Chem Factsheet

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Green Chemistry

Green chemistry (also called sustainable chemistry) is concerned with *changing or controlling the chemical methods* which are used to produce the substances and materials which we need in order *to increase sustainability and reduce the negative impact on the environment by minimizing the use and generation of hazardous substances*.

> **Sustainability or sustainable development** is a strategy for the use of all resources that aims to meet all human needs while preserving the environment so that these needs can be met, not only in the present, but also for future generations.

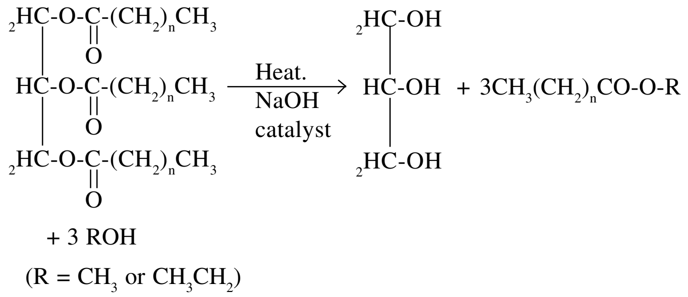
When studying green chemistry be prepared for questions which involve giving the advantages *and* disadvantages of a process.

It raises many different questions and problems, resulting in a wide variety of approaches to find solutions. Some of these will be considered in this FactSheet.

> ***Carbon footprint*** is the net amount of carbon released (as greenhouse gas) by a process in a year. This term is also applied to the net carbon emissions caused by individuals or groups of people in a year.

Changing from the use of non-renewable resources to renewable resources

Biodiesel fuel can be manufactured by the reaction of vegetable oils (triglycerides) with methanol or ethanol. Sodium hydroxide or potassium hydroxide can be used as a catalyst. Glycerol, which is a useful chemical, is produced as a byproduct of the reaction.



(R = CH_3 or CH_3CH_2)

Many different plants can be used as a source of triglycerides, including those which cannot be used as food. One main disadvantage of the process is that large amounts of land need to be used to grow plants and this land is then not available for other purposes, such as growing food crops. However, it is claimed that the process is *greenhouse gas neutral* or *carbon neutral* because the carbon dioxide given off when the fuel is burned was originally in the atmosphere and used for photosynthesis by the plants. This can be contrasted with the burning of fossil fuels, where the carbon has been 'locked in' for millions of years, only to be released during combustion.

> ***Carbon neutral*** means to have net carbon emissions of zero. That is, the carbon dioxide released is offset by an equivalent amount of carbon dioxide absorbed. It corresponds to a *carbon footprint of zero.*

The concept of carbon neutrality applied to burning fuels

Non-renewable fuels such as petrol made from crude oil give rise to emissions of carbon dioxide when burned and there is no intake of carbon dioxide in producing the fuel so this is not carbon neutral. Bio-ethanol and other renewable fuels produced from biomass are often regarded as effectively carbon neutral (as the plants absorbed the carbon dioxide during photosynthesis). However, if producing a fuel involved the emission of carbon dioxide, for example by heating a reaction, this would result in the fuel having a carbon footprint not equal to zero, so it could *not* be classified as carbon neutral.

Similarly, considering a fuel such as hydrogen produced from methane gas. The methane gas that is obtained from the North Sea Gas Fields has a similar carbon footprint to any other fossil fuel. If it states in the question that the methane gas has come from a renewable source involving biomass, then the carbon footprint would be less or zero.

> ***Biomass*** is biological material from *living* or *recently living organic organisms* and is a *renewable energy source.*

Finding ways in which energy can be used more efficiently

Microwave energy is used to heat reactions in the pharmaceutical industry. This is more efficient as all of the energy supplied is used to heat the reaction and a negligible amount is absorbed by the environment.
Methods of synthesis and purification should be designed for ambient temperature and pressure to avoid the energy use associated with high temperatures and pressures.

The use and development of new catalysts so that reactions have higher atom economies, thus reducing the waste produced in a chemical reaction

e.g. The production of ethanoic acid by the carbonylation of methanol using a rhodium metal iodide complex ion (*cis*-$[Rh(CO)_2I_2]^-$) as catalyst was developed in the 1970s.

A similar, but much faster process using an iridium metal iodide complex ion ($[Ir(CO)_2I_2]^-$) promoted by ruthenium as catalyst was developed in 1997 and is now used increasingly.

The development and use of this new catalyst made it a much greener process in that, for example:

1. It produces substantially lower amounts of propanoic acid byproduct compared to the rhodium process meaning much less energy is required to purify the product.
2. It operates at much lower water concentrations, thus reducing the amount of energy required to *dry* the product.
3. Total direct gaseous emissions (e.g. CO and CO_2) can be reduced by much more than 50 per cent.
4. Energy costs are much reduced e.g. steam usage is reduced by 30 per cent meaning less energy is required to generate the steam

Both processes have the same equations, although the reaction conditions required by the catalysts differ:

$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

$$CH_3I + CO \xrightarrow{\text{catalyst}} CH_3COI$$

$$CH_3COI + H_2O \rightarrow CH_3COOH + HI$$

All of the reactants are used to produce the ethanoic acid, except the hydrogen iodide, which is used as a reactant and then appears as a byproduct at the end. The recycling of the hydrogen iodide gives both processes a theoretical 100% atom economy.

Atom Economy is defined as (Molar mass of useful product(s) ÷ Sum of molar masses of all reactants) x 100%

Preventing the pollution of the environment

Many halogenoalkanes are excellent solvents and are extensively used as degreasing agents in industry. However, many are classed as VOCs (volatile organic compounds), some of which give rise to harmful vapours. Many are chloroalkanes, as chlorine is cheap and so these are inexpensive to produce. The vapour from some of these compounds can cause harm to the nervous system and internal organs such as liver and kidneys.

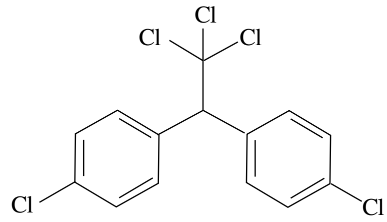
Examples include tetrachloromethane (carbon tetrachloride, CCl_4) which was once used in fire extinguishers until it was realized that its use on fires produced phosgene ($COCl_2$) which is a highly toxic gas – used in chemical warfare during World War 1! Others include tetrachloroethene (C_2Cl_4), 1,1,1-trichloroethane (CCl_3CH_3) and dichloromethane (CH_2Cl_2).

Green chemistry advocates the reduction or, if possible, the elimination of solvents, as well as the replacement of VOCs by green solvents such as glycerol, (a byproduct of the production of biodiesel). The properties looked for in a green solvent are low toxicity, solubility in water, low vapour pressure (i.e. not a VOC) and high boiling point as well as renewability, low cost and wide availability.

Organo-halogen compounds have been used as pesticides (especially against malaria carrying mosquitoes) with detrimental effect.

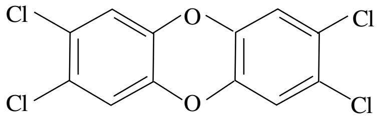
For example, the organo-chloride, DDT (**d**ichloro**d**iphenyl **t**richloroethane) was found to be non-degradable and, because it is fat soluble, entered and built up in the food chain.

DDT



Creatures at the end of the food chain suffered. For example, peregrine falcons (an endangered species) could not hatch their eggs due to DDT causing thin shells. Human beings would also potentially be damaged by the use of such chemicals, due to eating fish for example. The use of DDT is now restricted.

Polymers containing chlorine, such as poly(chloroethene) or PVC are also a cause for concern. The monomer, chloroethene, is highly toxic and the combustion of PVC gives high concentrations of carbon monoxide, carbon dioxide and hydrogen chloride. Under certain circumstances highly toxic dioxins (polychlorinated dibenzodioxins) may be formed.



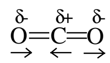
An example of a dioxin
(2,3,7,8-tetrachlorodibenzo-p-dioxin)

In 1994, the US EPA reported that "dioxins are a probable carcinogen, but non-cancer effects (reproduction and sexual development, immune system) may pose an even greater threat to human health".

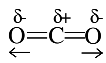
Reducing the emission of greenhouse gases and preventing global warming

The absorption of infra red radiation is due to the vibration of the bond(s) of the molecule giving rise to a *changing polarity* of the molecule. This interacts with the electromagnetic radiation and absorbs energy from it.

For example carbon dioxide has polar bonds, because oxygen is more electronegative than carbon, so certain vibrations of the bonds give rise to a fluctuating unequal electron distribution:



Asymmetrical bond stretching vibration gives rise to *changing polarity* → *absorbs infra-red radiation*



Symmetrical bond stretching vibration does not give rise to *changing polarity* → *does **not** absorb infra-red radiation*

This can be used to predict whether a given molecule will absorb infra-red radiation.

Common examples of molecules which will absorb infra-red radiation are CO_2, H_2O, CH_4, and NO, and these are greenhouse gases.

O_2 and N_2 are non-polar molecules and their bonds are non-polar. They cannot absorb infra-red radiation and so will not act as greenhouse gases.

A non-polar molecule has centres of positive and negative charge which coincide.

The importance of a gas when considering global warming will depend both on whether it will absorb infra red radiation and if it does, on the degree to which it absorbs it, that is the intensity of its infra red spectrum.

Methods of reducing greenhouse gas emissions have been suggested which include the removal of emissions of carbon dioxide by storing them underground in geological formations, injecting them as a liquid deep into the oceans, or reacting them with metal oxides to form stable carbonate minerals.

Carbon dioxide could be used in the production of expanded polymers as a blowing agent.

Deforestation and the loss of huge amounts of irreplaceable rainforest are important, as photosynthesis removes carbon dioxide from the air and replaces it by oxygen. Also a rainforest represents a unique, rich and diverse ecosystem. There are many initiatives concerned with planting trees, but these may be negligible compared with the clearing of rainforest to plant crops.

The difference between natural climate change and that caused by human activity

It is important to appreciate that natural climate change occurs over hundreds of thousands of years and that, superimposed on this, is *anthropogenic* climate change which is that caused by human activity! For example carbon dioxide content of the atmosphere has shown a natural fluctuation over hundreds of thousands of years, together with more recent increases which are believed to be due to human activity such as deforestation, burning of fuels and industrial activity. Warming of the Earth causes the release into the atmosphere of some of the carbon dioxide dissolved in the oceans, which in turn enhances global warming. Large computers are used in order to try to analyse the global situation.

International initiatives have been set up in order to monitor the progress in limiting greenhouse gas emissions, and reducing activities which are believed to be causing global warming.

Where at present very hazardous chemicals are being used, developing alternative reactions in which safer chemicals are used to produce the same product

The goal is to use less hazardous chemicals and also produce less hazardous byproducts. The problems associated with the disposal of hazardous chemical waste are storage, transport and treatment.

Chemical processes are redesigned to use chemical reagents which are non-toxic and reactions which take place under safe, lower energy reaction conditions. Reactions should give a minimum of waste which is non-toxic and which biodegrades rapidly.

Understanding how chemicals can damage the ozone layer and the effects which this damage causes

Chlorofluorocarbons (CFCs) were used extensively in refrigerators, aerosol cans, anaesthetics and plastics until about twenty years ago. The reason for their use was low toxicity, lack of reactivity and low flammability. It was then found that CFCs were damaging to the ozone layer, because they cause the breakdown of the ozone molecules (O_3). Before the CFCs reach the ozone layer the ultraviolet radiation is not intense and energetic enough to cause them to breakdown, but on reaching the region of the ozone layer they will remain there, producing ozone destroying chlorine radicals under the action of the very short wavelength (175-230 nm) ultraviolet light:

Initiation

$$CCl_2F_2 \xrightarrow{uv} \bullet CClF_2 + Cl\bullet \quad or \quad CCl_3F \xrightarrow{uv} \bullet CCl_2F + Cl\bullet$$

Propagation

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$

Followed by Cl• regeneration when ClO• reacts with either oxygen atoms or nitrogen monoxide

$$ClO\bullet + O \rightarrow Cl\bullet + O_2 \quad and \quad ClO\bullet + \bullet NO \rightarrow Cl\bullet + \bullet NO_2$$

One Cl radical can destroy many O_3 molecules by this chain of reactions

Termination

$$Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl \quad or \quad Cl\bullet + H_2 \rightarrow HCl + H\bullet$$

Also chlorine nitrate may be formed:

$$ClO\bullet + \bullet NO_2 \rightarrow ClNO_3$$

The chlorine nitrate cannot react with ozone, but does undergo photolysis to produce more chlorine atoms, Cl• , for further ozone depletion.

The general lack of reactivity of CFCs also means that they will not take part in other reactions which would make them harmless to the ozone layer.

This breakdown of the ozone caused a gradually increasing hole to appear in the ozone layer. This was increasingly allowing dangerous short wave ultraviolet radiation to reach Earth, resulting in an increased incidence of sun burn and skin cancers, especially in areas under the growing hole. Very large depletions in the ozone layer could let enough ultraviolet light through to have a detrimental effect on crop yields and larvae of fish, shrimps and crabs. Plankton, which are microscopic life forms in the oceans on which the food chain depends, could potentially be made extinct.

However, there are natural changes which occur to the ozone layer, and the atmospheric changes due to pollution are difficult to distinguish from natural changes. Agreements between fifty nations are in place to restrict the production and use of CFCs. Very powerful computers using highly complex programs and three dimensional modeling are used to predict the exact consequences of atmospheric pollution and it is predicted that it may take 100 years for existing CFCs to disperse.

Possible substitutes for CFCs are:

1. Hydrofluorocarbons, HFCs. (e.g. 1,1,1,2-tetrafluoroethane, CH_2FCF_3). The carbon-chlorine bond is much weaker than the carbon-fluorine bond and so these compounds which contain no chlorine would not be expected to form free radicals. The 175-230 nm ultraviolet radiation would not be energetic enough to break the carbon-fluorine bond, so no fluorine free radicals would be formed and no destruction of the ozone layer would occur.

2. Hydrochlorofluorocarbons, HCFCs. (e.g. 2,2-dichloro-1,1,1-trifluoroethane, $CHCl_2CF_3$). These all contain at least one hydrogen atom, which causes them to be much less stable so they will react in the lower atmosphere, and few of their molecules will reach the ozone layer. However, these compounds are greenhouse gases.

Practice Questions

1, Which of the following are ***not*** greenhouse gases:
CO_2, O_2, CH_4, H_2O, N_2?

2. From the following fuels, select the one with the ***smallest*** carbon footprint:
(a) Hydrogen produced from methane
(b) Petrol produced from crude oil
(c) Coal
(d) Ethanol produced from sugar.

3. One idea for the reduction of carbon dioxide emissions involves storing the gas in geological formations deep underground rather than releasing it into the air. Give two problems / disadvantages associated with this method. (3 marks)

4. Give a method (involving a chemical reaction) that you could use to compare carbon dioxide levels in the atmosphere at various locations/different times of day.

5. In an industrial process, use of which of the following would lead to greater sustainability?
(a) biofuels for heating
(b) a catalyst which improves atom economy
(c) a higher temperature
(d) recycling of unused reactants

6. The industrial production of ethanoic acid now uses a rhodium metal iodide complex ion catalyst or a iridium metal iodide complex ion catalyst. What is the ***main*** advantage of using these catalysts?

7. What measures have been adopted to prevent destruction of the ozone layer?

8. Give the equations which show how a CFC can destroy the ozone layer. Include an initiation, propagation, regeneration, and termination step. (3 marks)

9. Your school has just purchased an intra-red spectrometer. How might you use this to measure carbon dioxide levels?

10. Give the two main factors on which the 'greenhouse effect' of a given gas depend.

Answers

(One mark for each correctly answered question except questions 3 and 9)

1. O_2 and N_2
2. Ethanol produced from sugar.
3. Any two from: locating a suitable underground geological formation / the drilling of a vent through which the carbon dioxide could be pumped would use energy / pumping the carbon dioxide underground would use energy / the carbon dioxide may escape through another part of the underground rock.
4. Use a pump to draw the air through limewater for a given time.
Compare the degree of cloudiness.
5. All except c), using a higher temperature would lead to lower sustainability.
6. Very high/100% atom economy.
7. Restrictions on the production and use of CFCs.
8. Any four suitable equations (see text). One correct equation = 1 mark, two correct equations = 2 marks, four correct equations = 3 marks. Repeat equations for a step only count as one equation.
9. Set the instrument at the wavelength at which carbon dioxide absorbs radiation but no other gases will absorb / 2349 cm^{-1}.
10. Atmospheric concentration and ability to absorb intra red radiation.

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