

Catalysis Web Pages for Pre-University Students V1_0

By Tim Harrison

Bristol ChemLabS, School of Chemistry, University of Bristol

May 2014



Table of Contents

| | |
|---|----|
| Introduction | 3 |
| Rates of reactions and catalysis | 4 |
| The Arrhenius equation | 4 |
| Equilibrium and catalysis | 5 |
| Autocatalytic processes | 5 |
| Aspirin | 5 |
| Manganate (VII) ions and ethandioic (oxalic) acid | 5 |
| Tin pest..... | 5 |
| Transition chemistry and catalysis..... | 6 |
| Homogenous and heterogeneous catalysis..... | 6 |
| Homogeneous catalysis | 6 |
| Heterogeneous catalysis | 6 |
| Surface area and heterogeneous catalysts..... | 7 |
| Examples of traditional industrial processes that use catalysis..... | 8 |
| The polymerisation of ethane to form polythene | 8 |
| The manufacture of sulfuric acid | 8 |
| The Manufacture of Ammonia- The Haber Process | 8 |
| Catalytic hydrogenation of vegetable oils in margarine manufacture | 8 |
| Did you know?..... | 9 |
| Catalytic converters in car exhausts | 9 |
| Organic chemistry and catalysis..... | 10 |
| Hydrogenation of an alkene to form an alkane..... | 10 |
| Alcohol Production from alkenes..... | 10 |
| Reactions of primary, secondary and tertiary alcohols with hydrogen halides: the Lucas test ... | 10 |
| Oxidation of alcohols to carbonyls..... | 11 |
| Esterification | 11 |
| Alkene formation from alcohols | 11 |
| Friedel–Crafts reactions..... | 11 |
| Atmospheric chemistry, ozone and catalysis..... | 12 |
| Enzymes | 13 |
| Green chemistry and catalysis | 14 |
| Current research in catalysis..... | 15 |
| Butan-1-ol: An Advanced Biofuel? | 15 |

Acknowledgements..... 16

Introduction

Catalysis, the study and use of catalysts, is an extremely important facet of the world's chemical industry. Put simply, catalysts speed up chemical reactions and therefore enable more chemicals to be made in a shorter time, usually with less energy input, so that more profit can be made more quickly. Catalysts also have a major role to play in making a greener environment through greater yields of product, the reduction in use of scarce resources (both chemical and energy) and in the limiting waste. This reflects several of the Principles of Green Chemistry.

Pre-university students working through this resource should gain an excellent understanding of the basics of catalysis.

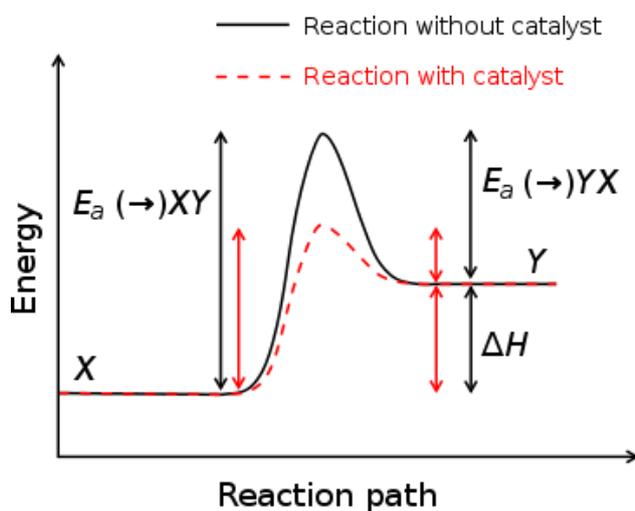
Rates of reactions and catalysis

An understanding of catalysis must start with an understanding of reactions and the factors that determine how fast reactions occur, if they occur at all.

For two chemicals react they must collide with sufficient energy. Most collisions between particles have insufficient energy to rearrange bonds. The minimum energy to react is called the activation energy, E_a . Once the activation energy barrier has been reached bonds are rearranged and energy can be released. In exothermic reactions all the activation energy is released and more. The excess energy is the heat of reaction. In endothermic reactions not all the activation energy is released: some is retained.

Catalysts work by providing an alternative reaction pathway with a lower activation energy. The lowering of the activation energy barrier results in more molecules having sufficient energy to react at any instant hence a faster reaction rate.

Table: An energy level diagram showing the effect of catalysis on reaction pathway. Taken from 1 http://upload.wikimedia.org/wikipedia/commons/thumb/2/24/Activation_energy.svg/540px-Activation_energy.svg.png



The catalyst speeds up a reaction without being consumed by the overall reaction; in other words there is as much catalyst at the end of reaction as at the start. In a homogenous reaction the catalyst takes part in the reaction and gets regenerated.

Catalysts can be transition metals or their compounds but they are not limited to this grouping. Protons (H^+), iodide ions, aluminium and proteins naming just a few examples of non-transition elements can be catalysts too.

The Arrhenius equation

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.

From the Arrhenius equation, the activation energy, E_a , can be expressed as

$$k = Ae^{-E_a/RT}$$

R is the Universal gas constant, T is the temperature (in kelvin), A is the frequency factor for the reaction and k is the reaction rate coefficient.

Equilibrium and catalysis

Many catalysed industrial processes are equilibria. It is important to note:

- A catalyst does not affect the position of equilibrium.
- The value of the equilibrium constant, K_c , is not affected by changes either in concentration or the addition of a catalyst
- Catalysis does affect the time taken to reach equilibrium as it reduces the time needed.

Autocatalytic processes

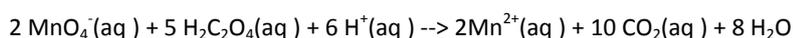
A chemical reaction is said to be autocatalytic, if a reaction product itself is the catalyst for the reaction in which it is made.. There are a few examples of this unusual catalytic activity.

Aspirin

Formulations containing high concentrations of aspirin often smell like vinegar because aspirin can decompose through hydrolysis in moist conditions, yielding salicylic (2-hydroxybenzoic acid) and ethanoic acid. The ethanoic acid created by hydrolysis can then bring about catalysed de-esterification.

Manganate (VII) ions and ethandioic (oxalic) acid

The classic example of autocatalysis is the reaction between manganate (VII) ions and ethandioic (oxalic) acid. The manganese (II) ions formed are a catalyst for the redox reaction.



This is an example of a homogenous catalysis so the reaction rate is dependent on the concentration of the catalyst, which itself increases in time. An intermediate, red in colour, is $[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}$.

Tin pest

Tin pest is an autocatalytic, allotropic transformation of the element tin. This causes deterioration of old tin objects at low temperatures. Tin pest is also called tin disease, tin blight or tin leprosy. Below 13.5 °C pure tin transforms from the β -form white metallic tin allotrope which is ductile to the brittle, non-metallic, α -form grey tin. Once the grey form of tin forms it autocatalyses the allotrope interconversion.

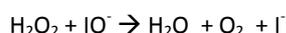
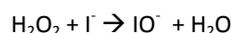
Transition chemistry and catalysis

Homogenous and heterogeneous catalysis

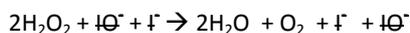
Homogeneous catalysis

Homogeneous catalysis is where the catalysts and reactants are in the same state/phase, the reaction proceeds through an intermediate. The rate of reaction is dependent on the concentration of the catalyst.

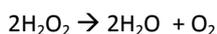
E.g the decomposition of hydrogen peroxide solution using potassium iodide solution



Adding the two equations together and eliminating iodide and iodate common factors:



Nett reaction:



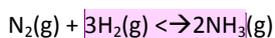
The catalyst is not used up but did provide an alternative chemical pathway.

Heterogeneous catalysis

Heterogeneous catalysis is where the catalyst in a different state of matter or 'phase' to that of the reactants. Often industrially heterogeneous catalysts are the d-block elements (also called transition metals).

Examples:

1. In the manufacture of the liquid methanol from the gases carbon monoxide and hydrogen solid chromium (VI) oxide, Cr_2O_3 , is used as a catalyst.
2. Iron, a solid, is used in the to manufacture ammonia where the reactants are both gases;



Here the transition metal provides a surface ('reaction site') for the reaction to occur. The reactant gases are both adsorbed on to the metal surface forming weak bonds with vacant d orbitals, and react at lower energy. The products then desorb from the surface.

Comment [TGH1]: Equil sign needed

Surface area and heterogeneous catalysts

Factors increasing available surface area favour increased reaction rates and vice versa. Whilst taking a block and powdering it up will make far more surface the effective surface will not be as great as the theoretical maximum. This is because some particles of powder will lie on top of others. When using gases under pressure it is inadvisable to use powdered catalysts as they are likely to be blown through the industrial pipework. Instead an inert (unreactive) support medium to maximise the surface area is used. A thin film of the catalyst (e.g. platinum/palladium/rhodium) is coated onto ceramic support in a car's catalytic converters exhaust. The use of support materials not only increases available surface but decreases the overall cost of the expensive catalysts as less is used. Other support materials can include coated glass wool, coated beads and, in the past, coated asbestos.

In acting as a catalytic surface the bonding of the reactant to the surface must be weak enough for adsorption and desorption to take place but strong enough to weaken bonds and allow the desired reaction to take place.

Catalysts can become poisoned by impurities. This reduces their efficiency and subsequently has a cost implication for reduced product formation, or for the disposal and replacement of the catalysts. Examples include the poisoning by sulfur in the Haber Process and by lead in car's catalytic converters.

Examples of traditional industrial processes that use catalysis

The polymerisation of ethane to form polythene

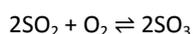
Titanium (III) chloride, (TiCl₃), titanium (IV) chloride (TiCl₄) and aluminium triethyl (Al₂(CH₃CH₂)₃) are Ziegler-Natta catalysts and are used in the polymerisation of ethene, C₂H₄, (an alkene) to high density poly(ethane). The pressure used is 50-75 °C. Poly(ethene), more commonly called polythene, is one of the world's top ten most used polymers.

Ziegler and Natta separately worked on the polymerisation of ethene and propene and were jointly awarded the Nobel Prize for their catalysis work in 1963.

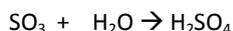
The manufacture of sulfuric acid

The traditional example of catalysis in the manufacture of another of the world's bulk chemicals is the Contact process for the manufacture of sulfuric acid. It used to be said that one measure of a country's wealth was its output of sulfuric acid.

In the three step process sulfur, or a sulfide is roasted (oxidised through reaction with air) to sulfur dioxide, SO₂. Further oxidation to sulfur trioxide requires catalytic oxidation. This uses vanadium (V) oxide, V₂O₅, but could use the more expensive platinum metal. This step is the Contact process:

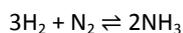


The SO₃ is then dissolved in a 98% sulfuric acid: 2% water mixture to make 98.5% sulfuric acid which is then diluted to make more 98% sulfuric acid.



The Manufacture of Ammonia- The Haber Process

Ammonia is another of the world's bulk chemicals and is important for a wide range of uses from producing synthetic fertilisers, dyestuffs, explosives, polymers and many more. It is the direct combination of two non-metal elements which will not occur efficiently unless catalysed at the correct temperature (~400-450 °C) and high pressure. The catalyst is simply iron.



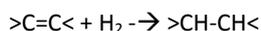
The catalyst does not increase the yield of the reaction but just decreases the time it takes to reach equilibrium. At equilibrium the catalyst increases the rate of the reaction reactants to products at the same rate as the back reaction, products to reactants.

Catalytic hydrogenation of vegetable oils in margarine manufacture

Unsaturated vegetable oils contain alkenic (carbon to carbon double bonds). Being an oil they are in the liquid state at room temperature. The cis and trans structures of the alkenes does not allow molecules to come close together for sufficiently strong intermolecular bond to occur hence they

are liquids. If the fatty acids are made saturated by the addition of hydrogen across the alkene the molecular shape change will allow the molecules to come much closer together and stronger intermolecular bonding can now occur. The result is a solid that at room temperature is not too far from its melting point so can spread easily.

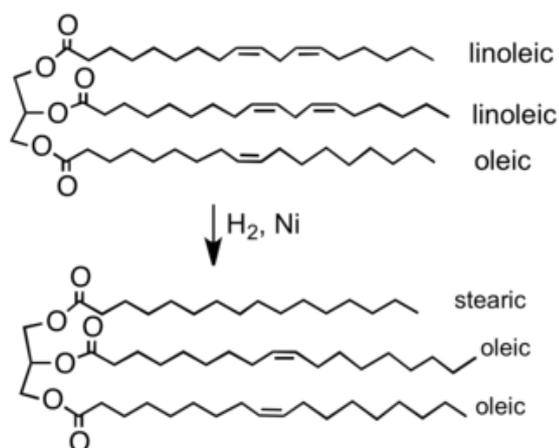
In the catalytic hydrogenation of oils, nickel is used as the catalyst. The reaction can be represented as:



Table

2:

<http://upload.wikimedia.org/wikipedia/commons/thumb/1/1a/H2forMargerin.png/480px-H2forMargerin.png>



Did you know?

Margarine was invented by a French chemist, Michel Eugène Chevreul in 1813 of margaric acid (later determined to be a mixture of stearic and palmitic acids) in response to a challenge laid down by Emperor Napoleon III of France who offered a prize to anyone who could make a satisfactory alternative for butter.

At one time in the USA margarine came with yellow food colour separately added so the customer could colour the off white (lard looking) solid to make it look like butter. It was the American dairy farmers, afraid of the competition with butter markets, which made it illegal for margarine to be sold ready-coloured.

Catalytic converters in car exhausts

Essentially a catalytic converter decreases carbon monoxide and nitrogen monoxide emissions from vehicle's internal combustion engines by three steps: (a) adsorption of carbon monoxide, CO, and nitrogen oxide, NO, to the catalyst's surface, (b) the chemical reaction, and (c) the desorption of CO₂ and N₂ from the catalyst surface.

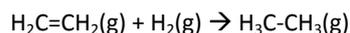
There is more than one type of catalytic converter in vehicle exhaust systems. Other catalysts present may oxidise unburnt hydrocarbons and/or toxic carbon monoxide from the fuel both to carbon dioxide.

Organic chemistry and catalysis

Many organic synthesis steps involve catalysis. Some common reaction steps are discussed below.

Hydrogenation of an alkene to form an alkane

The addition of hydrogen with a nickel catalyst at 300 °C to form an alkane



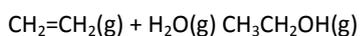
The nickel is usually finely divided and named Raney Nickel –after its inventor. Both palladium, Pa, and platinum, Pt, can catalyse this reaction at room temperature but are far more expensive to purchase.

This is of industrial importance in the hydrogenation of unsaturated vegetable oils in the manufacture of margarine-see elsewhere in this resource.

Alcohol Production from alkenes

The industrial manufacture of ethanol can be from ethene not just by fermentation.

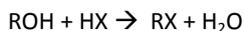
Steam and ethene under pressure are passed over a catalyst of phosphoric acid at a temperature of 300°C,



A pressure of 60-70 atmospheres, and a steam:ethene ratio of 0.6:1 are also used. The steam and ethene are recycled as there is only about 5% conversion per pass.

Reactions of primary, secondary and tertiary alcohols with hydrogen halides: the Lucas test

The general reaction, catalysed by anhydrous zinc chloride, is:



Where, X = -Cl, -Br or -I.

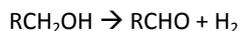
The alcohol is treated with anhydrous zinc chloride in concentrated hydrochloric acid.

Tertiary alcohols react quickly to form an insoluble, tertiary chloride compound, R₃C-Cl. The result is an almost instant cloudiness in the solution. The secondary alcohol will give delayed cloudiness and the primary alcohol gives no indication of reaction.

The test is based on the relative stabilities of carbocations formed during the reaction mechanism.

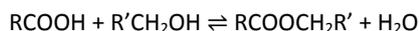
Oxidation of alcohols to carbonyls

One way of preparing aldehydes and ketones (other than oxidation of alcohols using acidified dichromate ions) is through passing the alcohol vapour over a copper catalyst at 500 °C.



Esterification

In the formation of an ester from a carboxylic acid and an alcohol, concentrated sulfuric acid or concentrated hydrochloric acid. The inorganic acid behaves as a homogeneous catalysis being involved in protonation of the alcohol in the mechanism.



In the alternative Fischer-Speier method dry hydrogen chloride gas is used as the catalyst to form an ester.

Alkene formation from alcohols

Alkenes can be formed from alcohols by elimination using concentrated phosphoric acid, H_3PO_4 or concentrated sulfuric acid, H_2SO_4 is usually the catalyst.

This provides a potential route for monomer formation making it possible to produce polymers without using monomers derived from oil.

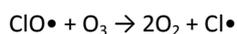
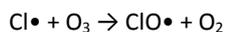
Friedel-Crafts reactions

The difficulty of plugging groups of atoms into a benzene ring is overcome using the Friedel-Crafts reactions. The group to be added should be attached to a halogen such as the chloro or bromo group. This is then worked up with a 'a halogen carrier' catalysts such as anhydrous aluminium chloride or iron (III) bromide before reacting with arenes (such as benzene or methyl benzene) through an electrophilic substitution reaction.

If the acylation (addition of $-\text{COCH}_3$) of benzene is taken as an example ethanoyl chloride is reacted with aluminium chloride, AlCl_3 . The chlorine from the ethanoyl chloride forms a dative covalent bond with the 'gap' in outer shell of the aluminium. The resulting rearrangement forms a positive charge on the carbonyl carbon. The electrophile created is attracted to the delocalised electrons in the ring. The resultant bond rearrangement causes the benzene to eliminate a hydrogen ion (H^+) as the acyl group takes its place. AlCl_3 .

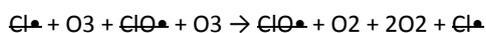
Atmospheric chemistry, ozone and catalysis

Chlorine atoms can exist in the atmosphere from the photolysis (breakdown using sunlight) of halocarbons and CFCs. Chlorine atoms are free radicals as they contain unpaired electrons. They catalyse the decomposition of ozone and contribute to the formation of a hole in the ozone layer

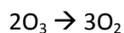


This is an example of homogenous catalysis: the chlorine atom used in the first reaction is regenerated in the second.

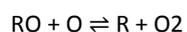
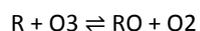
The overall reaction can be found by adding the two equations together and eliminating reactants and products from either side of the 'arrow'.



Becoming



Free radicals, eg from CFCs, and NO_x from thunderstorms or aircraft also catalyse the breakdown of ozone by the following simple representation:



where R represents Cl \cdot from a CFC or NO from nitrogen oxides.

Enzymes

Enzymes are often referred to as biological catalysts. Enzymes are proteins whose shape allows reactions to occur on their surfaces. Reactions in living bodies, ('life processes') are controlled by enzymes. Enzymes have been adapted to work in processes in the chemical industry such as in fermentation.

As the catalytic activity of enzymes depends on shape, and that shape is determined mainly by weak intermolecular bonding, it should be of no surprise that factors that alter the shape of enzymes slow or stop its catalytic activity. The action of an enzyme being determined by shape is usually referred to as the 'lock and key' model. Full discussion is beyond the scope of this resource.

Fermentation is the enzymic process that, in anaerobic conditions (no oxygen), converts glucose (a simple sugar) into ethanol and carbon dioxide using an enzyme found in yeast:

Equation: $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH$ and $2CO_2$

This important industrial process is the basis of the brewing, wine making and bread making industries. It can also be used to make biofuels such as methylated spirits and for solvent formation.

The enzyme involved in fermentation which is found in the yeast, 'zymase', is one of the first studied enzymes. This process serves to show the main differences between enzymes and inorganic catalysts. The enzyme has a narrow temperature range over which it functions with an optimum temperature at which there is a maximum rate of reaction. Heating an enzyme changes its shape and stops it working. This is referred to as denaturing. Inorganic catalysts increase reaction rate with increased temperature.

Changes in pH can also cause shape changes in the protein structure for the enzyme again stopping reaction. Enzymes therefore have an optimum pH at which they work the best.

In alcohol fermentation the product, ethanol, reaches a maximum of ~15% yield before the yeast is poisoned and the reaction stops working. Inorganic catalysts are poisoned when their surfaces become coated in a material that does not leave space for the desired reactions to occur.

Many diseases and symptoms are caused by enzymes that stop working properly or are turned on. Control of such processes by chemicals is the basis of much of the pharmaceutical industry.

There is much interest in extremophile organisms, those that survive in conditions usually hostile to life. Extremophiles can live in acidic, alkaline conditions, under extreme pressure or in hot or cold conditions. Enzymes from such organisms are already in industrial use such as in the manufacture of stone wash jeans where an enzyme from a thermoalkalophile is used to break down the indigo dye.

Green chemistry and catalysis

Catalysis affects the conditions that are needed in chemical reactions. Catalytic reactions often require lower temperatures and pressures and therefore reduce energy demand. Consequently less CO₂ emissions are produced from the burning of fossil fuels resulting in less climate change potential.

However there is an energy requirement in the mining and processing of the usually rare elements, such as platinum, in the first place. Ideally catalysts would all be from less rare metals such as iron.

The disposal of some currently used catalysts also poses an environmental problem as they, or the compounds formed on them may be toxic.

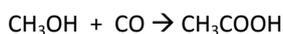
An example of a green use of catalysis is the conversion of (waste) vegetable oils into biodiesel by reaction with methanol in the presence of a catalyst. Biodiesel can be thought of as the methyl esters of fatty acids.

Current research in catalysis

The considerable importance of finding new and better catalysts, including the use of enzymes, in achieving many of the goals of green chemistry, cannot be underestimated. Large sums of money are being spent on research into catalysis allowing reactions to happen at lower temperatures and at lower pressure (therefore consuming less energy) and using more commonly available compounds or less environmentally hazardous compounds as catalysts/. Other researchers are looking at creating new catalysts for desirable reactions that cannot yet be done efficiently. Some of these new catalysts will involve catalysis by enzymes from extremophiles using milder conditions which save on energy and other expenses.

All these new developments are designed to make the chemical industry; more profitable with reduced energy and materials costs and more green in general.

One example is the development of new catalysts for ethanoic acid production from methanol and carbon monoxide (with a high atom economy).

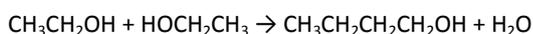


Butan-1-ol: An Advanced Biofuel?

The following article was adapted from the Science for All blogsite article (2013) of the same name by Tim Harrison and Duncan Wass and published in Brazil can be found at: <http://www.ccell11.com/2013/06/t71-butan-1-ol-advanced-biofuel-by-tim.html#ING>

Ethanol is a biofuel and has been known about since antiquity. It is produced by many fermentation processes. Ethanol in alcoholic drinks, such as beer and wine, is produced from the sugars in vegetable matter such as fruits. Ethanol can also be produced from other vegetable matter including some grasses and even corn husks. Vehicles that use 100% ethanol (E100) can be used where the engines are specifically designed for this fuel. In many countries, low-ethanol mixtures, known as gasohol, from E5 to E25, have been available since the late 1970s. However Ethanol is not a particularly good fuel but butan-1-ol is.

It has long been the target of the chemical industry to be able to make butan-1-ol by condensing two ethanol molecules together.



Butan-1-ol (29.2 MJ/l) would be a much better fuel additive than ethanol (19.6 MJ/l) as it has properties more aligned with petrol (32.0 MJ/l). This is why butan-1-ol is a so-called advanced biofuel. Butan-1-ol can be produced from biomass (biobutanol) and from fossil fuels (petrobutanol). These processes are either energy demanding or rely on biological catalysts (enzymes) and

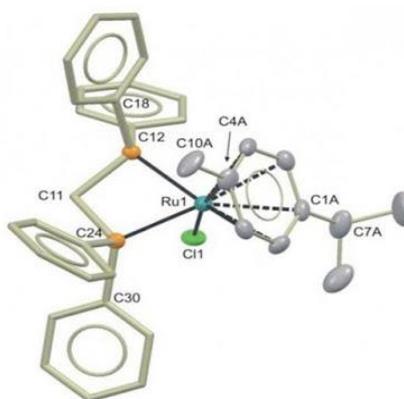


Figure 1 The complex ruthenium catalyst used to make butan-1-ol from ethanol.

produce low yields. The separation of the butan-1-ol from a mixture of products would also be energy demanding.

A recent (2013) breakthrough at the University of Bristol in the UK a way of producing butan-1-ol from ethanol in yields >95% has been found. Two molecules of ethanol can be made to react so that they join with the elimination of a water (H_2O) molecule. The key to the reaction was the design of a family of ruthenium compounds as catalysts.

Acknowledgements

In producing this resource I acknowledge the following UK examination boards and the specifications they produced for examinations up to 2015: WJEC, OCR, Edexcel and AQA.

I am grateful to the ESPRC for the grant under whose auspices this work has been produced.