# 34 Green Chemistry

Green chemistry involves the design, development and and implementation of chemical products and chemical processes which reduce, and hopefully will eliminate, the use and manufacture of hazardous substances that could harm people and the environment.

The idea is to use sustainable processes that carry out chemical reactions and produce chemical products in ways that do not produce pollution and thus prevent environmental pollution before it occurs – to stop it at its source.

Chemical synthesis using the principles of green chemistry, aims to use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products.

Green chemistry can be applied to both small laboratories and large industries. At all levels, it encourages chemists to look for processes which are sustainable, produce less waste, use safer practices and do not use or produce hazardous substances.

Two American chemists, **Paul Anastas** and **John Warner** have developed twelve principles of green chemistry which illustrate its aims.

**Figure 34 .1** Paul Anastas and John Warner.

## Principles of green chemistry

### 1. Prevent waste

Cleaning up after a chemical discharge and disposing of waste can be difficult and also very costly. Preventing waste is better than treating or cleaning up waste after it is formed. This ties in with the idea of atom economy.

### 2. Atom economy

Another American scientist, Barry Trost, is credited with suggesting the principle of atom economy in the 1990s. This is a way of describing the efficiency of a chemical reaction numerically – by dividing the molecular mass of the required product(s) by the combined molecular mass of all the reactants. The idea is that synthetic processes should be designed so that all materials used are incorporated into the final product. As much as possible of the mass of all the reactants should be included in the mass of the products.

An example is the anti-inflammatory drug ibuprofen, which was initially synthesised using a six-step process with low atom economy of 40.1%, and the formation of waste inorganic salt (sodium sulfite). Only 40.1% of the mass of the reactants ended up in the desired product. A greener, three-stage process was developed with an atom economy of 77.4%. This new process uses catalysts and there is no waste produced.

### 3. Less hazardous chemical synthesis

Wherever practicable, substances used and produced should have little or no toxicity to humans and the environment.

An example is the development of insecticides that target an insect's own hormones. The structure of the insect's hormone receptor is studied and then synthetic molecules are developed to interact with these receptors. This is an example of biomimicry, and in this case it can make the insect moult prematurely and die. Advantages are that only a small amount of the chemical is needed, the insect will not develop resistance, and the insecticide is only toxic to the target species of insect.

Another example involves the use of chemicals to destroy plants and animals growing on the hulls of ships. These need to be removed as the drag generated increases fuel costs. Early antifouling chemicals were toxic for marine animals and persisted in the environment. These have been replaced by toxins which exist for only a few hours in water and sediment, so they do not accumulate in shellfish or the environment.

### 4. Design safer chemicals

Chemical products should be designed to be as efficient as possible and have the least toxicity possible.

Chemicals such as tetrachloroethylene were used as dry cleaning fluids, however this is toxic and flammable. Perchlorethylene is still used extensively, although it is reputed to be carcinogenic and is being phased out. Siloxane may be safer, or else glycol ether may be used to wash garments which are then rinsed with liquid carbon dioxide.

Another example is the production of paints. Some companies are making resins and solvents from a mixture of soya oil and sugar instead of from fossil fuels.

### 5. Use safer auxiliaries

Auxiliary substances, such as solvents and separation agents should be used as little as possible and if needed they should be non-toxic. Solvents make up 50% or more of the total chemicals used in most processing plants and they are of concern because they are flammable, volatile and sometimes explosive. They also contribute to energy costs. A green solvent should be non-toxic, inexpensive, readily available and work well in the context.

Many of the solvents, e.g. chlorinated hydrocarbons, previously used in the synthesis of organic compounds are now considered too toxic and have been replaced by more environmentally friendly alternatives such as ethanol, supercritical carbon dioxide, ionic liquids and water.

### 6. Energy efficiency

Energy requirements should be minimised so as to have as little impact as possible on the environment and economy.

Energy is used during production for processes such as heating, cooling, separations such as isolating solvents and removing impurities, electrochemistry, pumping. Only about 2% of the energy in fossil fuels actually gets used usefully – the rest is lost in conversion. Also a lot of energy is lost in transportation. Wherever possible, synthesis should take place at ambient temperature and pressure to prevent the use of energy in maintaining high temperatures and pressures.

### 7. Use renewable feedstocks

A raw material (feedstock) should be renewable wherever this is technically and economically practicable. This will help prevent the depletion of finite resources such as fossil fuels.

Green chemistry supports the use of renewable feedstocks to produce not only chemicals but also fuels. Examples of fuels include biodiesel from plants and algae, as well as bioethanol and butanol from sugars and lignocelluloses. Examples of products from feedstocks include plastics, foams and thermoset plastics from lignin and plant oils and electronic materials including computer chips from the protein keratin in chicken feathers.

Polylactic acid polymers (PLAs) are recyclable, biodegradable polymers which are synthesised from lactic acid which can be largely derived from renewable sources. Their production also reduces the need for hazardous materials such as organic solvents, and catalysts are used to achieve high yields using less energy.

Scientists have also produced a biodegradable composite material of renewable resources – flax yarn embedded in a soy polymer resin. This product has tensile properties similar to steel and is suitable for some building applications.

### 8. Reduce derivatives

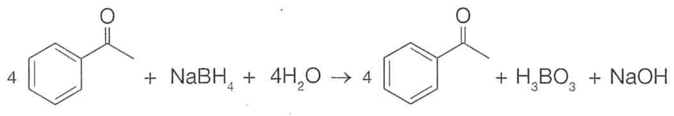
Avoid the unnecessary production of derivatives wherever possible. For example, in early production methods for penicillin a number of different stages were produced during its manufacture. The influence of green chemistry has led to a production process that is more direct, with fewer stages. This process is possible because of the use of an enzyme. Enzymes are biocatalysts; they are biodegradable and environmentally compatible. Using such catalysts, reactions can occur in water under mild conditions of temperature and pressure.

### 9. Using catalysts

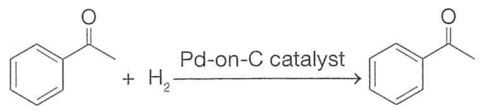
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents such as oxidants and reductants.

Catalysts can reduce the wastage of atoms and energy, they can be used in small amounts and can be re-used.

For example, the reduction of a ketone to a secondary alcohol is illustrated in the following two equations.



81% atom economy



100% atom economy

In the first reaction, sodium borohydride is used as a reductant and 81% of the atoms used are present in the product.

In the second equation, molecular hydrogen is used as the reductant, a process that can only take place with a catalyst present – in this case palladium on charcoal. The catalyst provides an alternative pathway with lower activation energy. This process allows all atoms to be incorporated in the product, and the catalyst can be re-used.

Biocatalysts are also being used to replace metal catalysts in some processes such as the synthesis of drugs for diabetes.

### 10. **Design products that degrade**

Chemical products should be designed so that at the end of their function they break down (degrade) rather than persist in the environment. This reduces the time they are available in the environment to cause damage. An example is the biodegradable bags now being made from cassava starch and calcium carbonate.

### 11. **Real time analysis and monitoring**

Analytical methodologies need to be further developed to allow for real time monitoring and control, during a chemical process, before hazardous substances are formed. Any changes, such as in pH, temperature or the poisoning of catalysts, needs to be detected immediately, before any serious damage occurs.

Technological developments that help in this area include the ability to analyse using increasingly small samples, and the ability to analyse quickly and accurately using instrumental methods, such as spectroscopy, rather than the slower conventional methods of ‘wet chemistry’. Such techniques not only promote the principles of green chemistry but also improve the safety and efficiency of chemical plants.

### 12. **Accident prevention**

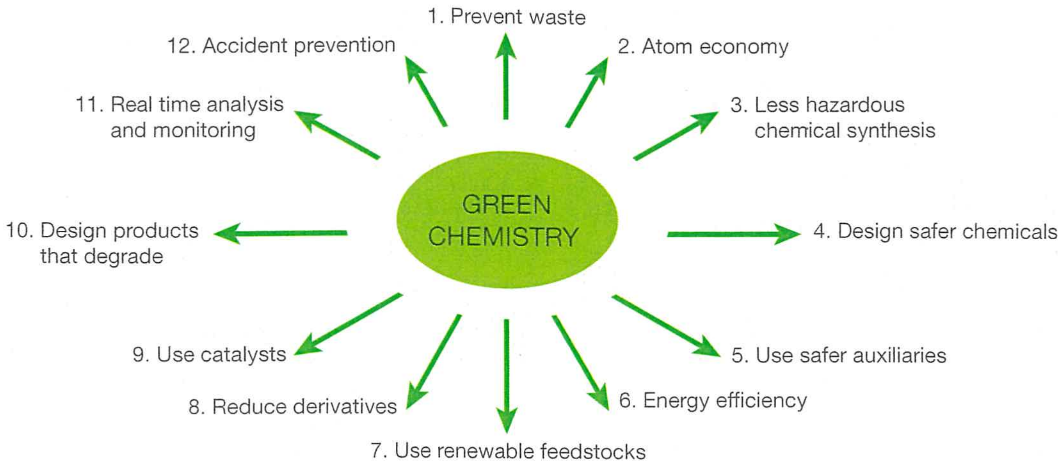
Substances and the form of a substance used in a chemical process should be chosen to minimise potential for chemical **accidents**, including releases, explosions, and fires. We already have in place engineering controls, administrative and work practice controls, and the use of personal protective equipment by workers, to reduce the likelihood of an accident involving hazardous substances. Green chemistry goes further. It asks for the elimination of hazardous substances from the workplace wherever possible.

## QUESTIONS

1. What is meant by green chemistry?
2. Why is green chemistry sometimes referred to as sustainable chemistry?
3. Green chemistry is sometimes classified into four main areas of action.
   (a) Efficient use of energy and chemicals.
   (b) Hazard reduction.
   (c) Waste minimisation.
   (d) Use of renewable resources.
   For each of these four areas, research an example of how green chemists are introducing practices to accommodate these aims.
4. Green chemistry has been criticised in a number of ways.
   (a) It has been said that green chemistry is not new. Discuss this statement.
   (b) Green chemistry is not economically viable. Evaluate this claim.

Research to answer one or more of the following questions.

5. The 2005 Nobel Prize for Chemistry was awarded to Yves Chauvin, Robert Grubbs and Richard Schrock for developing a chemical process called metathesis in organic chemistry.
   Metathesis is a reaction mechanism in organic chemistry which uses specially designed catalysts to rearrange fragments of the carbon chains and hence make new products.
   Research the importance of this process.
6. Research the significance of each of the following developments in synthesis.
   (a) In 1929 Wohler synthesised urea from a compound called ammonium isocyanate.
   (b) In 1856, the chemist Perkin produced a synthetic purple dye.
7. Find out about awards given in countries such as Australia and the United States to encourage the development of green chemistry. Describe two innovations that have received such an award.



## 33 Reagents, Conditions and Yield

1. (a) Stoichiometric means in the proportions in which substances will react based on mole ratios as shown in equations.
   (b) By-product is a chemical produced in a reaction which is not the product initially wanted.
   (c) Yield means the amount of a product that is produced by a chemical reaction.
2. 
   - Economics – profits need to be maximised and this requires relatively low costs and high yield.
   - Reducing waste and environmental damage – mixing reactants in stoichiometric proportions will reduce waste of chemicals and energy.
   - Safety of workers is essential. This may limit the temperature and pressure used for the reaction. It is not acceptable to use conditions that produce a higher yield if this risks the health of employees.
   - Purity and quality of product are important – it is not acceptable to increase the yield at the expense of the purity and quality of the product.
   - By-products produced need to be minimised if there is no market available for them.
3. Molar mass of glucose $C_6H_{12}O_6$
   $= (6 \times 12.01) + (12 \times 1.008) + (6 \times 16)$
   $= 180.156$ g
   Moles glucose $= \frac{\text{mass}}{\text{molar mass}} = \frac{1000}{180.156} = 5.5507$
   Moles ethanol $= \frac{15}{100} \times (2 \times 5.5507) = 1.665$ moles
   Molar mass of ethanol $C_2H_5OH$
   $= (2 \times 12.01) + (6 \times 1.008) + 12.01 = 46.068$ g
   Mass ethanol $= 1.665 \times 46.068$
   $= 76.77$ g or 77.0 g
4. Various.
   (a) Examples of the use of the word reagent include:
   - Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst. It can be used to destroy organic compounds found as contaminants in water and soils, for example oil spills and toxic industrial wastes such as phenol and formaldehyde.
   - Grignard reagent can be added to a carbonyl group in an aldehyde or ketone to help in the formation of carbon-carbon bonds.
   - Millon's reagent is used to confirm the presence of soluble proteins. A few drops of Millons reagent is added to an unknown substance in a test tube and the test tube is warmed. If a reddish-brown precipitate forms, then protein is present.
   - Some reagents are impregnated onto strips for ease of use, e.g. test strips used by doctors to detect glucose or blood in urine.

   (b) Examples of catalysts include the following.
   - Iron oxide is used as a catalyst in the Haber process for the production of ammonia.
   - $3H_2(g) + N_2(g) \overset{Fe}{\rightleftharpoons} 2NH_3$
   - Zeolites (aluminosilicate minerals) are used in the catalytic cracking of crude oil into fractions including petrol for cars.
   - Vanadium pentoxide ($V_2O_5$) (or platinum metal) in the contact process during the production of sulfuric acid.
     $2SO_2(g) + O_2(g) \overset{V_2O_5}{\rightleftharpoons} 2SO_3(g)$
     The reacting molecules of sulfur dioxide and oxygen are adsorbed onto the catalyst. This distorts and weakens their bonds so they can more readily react together.
   - Platinum is used, in the catalytic converter of a car, to catalyse the conversion of carbon monoxide to carbon dioxide.
     $2CO(g) + O_2(g) \xrightarrow{Pt} 2\,CO_2(g)$
     Platinum can also be used as a catalyst in the hydrogenation of alkenes.
     $H_2C{=}CH_2(g) + H_2(g) \xrightarrow{Pt} H_3C{-}CH_3(g)$

   (c) Separation processes include the following.
   - The product may be able to be precipitated out as a solid and separated by filtration. In the production of sodium carbonate a mixture of ammonium chloride and sodium hydrogen carbonate is produced.
     $NaCl(aq) + NH_3(g) + H_2O(l) + CO_2(g) \rightarrow NH_4Cl(aq) + NaHCO_3(aq)$
     This mixture is cooled. At lower temperatures sodium hydrogen carbonate becomes less soluble, so it precipitates out, leaving the ammonium chloride in solution. Filtering will then separate the two products.
   - Semipermeable membranes may be used to separate substances such as in the membrane cell used in the manufacture of sodium hydroxide by electrolysis of sodium chloride (salt) solution. In membrane cells, hydroxide and chloride ions cannot pass through the membrane used, ensuring the production of pure sodium hydroxide solution.
   - Volatile reactants and products may be separated out by fractional distillation. One example of this is the production of an ester from an alcohol and a carboxylic acid. The temperature of the reacting mixture plus products is carefully controlled so that different substances vaporise and can be collected at different temperatures.
5. (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) From the equation, 1 mol nitrogen reacts with 3 mol hydrogen.
   100 mol $N_2$ would need 300 mol $H_2$ for complete reaction.
   There is only 100 mol $H_2$, so hydrogen is the limiting reagent – it will run out before all the nitrogen is used.
   (c) (i) 50 g $H_2 = \frac{50}{2} = 25$ mol $H_2$
   (ii) 50 g $H_2 = \frac{50}{2} = 25$ moles $H_2$
   From the equation, 1 mol $H_2$ reacts with $\frac{1}{3}$ mol $N_2$
   25 mol $H_2$ will need $\frac{1}{3} \times 25 = 8.33$ g $N_2$
   8.33 mol $N_2 = 8.33 \times 28 = 233.3$ gram $N_2$
   (iii) 112 g $N_2 = \frac{\text{mass}}{\text{molar mass}} = \frac{112}{28} = 4$ mol.
   From the equation 1 mol $N_2$ produces 2 mol ammonia.
   4 mol $N_2$ would produce 8 mol $NH_3$
   The process is 95% efficient, so amount produced
   $= \frac{95}{100} \times 8 = 7.6$ mol.
   7.6 mol $NH_3$ = moles × molar mass
   $= 7.6 \times 17 = 129.2$ g.
6. (a) Molar mass $CaCO_3 = 40.1 + 12.0 + 48.0 = 100.1$ g
   Molar mass of $NaCl = 23.0 + 35.5 = 58.5$ g.
   (b) Moles in 53 kg $CaCO_3 = \frac{\text{mass}}{\text{molar mass}}$
   $= 53 \times \frac{10^3}{100.1} = 529.47$ mol.
   Moles NaCl $= 30.0 \times \frac{10^3}{58.3} = 512.82$ mol.
   From the overall reaction equation,
   1 mol $CaCO_3$ needs to react with 2 mol NaCl
   529.1 mol $CaCO_3$ would need $2 \times 529.1 = 1058.2$ mol NaCl,
   but there is only 512.82 mol NaCl
   So NaCl will run out first and thus NaCl is the limiting reagent.
   (c) From the equation, 2 mol NaCl produce 1 mol $Na_2CO_3$
   1 mol NaCl would produce 0.5 mol $Na_2CO_3$
   512.82 mol NaCl would need 256.41 mol $Na_2CO_3$
   $= 256.41 \times$ molar mass $Na_2CO_3$
   $= 256.41 \times 106.0 = 27.2$ kg $Na_2CO_3$

## 34 Green Chemistry

1. Green chemistry involves the design, development and implementation of chemical products and chemical processes which will reduce (and hopefully even eliminate) the use and manufacture of hazardous substances that could harm people and the environment.

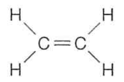
2. Green chemistry can be considered as sustainable chemistry because in reducing the wastage of resources, improving the recycling of chemicals wherever possible, and eliminating or reducing the use of hazardous chemicals involved, it increases the likelihood that chemicals and processes will continue to be used over a longer time span.
3. Various, for example:
   (a) Efficient use of energy and chemicals – the use of catalysts allows a reduction in the quantities of chemicals needed. Also catalysts can be used over and over again as they are not changed by the reaction. Catalysts are also being improved. For example, a new catalyst developed for the manufacture of methanol has allowed plants to operate at lower temperatures and pressures, thus saving energy and having less harmful environmental effects.
   (b) Hazard reduction – Instead of using toxic insecticide sprays, synthetic chemicals are being developed that target the receptors of specific pest insects causing them to die without damage to other species or the environment.
   Other examples include the development of water-based paints, the replacement of chlorofluorocarbons, and the uniform classification and labelling of chemicals (GHS) in terms of how hazardous they are.
   (c) Waste minimisation – Toxic solvents are being phased out. In some cases ethanol is able to be used in their place. Nanoparticles of chemicals are being used as catalysts to reduce waste.
   (d) Use of renewable resources – Polylactic acid (PLAs) polymers are being manufactured from lactic acid to replace some polymers manufactured from fossil fuels.
   PLAs are renewable, biodegradeable and manufactured from renewable resources and they are used for clothing and packaging.
4. (a) In a discussion question like this you would first define green chemistry. Then you would write about examples of how, in the past, chemists have stopped using chemicals which had been found to be dangerous. These could include lead in petrol, mercury in batteries and in chemical plants carrying out electrolysis of brine to produce chlorine and sodium hydroxide.
   (b) For an evaluation question, you would again start with a definition of green chemistry. You would then discuss ideas in favour of and against this view. You might like to research some companies that have tried a green chemistry approach and see if they found the process economical. You might also like to consider how starting a new process, or changing an existing process might be initially more expensive. You could also consider the growing consumer demand for the use of less hazardous chemicals and processes and whether or not government subsidies are advisable and available.
   Always finish with an evaluation statement, e.g. 'I think that green chemistry is definitely (or is not) economically viable based on the arguments I have presented.' You are presenting your view here so there is no right or wrong approach, however your statement must be backed up with evidence.
5. It allows reactions to take place with fewer steps, producing less wastes as by-products, and also using lower temperatures and pressures.
6. (a) Urea is the waste product produced in the body from nitrogenous wastes. We now know that this and other body substances can be produced in the laboratory. Wohler's experiment helped establish that substances produced by living organisms can also be synthesised in the laboratory.
   (b) This synthetic purple dye was the first dye ever produced by synthesis. This replaced the natural purple dye used at the time (Tyrian purple) which was being extracted from a Mediterranean snail and was more expensive than gold. This was the beginning of an industry based on the synthesis of dyes from coal tar – a waste product from steel manufacture. This discovery is also an example of serendipity – an accidental discovery. At the time, Perkin was actually trying to synthesise not a dye but the antimalaria drug called quinine.
7. Various. In Australia the RACI (Royal Australian Chemical Institute) provides Green Chemistry Challenge awards to recognise and promote fundamental and innovative chemical methods that accomplish pollution prevention. In the United States, the Presidential green chemistry challenge provides similar incentives. You should describe two such awards that interest you.

## 35 Synthesis of Polymers

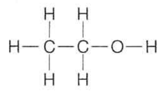
1.

| Feature | Addition reactions | Condensation reactions |
|---|---|---|
| What happens? | Double bond is broken and other atoms are added. | Two functional groups react to exclude a small molecule. |
| Occurs in saturated or unsaturated compounds. | Unsaturated. | Saturated. |
| One or two products. | One. | Two. |
| Is energy needed? | Not needed. | Needed. |
| Example | Synthesis of ethylene and PVC. | Synthesis of nylon and polyesters. |

2. Both addition and condensation polymers consist of many small monomer units joined together. Addition polymers are synthesised by breaking double bonds and adding on monomer units, e.g. poly(ethylene) and poly(vinyl chloride). Condensation polymers are formed when monomers join by the release of a small molecule such as water, e.g. nylon and cellulose.
3. Petroleum is non-renewable. There are finite reserves of this resource, which is being used up and cannot be replaced. The continued use of petroleum for this purpose on such a large scale is not sustainable.
4. (a) Ethylene (ethene) is a colourless, gaseous hydrocarbon and is the simplest alkene. It occurs naturally and is produced by the cracking of larger hydrocarbons. It affects the ripening of fruit and is used to manufacture many polymers, e.g. polyethylene and polyvinyl chloride.

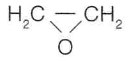


Ethanol is the alcohol which occurs in most alcoholic drinks.

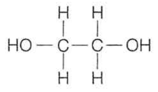


$H{-}CH_2{-}CH_2{-}O{-}H$

Ethylene oxide is a colourless, flammable, explosive, poisonous gas at room temperature and it is carcinogenic. It is used to make many products including detergents, thickeners, solvents, polymers, disinfectants and polymers.



Ethylene glycol is a colourless, toxic liquid used in antifreeze for cars. Its systematic name is ethane-1,2-diol.



$HO{-}CH_2{-}CH_2{-}OH$

Polyethylene glycol (PEG) is a polymer of repeating ethylene glycol units.