

anode: $6O^{2-} \rightarrow 3O_2(g) + 12e^-$

cathode: $4Al^{3+} + 12e^- \rightarrow 4Al\ (l)$

Extracting aluminum from bauxite ore (A soft, whitish to reddish-brown rock consisting mainly of hydrous aluminum oxides and aluminum hydroxides along with silica, silt, iron hydroxides, and clay minerals. Bauxite forms from the breakdown of clays and is a major source of aluminum.)

Aluminium is manufactured by the electrolysis of a molten mixture of aluminium oxide and cryolite.

- Aluminium forms at the negative electrode (cathode) and oxygen at the positive electrode (anode).

- The positive anode is made of carbon(graphite), which reacts with the oxygen to produce carbon dioxide.

Cryolite is used to dissolve the aluminum oxide so that the melting point of the electrolyte is lowered to about 970 degrees. It improves the electrical conductivity of the electrolyte.

The purification of copper

Copper is not *extracted* using electrolysis, it is *purified* using this process (Figure 6.3). This is because large amounts of copper are used in electrical wiring and the presence of impurities would increase the resistance of the wire, resulting in overheating.

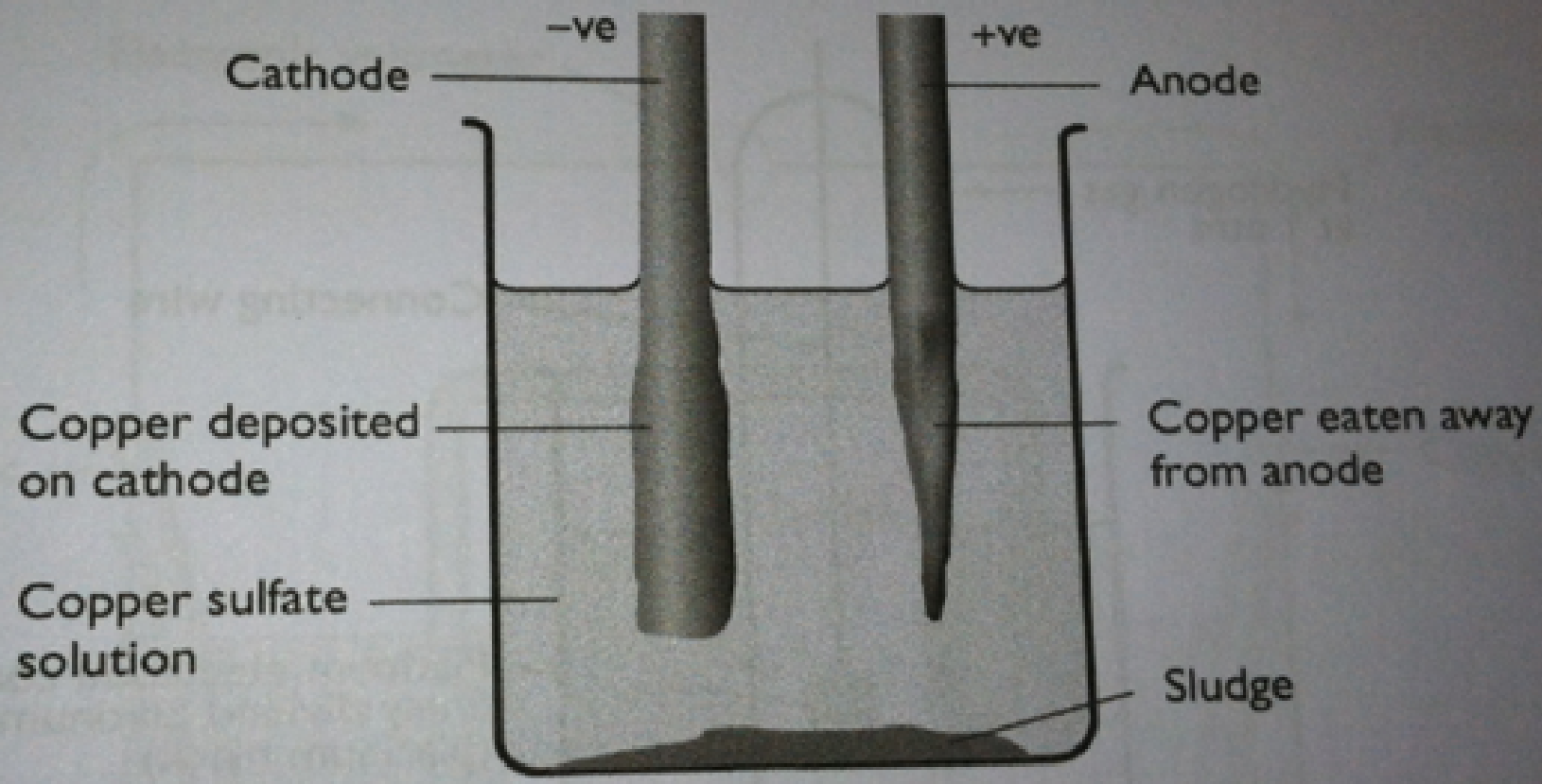


Figure 6.3 Purification of copper

Check-up

5 Give the full systematic names of the following:

a Na_2SO_3

b Na_2SO_4

c $Fe(NO_3)_2$

d $Fe(NO_3)_3$

e $FeSO_4$

f Cu_2O

g H_2SO_3

h Mn_2O_7

8 In the extraction of aluminium by electrolysis, why is it necessary to dissolve aluminium oxide in molten cryolite?

A to reduce the very high melting point of the electrolyte

B cryolite provides the ions needed to carry the current

C cryolite reacts with the aluminium oxide to form ions

D molten aluminium oxide alone would not conduct electricity

9 A cheap carbon monoxide detector for a gas heater consists of a patch containing palladium chloride crystals. When carbon monoxide is present, the crystals turn from orange to black as the following reaction takes place.

$$\underset{\text{orange}}{CO(g) + PdCl_2(s)} + H_2O(l) \rightarrow CO_2(g) + \underset{\text{black}}{Pd(s)} + 2HCl(aq)$$

Which is the element whose oxidation number **decreases** in this reaction?

A carbon

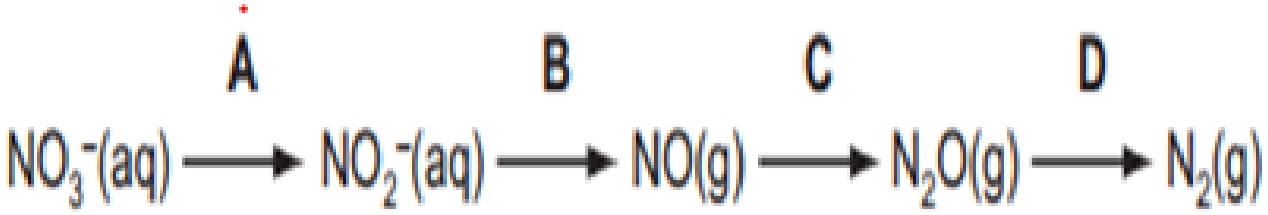
B chlorine

C hydrogen

D palladium

2 In flooded soils, like those used for rice cultivation, the oxygen content is low. In such soils, anaerobic bacteria cause the loss of nitrogen from the soil as shown in the following sequence.

In which step is the change in oxidation number (oxidation state) of nitrogen different to the changes in the other steps?



3 In the extraction of aluminium by the electrolysis of molten aluminium oxide, why is cryolite added to the aluminium oxide?

A to ensure the aluminium is not oxidised

B to ensure the anode is not oxidised

C to lower the melting point of the aluminium oxide

D to prevent corrosion of the cathode

6 Ammonium nitrate, NH_4NO_3, can decompose explosively when heated.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

What are the changes in the oxidation numbers of the two nitrogen atoms in NH_4NO_3 when this reaction proceeds?

A −2, −4 B +2, +6 C +4, −6 D +4, −4

10 The oxide of titanium, TiO_2, is used as a 'whitener' in toothpaste. It is obtained from the ore iron(II) titanate, $FeTiO_3$.

What is the change, if any, in the oxidation number (oxidation state) of titanium in the reaction $FeTiO_3 \rightarrow TiO_2$?

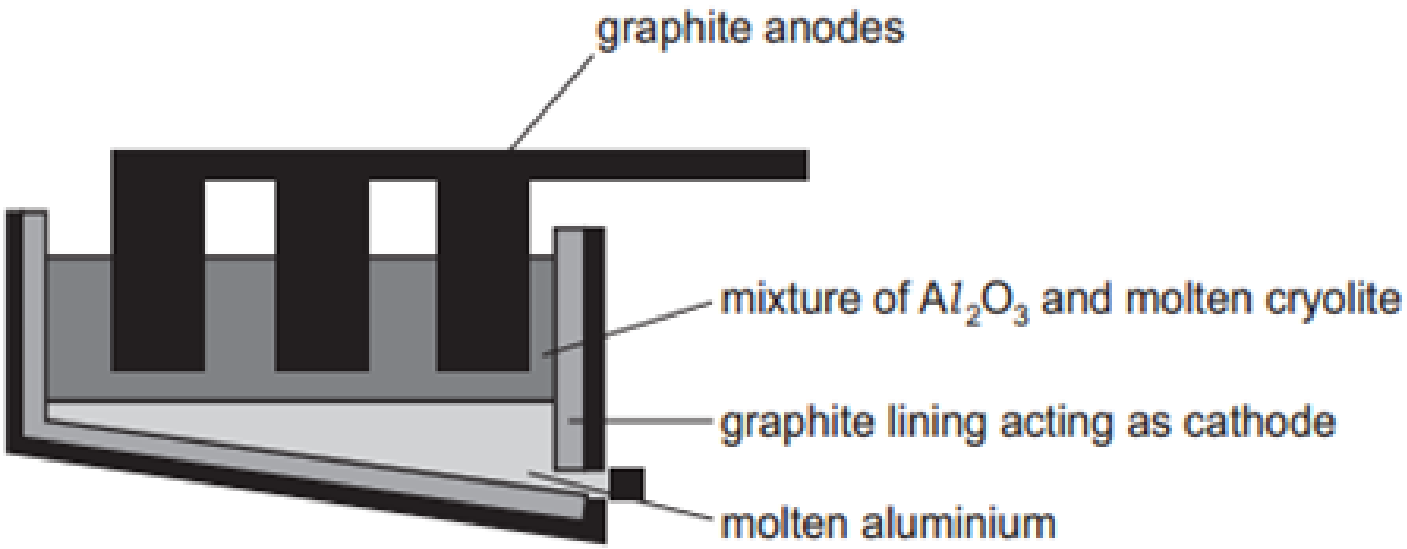
A It is oxidised from +3 to +4.

B It is reduced from +3 to +2.

C It is reduced from +6 to +4.

D There is no change in the oxidation number.

11 The diagram shows a cell for the manufacture of aluminium.



Which statement is **incorrect**?

A Aluminium ions are oxidised in this process.

B Aluminium is liberated at the cathode by the reaction $Al^{3+} + 3e^- \rightarrow Al$.

C The cryolite acts as a solvent.

D The graphite anode burns away.

16 In the treatment of domestic water supplies, chlorine is added to the water to form HC*l*O.

$$Cl_2(aq) + H_2O(l) \rightarrow H^+(aq) + Cl^-(aq) + HClO(aq)$$

The HC*l*O reacts further to give ClO^- ions.

$$HClO(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO^-(aq)$$

Both HC*l*O and ClO^- kill bacteria by oxidation.

What is the overall change in oxidation number of chlorine when forming the ClO^- ion from the aqueous chlorine?

A –1 **B** 0 **C** +1 **D** +2

15 In the treatment of domestic water supplies, chlorine is added to the water to form chloric(I) acid, HClO.

$$Cl_2(aq) + H_2O(l) \rightarrow H^+(aq) + Cl^-(aq) + HClO(aq)$$

This reacts further to give the chlorate(I) ion.

$$HClO(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO^-(aq)$$

Both HClO and ClO^- kill bacteria by oxidation.

What is the change in oxidation number of chlorine in forming the chlorate(I) ion from the aqueous chlorine?

A –1 **B** 0 **C** +1 **D** +2

8 When ammonia is converted into nitric acid on a commercial scale, the following reactions can occur.

In which reaction does the greatest change in oxidation number of the nitrogen occur?

reaction	
A	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
B	$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
C	$2NO + O_2 \rightarrow 2NO_2$
D	$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$

9 At the age of 17, in a woodshed in Ohio, Charles Martin Hall discovered the commercial process for the production of aluminium metal by the electrolysis of a mixture of bauxite, Al_2O_3, and cryolite, Na_3AlF_6.

What is the main purpose of the cryolite?

A Al_2O_3 is covalent, and AlF_6^{3-} ions interact with it to produce Al^{3+} ions which can be discharged at the cathode.

B Cryolite is a base, forming $NaAlO_2$ with bauxite, enabling aluminium to be discharged at the anode.

C Cryolite reduces the melting point of the bauxite.

D Cryolite minimises the release of O^{2-} ions at the graphite anodes, which are otherwise burnt away to CO.

9 The nickel-cadmium rechargeable battery is based upon the following overall reaction.

$$Cd + 2NiOOH + 4H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2.H_2O$$

What is the oxidation number of nickel at the beginning and at the end of the reaction?

	beginning	end
A	+1.5	+2
B	+2	+3
C	+3	+2
D	+3	+4

15 Which element has the same oxidation number in all of its known compounds?

A beryllium

B chlorine

C nitrogen

D sulphur

1. $Cl_2(g) + S_2O_3^{2-}(aq) \rightarrow Cl^-(aq) + SO_4^{2-}(aq)$ *in acid solution.*

Answers:

(a) $S_2O_3^{2-}(aq) + 5\ H_2O \rightarrow 2\ SO_4^{2-}(aq) + 10\ H^+(aq) + 8\ e^-$ *(oxidation half-reaction – LEO);*

$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ *(reduction half-reaction – GER).*

(b) $S_2O_3^{2-}(aq) + 5\ H_2O + 4\ Cl_2(g) \rightarrow 2\ SO_4^{2-}(aq) + 10\ H^+(aq) + 8\ Cl^-(aq)$

(c) $S_2O_3^{2-}(aq)$ *is the reducing agent;* $Cl_2(g)$ *is the oxidizing agent.*

2. $O_3(g) + Br^-(aq) \rightarrow O_2(g) + BrO^-(aq)$ *in basic solution.*

(a) $Br^-(aq) + H_20 + 2\ OH^-(aq) \rightarrow BrO^-(aq) + 2H_2O + 2\ e^-$ or, after simplifying,

$Br^-(aq) + 2\ OH^-(aq) \rightarrow BrO^-(aq) + H_2O + 2\ e^-$ (oxidation half-reaction – LEO);

$O_3(g) + 2\ H_2O + 2\ e\text{-} \rightarrow O_2(g) + H_2O + 2\ OH^-(aq)$ or, after simplifying,

$O_3(g) + H_2O + 2\ e\text{-} \rightarrow O_2(g) + 2\ OH^-(aq)$ (reduction half-reaction – GER).

(b) *$Br^-(aq) + O_3(g) \rightarrow BrO^-(aq) + O_2(g)$*

(c) *$Br^-(aq)$ is the reducing agent; $O_3(g)$ is the oxidizing agent.*

3. Balance the reaction, $Br_2(l) \rightarrow Br^-(aq) + BrO_3^-(aq)$ in basic solution.

Answer: this is a disproportion reaction

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$6\ Br_2(l) + 12\ OH^-(aq) \rightarrow 10\ Br^-(aq) + 2\ BrO_3^-(aq) + 6\ H_2O$