

# Reactivity 3.2

## Answers

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IB CHEMISTRY SL

25 <b>Mn</b> Manganese 54.938045	16 <b>S</b> Sulfur 32.065	<b>J</b>	6 <b>C</b> Carbon 12.0107	2 <b>He</b> Helium 4.002602	25 <b>Mn</b> Manganese 54.938045
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### Reactivity 3.2.1

#### Understandings:

- Oxidation and reduction can be described in terms of electron transfer, change in oxidation state, oxygen gain/loss or hydrogen loss/gain.

#### Learning outcomes:

- Deduce oxidation states of an atom in a compound or an ion.
- Identify the oxidized and reduced species and the oxidizing and reducing agents in a chemical reaction.

#### Additional notes:

- Include examples to illustrate the variable oxidation states of transition element ions and of most main group non-metals.
- Include the use of oxidation numbers in the naming of compounds.

#### Linking questions:

- Structure 3.1 What are the advantages and limitations of using oxidation states to track redox changes?
- Structure 2.3 The surface oxidation of metals is often known as corrosion. What are some of the consequences of this process?

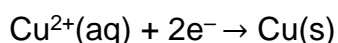
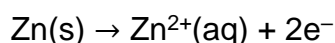
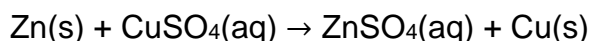
## Definitions of oxidation and reduction

Oxidation and reduction can be defined in terms of:

- Loss or gain of electrons and change in oxidation state.
- Loss or gain of oxygen.
- Loss or gain of hydrogen.

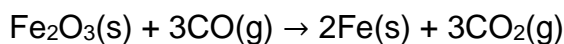
## Electron transfer

- Oxidation is the loss of electrons and an increase in oxidation state.
- Reduction is the gain of electrons and a decrease in oxidation state.



## Loss or gain of oxygen

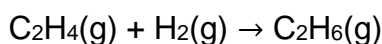
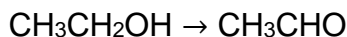
- Oxidation is the gain of oxygen.
- Reduction is the loss of oxygen.



- In the above reaction,  $\text{Fe}_2\text{O}_3$  has been reduced (loss of oxygen) and CO has been oxidised (gain of oxygen).

## Loss or gain of hydrogen

- Oxidation is the loss of hydrogen.
- Reduction is the gain of hydrogen.



- Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) has been oxidised (loss of hydrogen) and ethene ( $\text{C}_2\text{H}_4$ ) has been reduced (gain of hydrogen).

**Exercise:** Complete the following table.

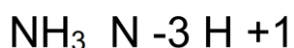
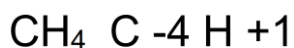
	Electron transfer	Loss or gain of oxygen	Loss or gain of hydrogen
Definition of oxidation	Loss of electrons	Gain of oxygen	Loss of hydrogen
Definition of reduction	Gain of electrons	Loss of oxygen	Gain of hydrogen

## Oxidation states

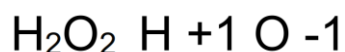
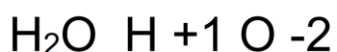
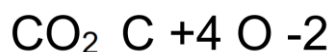
- The oxidation state is the hypothetical charge an atom would have if the bonds were assumed to be 100% ionic with no covalent character.
- Oxidation states are written with the + or – first followed by the number (+2, not 2+).

## Assigning oxidation states

- Elements have an oxidation state of zero.
- Examples include Cu(s), Fe(s), Be<sub>2</sub>(l), Cl<sub>2</sub>(g), O<sub>2</sub>(g), etc.
- The sum of the oxidation states in a compound is equal to zero.



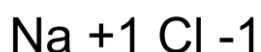
- Oxygen in a compound has an oxidation state of -2, except in peroxides when it is -1.



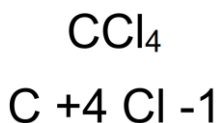
- Hydrogen in a compound has an oxidation state of +1, except in metal hydrides when it is -1.



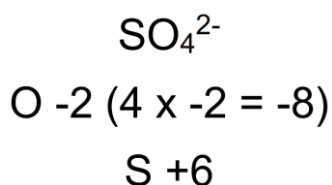
- Group 1 and 2 elements in compounds have oxidation states of +1 and +2 respectively.
- Fluorine in compounds always has an oxidation state of -1.
- In metals, the charge on the ion is the same as the oxidation state, for example in Cu<sup>2+</sup> the oxidation state of the copper ion is +2.
- In an ionic compound, the oxidation state of each species is the same as the charge on the ion.



- For covalent compounds, assume that the more electronegative atom has a negative oxidation state and the less electronegative atom has a positive oxidation state.



- The sum of the oxidation states in a polyatomic ion is equal to the charge on the ion.



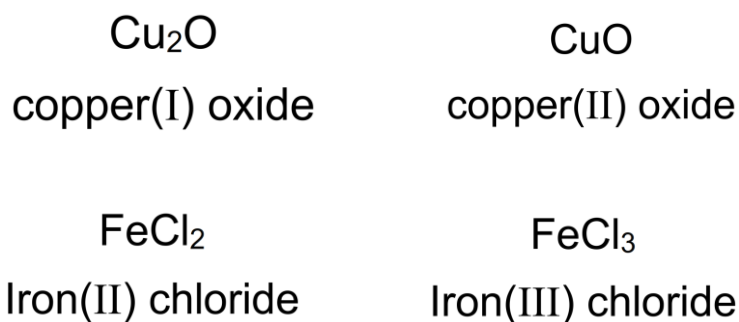
### Summary:

Rules for determining oxidation states	
1.	Free elements are assigned an oxidation state of zero.
2.	The sum of the oxidation states of all the atoms in a compound must be equal to zero.
3.	The alkali metals (Li, Na, K, Rb, and Cs) in compounds are always assigned an oxidation state of +1.
4.	Fluorine in compounds is always assigned an oxidation state of -1.
5.	The alkaline earth metals (Be, Mg, Ca, Sr, Ba, and Ra) and Zn in compounds are always assigned an oxidation state of +2.
6.	Hydrogen in compounds is assigned an oxidation state of +1 except in certain metal hydrides (e.g. NaH) which is -1.
7.	Oxygen in compounds is assigned an oxidation state of -2 unless it is combined with fluorine or in peroxides (e.g. H <sub>2</sub> O <sub>2</sub> ) which is -1.
8.	Chlorine is assigned an oxidation state of -1 unless it is combined with oxygen or fluorine.
9.	The charge on a metal ion is the same as its oxidation state, e.g. Zn <sup>2+</sup> has an oxidation state of +2.

## Oxidation numbers

- Oxidation states can be represented by a Roman numeral - note that these are actually called oxidation numbers but are used interchangeably with oxidation state.
- Transition elements such as copper and iron can have variable oxidation states/numbers.

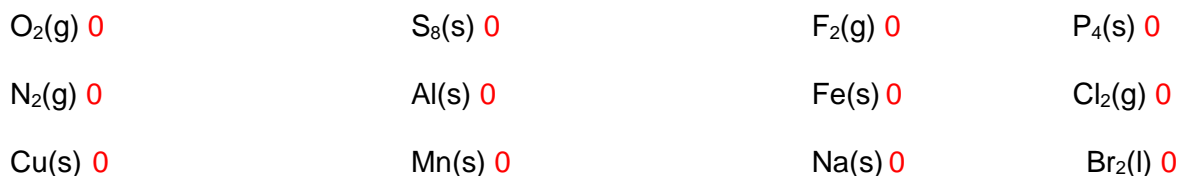
### Examples:



### Exercises:

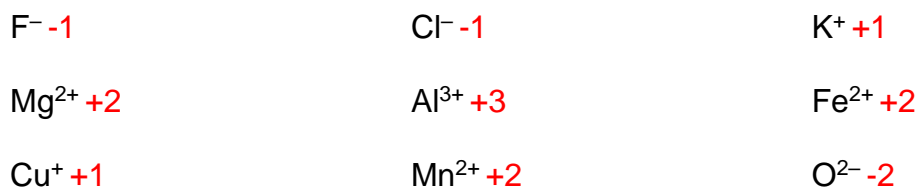
1) Deduce the oxidation states of the following.

All are elements therefore the oxidation state is zero.



2) Deduce the oxidation states of the following ions.

For ions, the oxidation state is the same as the charge on the ion.



3) Deduce the oxidation states of the species in bold in the following compounds.

All are neutral compounds so the sum of the oxidation states is zero.

**C**O<sub>2</sub> +4

**P**H<sub>3</sub> -3

H<sub>2</sub>**S**O<sub>3</sub> +4

**F**e<sub>2</sub>O +3

**S**iF<sub>4</sub> +4

**K**IO<sub>3</sub> +5

Na<sub>2</sub>**S**O<sub>4</sub> +6

H<sub>2</sub>**O**<sub>2</sub> -1

Na<sub>2</sub>**Cr**<sub>2</sub>O<sub>7</sub> +6

4) Deduce the oxidation state of the species in bold in the following polyatomic ions.

The sum of the oxidation states is equal to the charge on the ion.

**C**O<sub>3</sub><sup>2-</sup> +4

**N**O<sub>3</sub><sup>-</sup> +5

**S**O<sub>4</sub><sup>2-</sup> +6

**P**O<sub>4</sub><sup>3-</sup> +5

**N**O<sub>2</sub><sup>-</sup> +3

**S**O<sub>3</sub><sup>2-</sup> +4

5) Deduce the oxidation number of the metal ion in the following.

The Roman numerals are oxidation numbers.

iron(II) oxide +2

manganese(IV) oxide +4

manganate(VII) ion +7

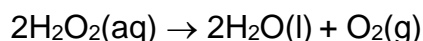
chromium(III) oxide +3

copper(I) chloride +1

copper(II) chloride +2

### Disproportionation reactions

- A disproportionation reaction is a redox reaction in which one species is simultaneously oxidised and reduced (one species acts as both the oxidising and reducing agent).



- In the reaction, oxygen has both been both oxidised (increase in oxidation state) and reduced (decrease in oxidation state).

**Exercise:** Copper chloride in solution reacts as follows.



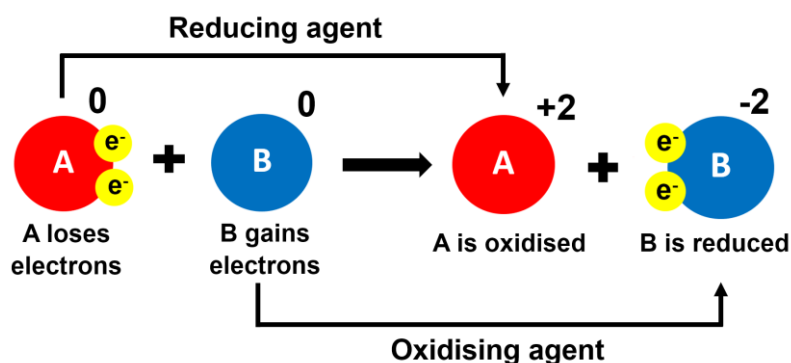
Determine the oxidation states of the species in the reaction and explain why this is a disproportionation reaction.

Reactants: Cu<sup>+</sup> : +1, Cl<sup>-</sup> : -1 Products: Cu : 0, Cu<sup>2+</sup> : +2, Cl<sup>-</sup> : -1

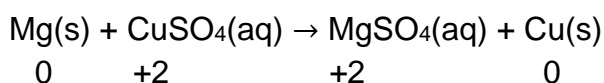
The Cu<sup>+</sup> ion has been oxidised to form the Cu<sup>2+</sup> ion and reduced to form Cu.

## Oxidising and reducing agents

- An oxidising agent oxidises another species (an oxidising agent is reduced).
- A reducing agent reduces another species (a reducing agent is oxidised).

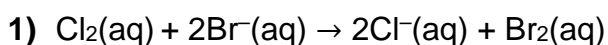


- Example – magnesium reacts with copper sulfate as follows.



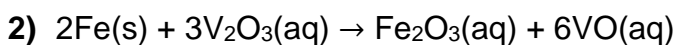
- The magnesium has been oxidised therefore it is the reducing agent.
- The  $\text{Cu}^{2+}$  ion has been reduced therefore it is the oxidising agent.

**Exercise:** Identify the oxidising and reducing agents in the following reactions.



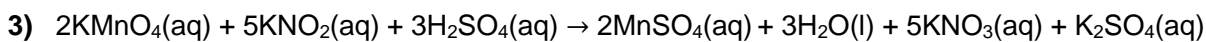
Oxidising agent:  $\text{Cl}_2$

Reducing agent:  $\text{Br}^-$



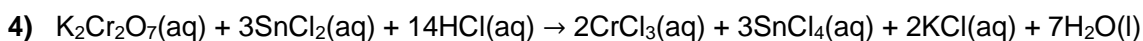
Oxidising agent:  $\text{V}_2\text{O}_3$

Reducing agent:  $\text{Fe}$



Oxidising agent:  $\text{KNO}_2$

Reducing agent:  $\text{KMnO}_4$



Oxidising agent:  $\text{K}_2\text{Cr}_2\text{O}_7$

Reducing agent:  $\text{SnCl}_2$



## Reactivity 3.2.2

### Understandings:

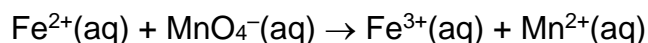
- Half-equations separate the processes of oxidation and reduction, showing the loss or gain of electrons.

### Learning outcomes:

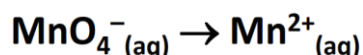
- Deduce redox half-equations and equations in acidic or neutral solutions.

### Balancing redox equations in acidic solutions

Example: Balance the following equation in acidic solution.



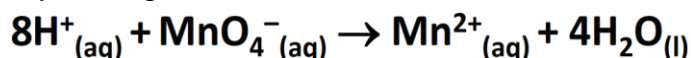
- 1) Balance for atoms other than H or O.



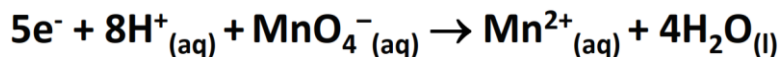
- 2) Balance for O by adding water (H<sub>2</sub>O) to the side with fewer number of O atoms.



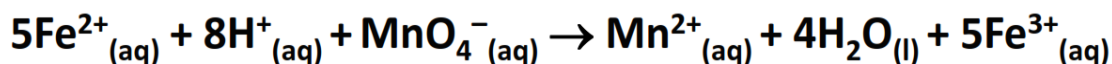
- 3) Balance for H by adding H<sup>+</sup> ions to the side with the fewer number of H atoms.



- 4) Balance for charge by adding electrons to make the charge the same on both sides of the arrow.



- 5) Combine both equations and cancel out the electrons.

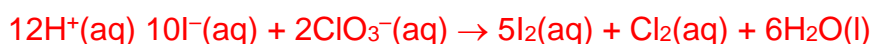


**Exercise:** Balance the following redox equations in acidic solution.

- 1)  $\text{Ag}(\text{s}) + \text{NO}_3^{-}(\text{aq}) \rightarrow \text{Ag}^{+}(\text{aq}) + \text{NO}(\text{aq})$



- 2)  $\text{I}^{-}(\text{aq}) + \text{ClO}_3^{-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + \text{Cl}_2(\text{aq})$



### Reactivity 3.2.3

#### Understandings:

- The relative ease of oxidation and reduction of an element in a group can be predicted from its position in the periodic table.
- The reactions between metals and aqueous metal ions demonstrate the relative ease of oxidation of different metals.

#### Learning outcomes:

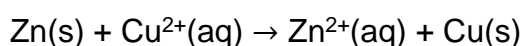
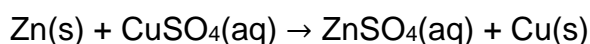
- Predict the relative ease of oxidation of metals.
- Predict the relative ease of reduction of halogens.
- Interpret data regarding metal and metal ion reactions.

#### Additional notes:

- The relative reactivity of metals observed in metal/ metal ion displacement reactions does not need to be learned; appropriate data will be supplied in examination questions.

## Displacement reactions

- In a displacement reaction, a more reactive metal displaces the ions of a less reactive metal from solution.
- Metals at the top of the activity series are stronger reducing agents (more readily oxidised).
- Metals at the bottom of the activity series are weaker reducing agents (less readily oxidised).
- A metal at the top of the activity series can reduce the ions of a metal lower in the activity series.
- Example – in the reaction below, a piece of zinc is added to an aqueous solution of copper(II) sulfate.



- Zinc is above copper on the activity series, so it displaces the copper ions from solution.

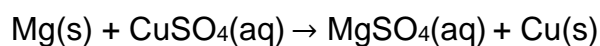
## Writing net-ionic equations

- A net-ionic equation is an equation for a redox reaction that includes only those species that participate in the reaction.
- Species that do not take part in the reaction are known as spectator ions and are not included in the net-ionic equation.

### How to write net-ionic equations:

1. Write the molecular equation for the reaction.
2. Write the complete ionic equation that shows all aqueous species broken down into their constituent ions.
3. Cancel out the spectator ions (ions that appear unchanged on both sides of the equation).
4. Write the net-ionic equation.

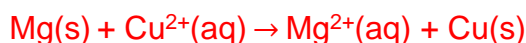
**Example:** Magnesium reacts with copper(II) sulfate as follows. Write the net-ionic equation for the reaction.



- 1) Write the complete ionic equation that shows all aqueous species broken down into their constituent ions.



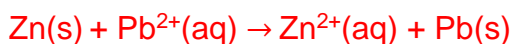
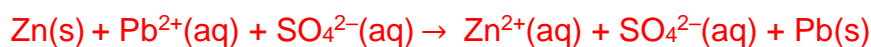
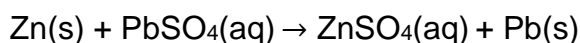
- 2) Cancel out the spectator ions (ions that appear unchanged on both sides of the equation).



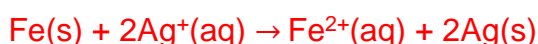
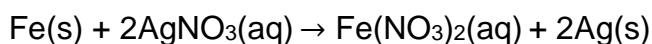
## Exercises:

1) Write the net-ionic equations for the following reactions:

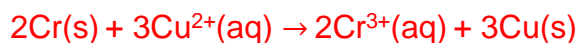
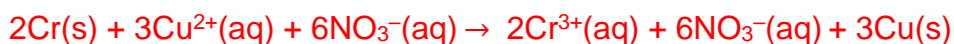
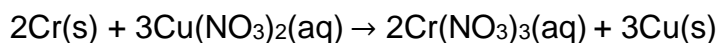
(a) Zinc reacts with lead sulfate to produce zinc sulfate and lead.



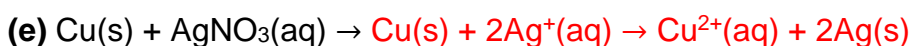
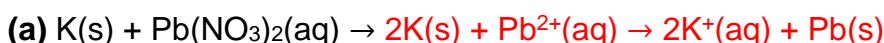
(b) Iron reacts with silver nitrate to produce iron(II) nitrate and silver.



(c) Chromium reacts with copper(II) nitrate to produce chromium(III) nitrate and copper.



2) Use the activity series to predict if the following reactions will take place or not. If the reaction takes place, write the net-ionic equations for the reaction.



### Reactivity 3.2.4

#### Understandings:

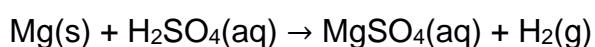
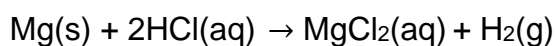
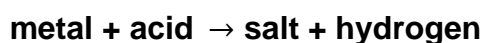
- Acids react with reactive metals to release hydrogen.

#### Learning outcomes:

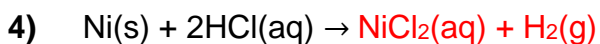
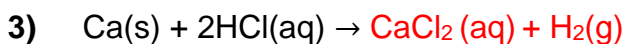
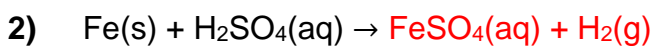
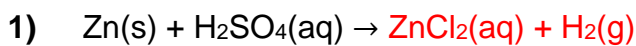
- Deduce equations for reactions of reactive metals with dilute HCl and H<sub>2</sub>SO<sub>4</sub>.

#### Reactions of metals and acids

- Acids react with reactive metals (those above hydrogen on the activity series) to produce a salt and hydrogen gas.



**Exercise:** Complete and balance the following equations.



### Reactivity 3.2.5

#### Understandings:

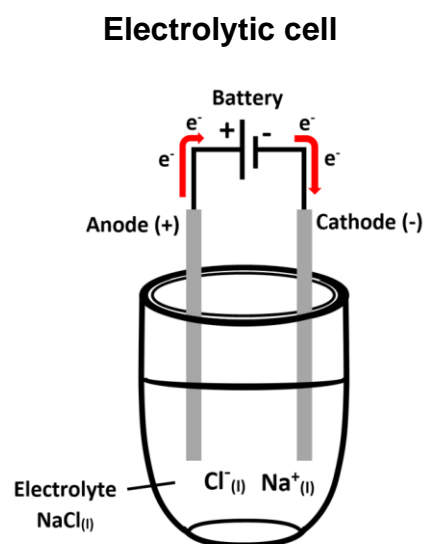
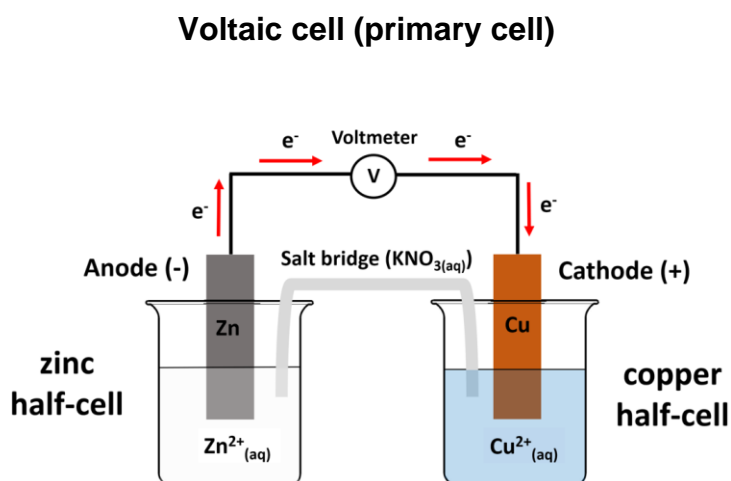
- Oxidation occurs at the anode and reduction occurs at the cathode in electrochemical cells.

#### Learning outcomes:

- Label electrodes as anode and cathode, and identify their signs/polarities in voltaic cells and electrolytic cells, based on the type of reaction occurring at the electrode.

#### Electrochemical cells

- Voltaic cells (or primary cells) and electrolytic cells are collectively known as electrochemical cells.



#### Electrochemical cells comparison

Voltaic cell	Electrolytic cells
A spontaneous reaction produces an electric current.	An electric current drives a non-spontaneous reaction.
Current is conducted by electron flow in wires and movement of ions in salt bridge	Current is conducted by electron flow in wires and movement of ions in electrolyte
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Chemical energy is converted to electrical energy	Electrical energy is converted to chemical energy
Reaction is exothermic	Reaction is endothermic
Oxidation occurs at the anode and reduction at the cathode	Oxidation occurs at the anode and reduction at the cathode

### Reactivity 3.2.6

#### Understandings:

- A primary (voltaic) cell is an electrochemical cell that converts energy from spontaneous redox reactions to electrical energy.

#### Learning outcomes:

- Explain the direction of electron flow from anode to cathode in the external circuit, and ion movement across the salt bridge.

#### Additional notes:

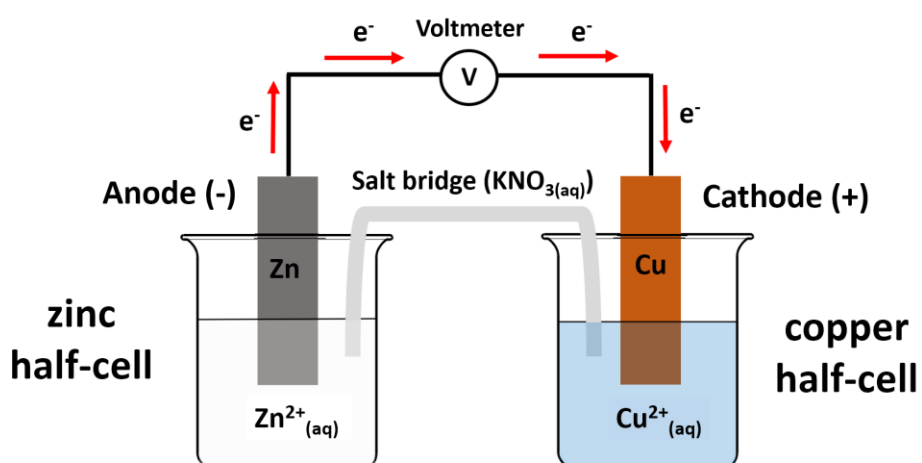
- Construction of primary cells should include: half-cells containing metal/metal ion, anode, cathode, electric circuit, salt bridge.

#### Linking questions:

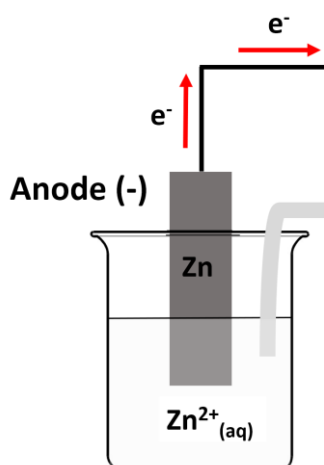
- Reactivity 1.3 Electrical energy can be derived from the combustion of fossil fuels or from electrochemical reactions. What are the similarities and differences in these reactions?

#### Voltaic cells

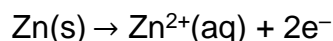
- Voltaic cells are also known as primary cells, galvanic cells or batteries.
- Voltaic cells are composed of two half cells, a salt bridge and an external circuit.
- A half-cell is an electrode (usually a metal) in a solution of its own ions.
- The metal higher up in the activity series (the more reactive metal) will be the anode.
- The metal lower down in the activity series (the less reactive metal) will be the cathode.
- The example below shows a voltaic cell made from a zinc half-cell and a copper half-cell.
- Zinc is above copper in the activity series, so the zinc half-cell is the anode and the copper half-cell is the cathode.



### At the anode (oxidation)



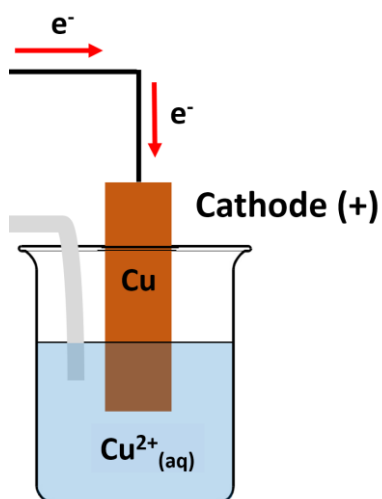
The Zn(s) undergoes oxidation.



The electrons flow in the wire to the cathode (copper half-cell).

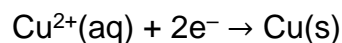
The mass of the zinc electrode decreases.

### At the cathode (reduction)

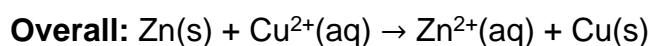
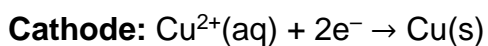
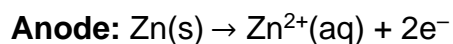


Electrons flow to the cathode from the anode.

The Cu<sup>2+</sup>(aq) ions undergo reduction.



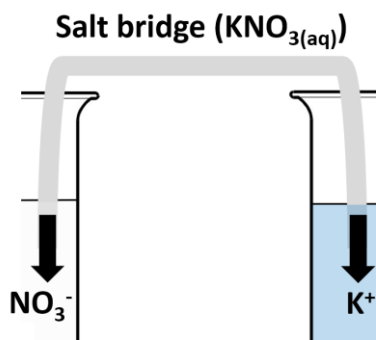
The mass of the copper electrode increases.





## Salt bridge

- The salt bridge allows movement of ions between half-cells which balances the charge and completes the circuit.
- Positive ions flow to the cathode and negative ions flow to the anode.



## Summary

- Oxidation occurs at the anode (negative electrode).
- Reduction occurs at the cathode (positive electrode).
- Current is conducted by electron flow in the external circuit (from the anode to cathode) and movement of ions in the salt bridge.
- Cations (positive ions) move in the salt bridge to the cathode.
- Anions (negative ions) move in the salt bridge to the anode.

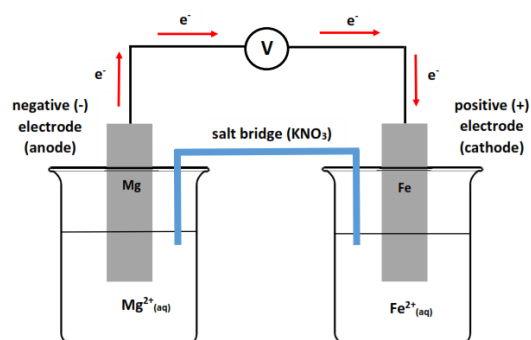
## Cell diagram convention

- The species on the left is oxidised (Zn) and the species on the right is reduced (Cu<sup>2+</sup>).
- The double vertical line represents the salt bridge.



**Exercise:** Magnesium is higher in the activity series than iron. Draw an annotated diagram of a voltaic cell made from a magnesium half-cell and an iron half-cell. Write half equations for the reactions that occur in each half-cell and describe how the current is conducted.

Mg is higher in the activity series than Fe, therefore Mg is oxidized at the anode and Fe<sup>2+</sup> ions are reduced at the cathode.



At the anode (oxidation):  $\text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^{-}$

At the cathode (reduction):  $\text{Fe}^{2+}(aq) + 2e^{-} \rightarrow \text{Fe}(s)$

Overall reaction:  $\text{Mg}(s) + \text{Fe}^{2+}(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Fe}(s)$

Anions move in the salt bridge from cathode to anode.

Cations move in the salt bridge from anode to cathode.

Electrons flow in the wires from anode to cathode.

### **Reactivity 3.2.7**

#### **Understandings:**

- Secondary (rechargeable) cells involve redox reactions that can be reversed using electrical energy.

#### **Learning outcomes:**

- Deduce the reactions of the charging process from given electrode reactions for discharge, and vice versa.

#### **Additional notes:**

- Include discussion of advantages and disadvantages of fuel cells, primary cells and secondary cells.

#### **Linking questions:**

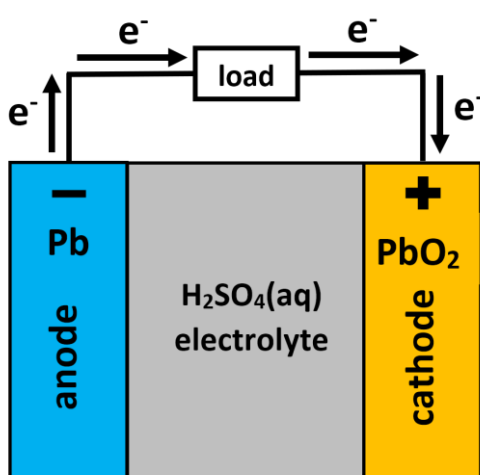
- Reactivity 2.3 Secondary cells rely on electrode reactions that are reversible. What are the common features of these reactions?

## Primary and secondary cells

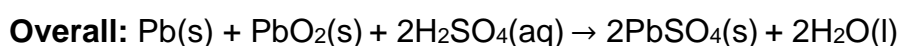
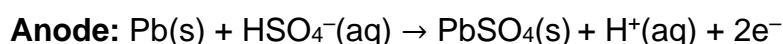
- In a primary cell, the electrochemical reaction is not reversible.
- Primary cells are designed to be used once and then discarded.
- Secondary cells are rechargeable – they involve redox reactions that can be reversed using electricity.
- Examples of secondary cells include lead-acid and lithium-ion batteries.

## Lead-acid battery

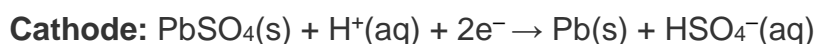
- Lead-acid batteries have a Pb anode, a PbO<sub>2</sub> cathode and electrolyte is H<sub>2</sub>SO<sub>4</sub>(aq).
- The H<sub>2</sub>SO<sub>4</sub> is used up when the battery produces a current.



- When being discharged the following reactions take place.

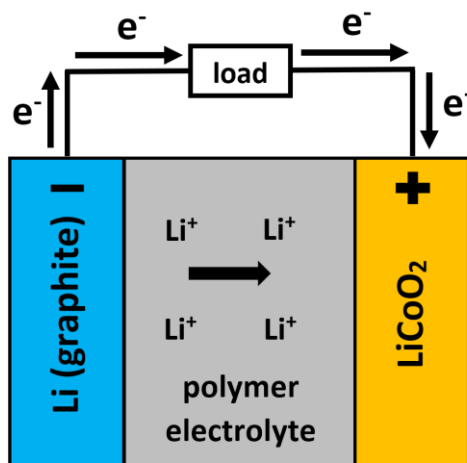


- When being recharged the following reactions take place.

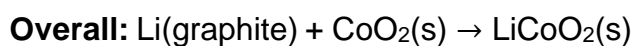
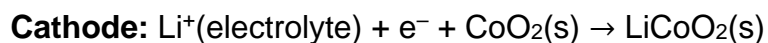
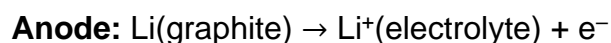


## Lithium-ion battery

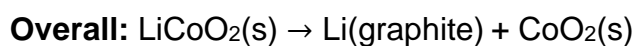
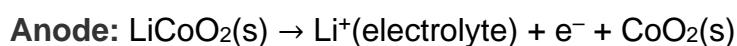
- Lithium-ion batteries use lithium atoms absorbed into a lattice of graphite electrodes for the anode and a lithium cobalt oxide complex ( $\text{LiCoO}_2$ ) for the cathode.



- When being discharged the following reactions take place.



- When being recharged the following reactions take place.



### Advantages and disadvantages of secondary cells

Type of cell	Advantages	Disadvantages
Lead-acid	Easy to manufacture, low cost and have low self-discharge rates.	Lead is toxic. Overcharging can produce hydrogen gas which is an explosion risk.
Lithium-ion	High energy density and low discharge rates.	Explosion risk and difficult to extinguish lithium fires.

### Comparison of primary, secondary and fuel cells.

- Primary cells can only be used once and are discarded; however, they are cheap and portable.
- Secondary cells can be recharged e.g., lithium-ion batteries are suitable for use in electrical devices.
- Some secondary cells contain toxic metals such as lead.
- Hydrogen fuel cells need a constant source of fuel to produce an electric current.
- The fuel, hydrogen gas, is highly flammable and care must be taken with its handling and storage to prevent accidents.
- Fuel cells require expensive metal catalysts such as platinum.
- Direct methanol fuel cells produce carbon dioxide, a potent greenhouse gas.

### Reactivity 3.2.8

#### Understandings:

- An electrolytic cell is an electrochemical cell that converts electrical energy to chemical energy by bringing about non-spontaneous reactions.

#### Learning outcomes:

- Explain how current is conducted in an electrolytic cell.  
Deduce the products of the electrolysis of a molten salt.

#### Additional notes:

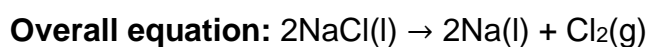
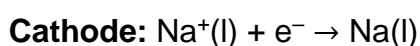
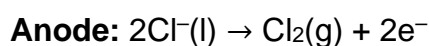
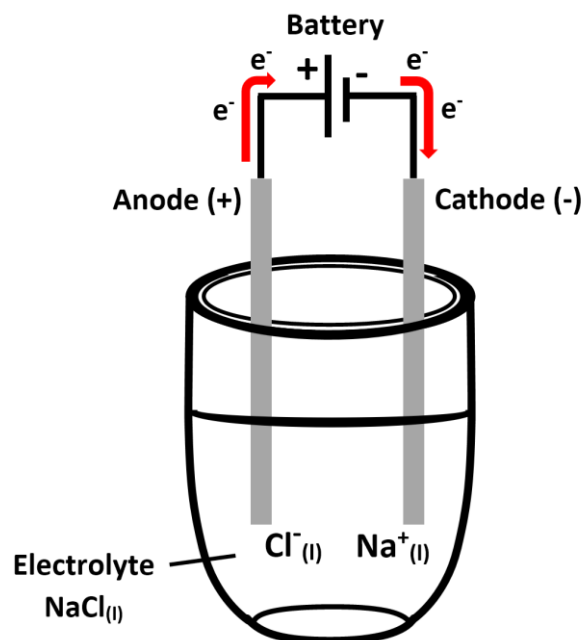
- Construction of electrolytic cells should include: DC power source connected to anode and cathode, electrolyte.

#### Linking questions:

- Structure 2.1 Under what conditions can ionic compounds act as electrolytes?

## Electrolytic cells

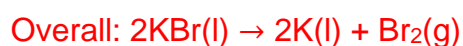
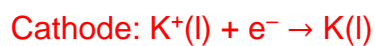
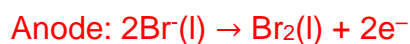
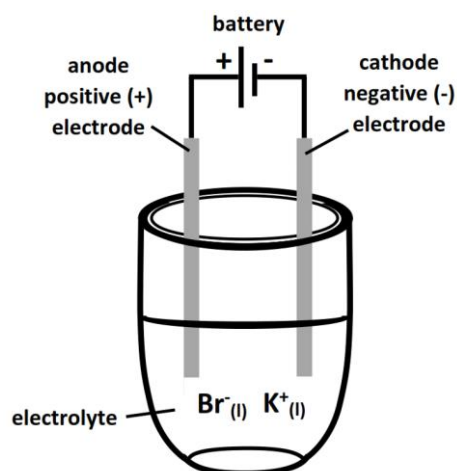
- An electrolytic cell uses a single container in which an ionic compound is heated until it melts (becomes molten).
- An electric current is supplied from a battery and the oppositely charged ions are attracted to the anode or cathode where they are either oxidised or reduced.
- Current is conducted by electron flow in the wires and ion flow in the electrolyte.



- The ratio of Na to  $\text{Cl}_2$  is 2:1

## Exercises:

- 1) Draw a diagram of apparatus that could be used to electrolyse molten potassium bromide, KBr. Label the diagram to show the polarity of each electrode and the product formed. Write half equations to show the formation of the product at each electrode.



molar ratio K : Br<sub>2</sub> = 2:1

- 2) Describe the two ways in which the current is conducted in an electrolytic cell.

Electrons flow through the wires and ions move through the electrolyte.



### Reactivity 3.2.9

#### Understandings:

- Functional groups in organic compounds may undergo oxidation.

#### Learning outcomes:

- Deduce equations to show changes in the functional groups during oxidation of primary and secondary alcohols, including the two-step reaction in the oxidation of primary alcohols.

#### Additional notes:

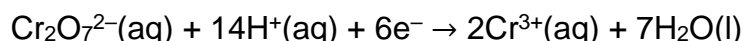
- Include explanation of the experimental set-up for distillation and reflux.
- Include the fact that tertiary alcohols are not oxidized under similar conditions.
- Names and formulas of specific oxidizing agents and the mechanism will not be assessed.

#### Linking questions:

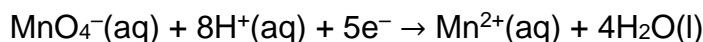
- Structure 3.2 How does the nature of the functional group in a molecule affect its physical properties, such as boiling point?
- Reactivity 1.3 What is the difference between combustion and oxidation of an alcohol?

## Oxidation reactions of the alcohols

- Alcohols undergo oxidation reactions when reacted with a suitable oxidising agent such as acidified potassium dichromate(VI),  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ .
- Colour change is orange to green ( $\text{Cr}_2\text{O}_7^{2-}$  ion is reduced to the  $\text{Cr}^{3+}$  ion).

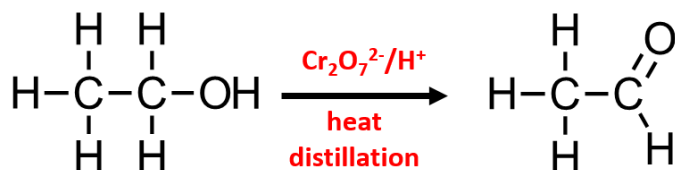


- An alternative oxidising agent is acidified potassium manganate(VII) solution which changes colour from purple to colourless as the manganate(VII) ion,  $\text{MnO}_4^-$ , is reduced to the manganese(II) ion,  $\text{Mn}^{2+}$ .

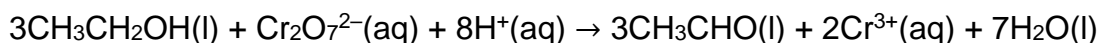


## Primary alcohols

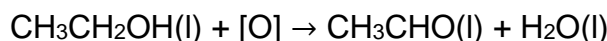
- Primary alcohols undergo partial oxidation to form aldehydes.



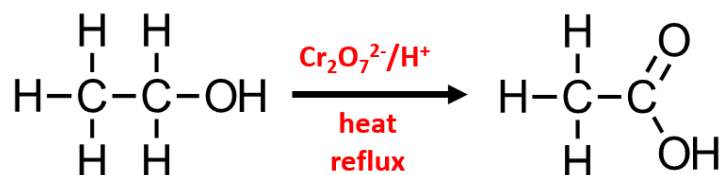
- An excess of alcohol is used in the reaction and the aldehyde is distilled off as it is produced.
- The balanced redox equation is as follows.



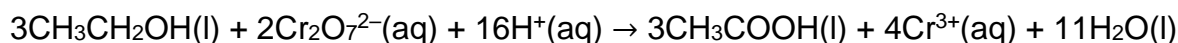
- The simplified equation is as follows, where [O] represents the oxidising agent.



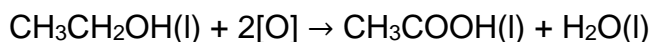
- Primary alcohols can also undergo complete oxidation to form carboxylic acids.



- An excess of oxidising agent is used in the reaction.
- The balanced redox equation is as follows.

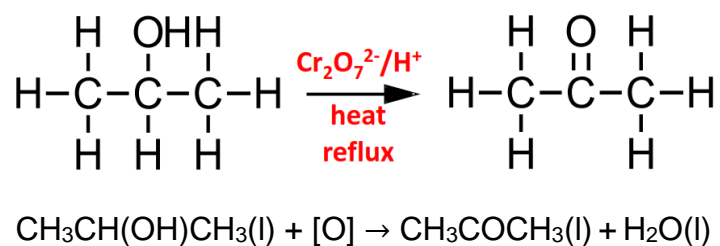


- The simplified equation is as follows, where [O] represents the oxidising agent.



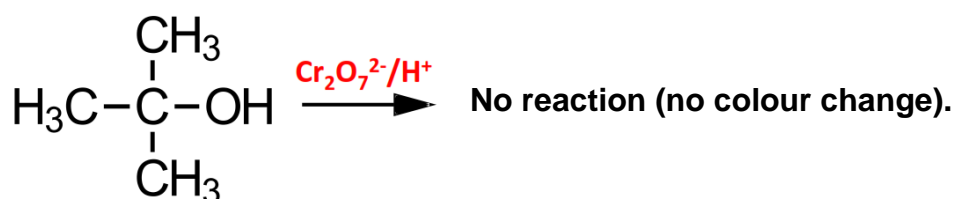
## Secondary alcohols

- Secondary alcohols are oxidised by acidified potassium dichromate(VI) ( $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ ) and heat to form ketones.



## Tertiary alcohols

- Tertiary alcohols do not undergo oxidation because there are no H atoms bonded directly to the C-OH.



## Distillation

- Distillation is used to separate the components of a mixture that have different boiling points.
- Aldehydes, due to their weaker intermolecular forces, have lower boiling points than alcohols.
- The aldehyde evaporates, rises up the fractionating column and condenses to form a liquid.

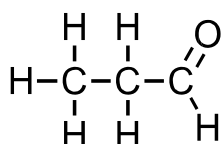
## Reflux

- A reflux condenser is used to prevent the loss of a solvent from a mixture.
- The vapours rise up the column, condense, and flow back down to the flask.
- The reaction mixture and oxidising agent are kept in contact for a longer period of time.

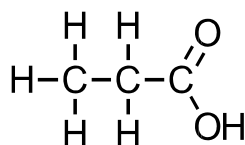
**Exercises:** Propan-1-ol and propan-2-ol are two structural isomers of C<sub>3</sub>H<sub>8</sub>O. Both propan-1-ol and propan-2-ol can be oxidised in aqueous solution.

- (a) When propan-1-ol is oxidized using a warm acidified solution of potassium dichromate(VI) two different organic products can be obtained. Deduce the name and structural formula for each of these two products.

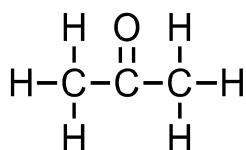
Propanal CH<sub>3</sub>CH<sub>2</sub>CHO



Propanoic acid CH<sub>3</sub>CH<sub>2</sub>COOH



- (b) Identify the class of alcohols that propan-2-ol belongs to and state the name of the organic product formed when it is oxidized by an acidified solution of potassium dichromate(VI).



Propan-2-ol is a secondary alcohol  
oxidises to propanone

### Reactivity 3.2.10

#### Understandings:

- Functional groups in organic compounds may undergo reduction.

#### Learning outcomes:

- Deduce equations to show reduction of carboxylic acids to primary alcohols via the aldehyde, and reduction of ketones to secondary alcohols.

#### Additional notes:

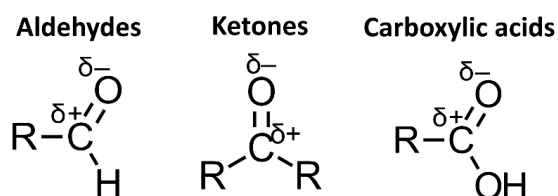
- Include the role of hydride ions in the reduction reaction.
- Names and formulas of specific reducing agents and the mechanisms will not be assessed.

#### Linking questions:

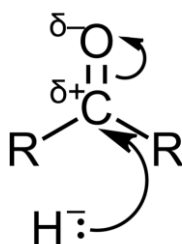
- Structure 3.1 How can oxidation states be used to show that the following molecules are given in increasing order of oxidation: CH<sub>4</sub>, CH<sub>3</sub>OH, HCHO, HCOOH, CO<sub>2</sub>?

### Reduction of carbonyl compounds

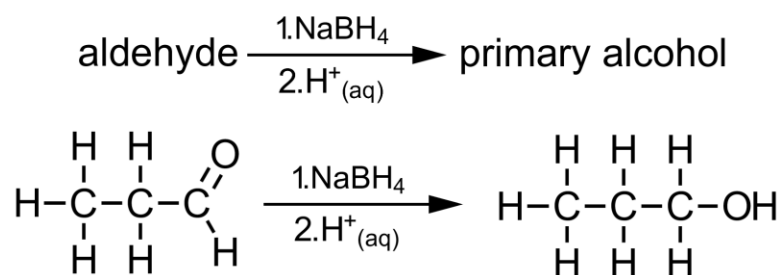
- Carbonyl compounds are compounds that contain a carbonyl group (C=O).



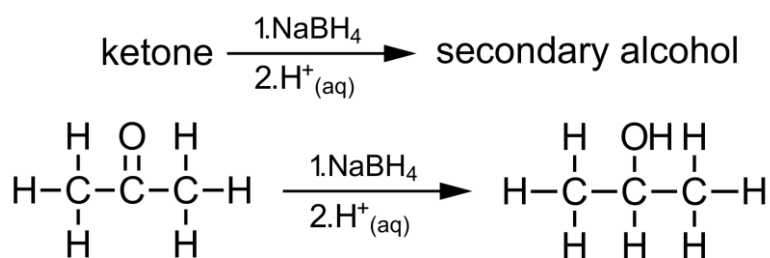
- Primary and secondary alcohols can be oxidised to aldehydes, ketones or carboxylic acids depending on the conditions; these oxidation reactions can be reversed by using a suitable reducing agent.
- The reducing agents used are either sodium borohydride (NaBH<sub>4</sub>), in aqueous or alcoholic solution (protic solvent) or lithium aluminium hydride (LiAlH<sub>4</sub>) in anhydrous conditions such as dry ether (aprotic solvent). The reaction is then acidified to obtain the product.
- These reducing agents provide hydride ions (H<sup>-</sup>) that act as nucleophiles **and** undergo a nucleophilic addition reaction with the electron deficient carbon atom of the carbonyl group.



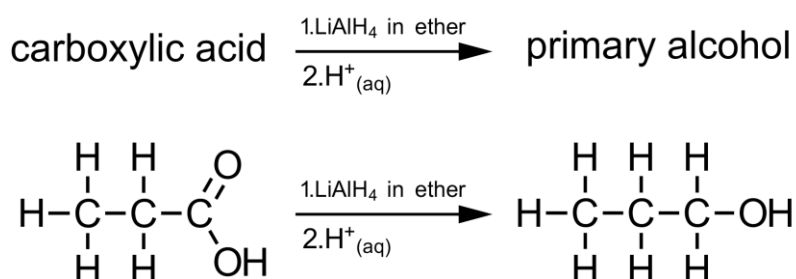
### Reduction of aldehyde to primary alcohol



### Reduction of ketone to secondary alcohol



### Reduction of carboxylic acid to primary alcohol (via the aldehyde)



- Conditions: heat with  $\text{LiAlH}_4$  in dry ether, then acidify ( $\text{NaBH}_4$  is not a strong enough reducing agent to reduce carboxylic acids).
- Note that the reduction reaction first involves the formation of an aldehyde, but because lithium aluminium hydride reacts rapidly with aldehydes, it is not possible to stop the reaction at this point.

### Summary:

Reactant	Reducing agent	Product
Aldehyde	$\text{NaBH}_4$ or $\text{LiAlH}_4$	Primary alcohol
Ketone	$\text{NaBH}_4$ or $\text{LiAlH}_4$	Secondary alcohol
Carboxylic acid	$\text{LiAlH}_4$ only	Primary alcohol (via the aldehyde)

### Reactivity 3.2.11

#### Understandings:

- Reduction of unsaturated compounds by the addition of hydrogen lowers the degree of unsaturation.

#### Learning outcomes:

- Deduce the products of the reactions of hydrogen with alkenes and alkynes.

#### Linking questions:

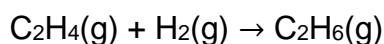
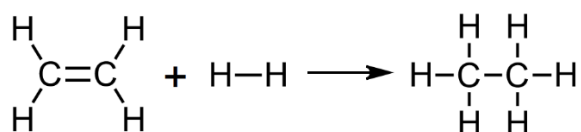
- Reactivity 3.4 Why are some reactions of alkenes classified as reduction reactions while others are classified as electrophilic addition reactions?

#### Degree of unsaturation

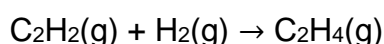
- The degree of unsaturation, also known as the index of hydrogen deficiency (IHD), is a count of how many molecules of H<sub>2</sub> need to be added to convert the molecule to the corresponding saturated, non-cyclic molecule.
- Unsaturated compounds such as alkenes and alkynes have carbon to carbon double bonds and carbon to carbon triple bonds respectively.
- The degree of unsaturation (IHD) of a molecule with one carbon to carbon double bond is one.
- The degree of unsaturation (IHD) of a molecule with one carbon to carbon triple bond is two.

#### Addition reactions of unsaturated compounds with hydrogen (hydrogenation)

- Alkenes and alkynes react with hydrogen in the presence of a catalyst and at high pressures and temperatures.
- These are electrophilic addition reactions.
- Example – the reaction of ethene, C<sub>2</sub>H<sub>4</sub>, with hydrogen produces ethane, C<sub>2</sub>H<sub>6</sub>.



- The degree of unsaturation has decreased from one to zero.
- Ethyne, C<sub>2</sub>H<sub>2</sub>, reacts with hydrogen to produce ethene.



- The degree of unsaturation has decreased from two to one.