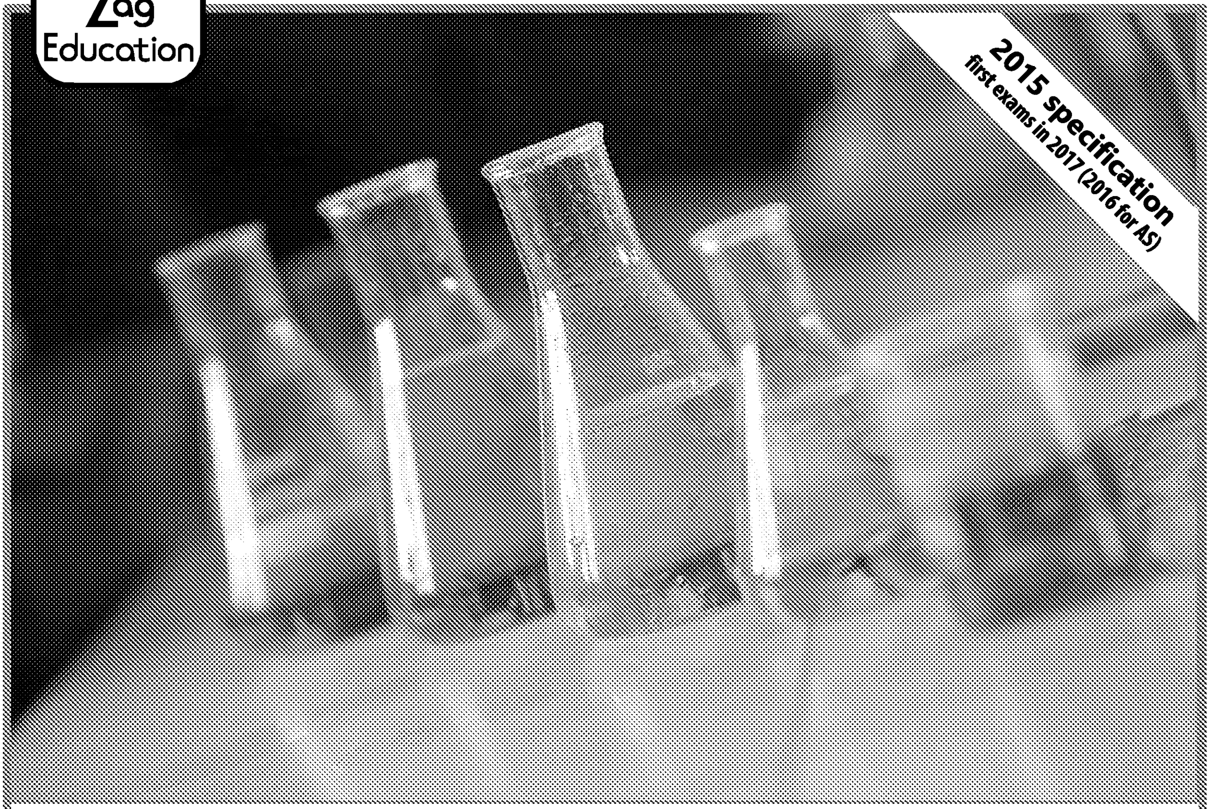
Chemistry AS / A Level Year 1 | Edexcel | 8CH0/9CH0



Stretch and Challenge Articles

for AS / A Level Edexcel Year 1 Chemistry

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Teacher’s Introduction

This resource contains 11 ‘Stretch and Challenge’ articles, written to stimulate and inspire able Edexcel AS / A Level Chemistry students.

While the material covered is largely beyond the scope of the AS / A Level course, each article is linked to a topic from the specification, as outlined on the ‘Specification information’ page. This allows students to apply and reinforce their existing knowledge in unfamiliar situations, while also learning new concepts and skills. This pack covers the first year of the course, and includes physical, inorganic and organic chemistry content.

Each article is between 1,500 and 2,000 words, and is expected to take students around 30 minutes to read. Following the article, several questions are provided, divided into three groups:

- **Comprehension questions**, which encourage students to review the article in order to cement their understanding of new ideas.
- **Application questions**, which prompt students to think more deeply about the article, and to apply concepts.
- **‘Taking it further’ questions**, which invite students to research and make notes on additional aspects of the topic. Some questions ask students to choose an area to explore, allowing them to delve more deeply into the areas of chemistry that most interest them.

Questions in the first two groups are fairly short, and are suitable as classwork. Students could tackle them individually, in groups, or as a class. Suggested answers for the questions are provided for each article. ‘Taking it further’ questions are envisaged as homework tasks, though students could discuss and share their findings in class.

While the articles are intended to appeal to any enthusiastic Chemistry student, they would be particularly suited to those hoping to pursue the subject at a higher level and will provide ample talking points for any admissions interviews.

We hope you enjoy reading and using this resource.

October 2021

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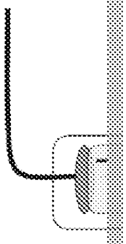
What are orbitals?

Throughout school, Chemistry students are introduced to different models descri
in an atom, each more nuanced and more complex than the last. When first intro
described as a negative particle that orbits the nucleus, and then sometime later t
By A Level, the idea of circular orbits is replaced with atomic orbitals of different s
electrons. But what actually is an orbital – is it anything more than a description?
shapes? This article will explore electrons a bit further and bring in quantum theo
gain a better understanding of a particle that is central to chemical reactions.

A bit of history: wave-particle duality



The electron was first discovered in 1897 by J Thomson. He used a heated cathode (negative electrode) to produce a 'cathode ray', and then used the fact that this beam could be deflected by discrete amounts in an electric field to show that the ray was actually a beam of negative particles, since the beam was attracted towards a positive electrode (anode). We now understand that by heating the cathode, Thomson was ionising the outer electrons in the metal that formed the beam. The degree of deflection also allowed Thomson to work out the charge-to-mass ratio of an electron (e/m).

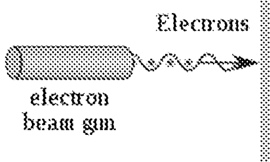
Thomson's work was followed by the work of Robert Millikan in 1906. Millikan de
experiment in which he used tiny negatively charged oil drops to work out the ma
oil drops to fall due to their weight caused by gravity, but then balanced this out b
above the oil drops pulling them upwards. He adjusted the electric field causing t
plate until the oil drops were suspended in mid-air. This meant that for an indivi

$$F_{down} = mg = F_{up} = qE$$

$$\text{So: } mg = qE$$

By working out the mass of an oil drop (m), and knowing E (the field strength that
drop) and g (acceleration due to gravity), Millikan was able to calculate q, the cha
that this was always a multiple of 1.60×10^{-19} C (coulombs), meaning that the cha
was exactly that number. This is e, the charge of one electron. Because Thomson
Millikan was then able to work out m, the mass of an electron, as well. All of this
a particle with a mass of 9.11×10^{-31} kg and a charge of 1.60×10^{-19} C.

Fifty-five years later, Claus Jönsson showed that as well as being particles, electrons are also waves. By passing a beam of electrons through two slits, an interference pattern was observed – this only happens with waves. As a wave passes through a slit, diffraction occurs and the wave spreads out. If this happens with two slits, the two waves interfere with each other once they've passed through the slit, causing a distinctive pattern of where the waves interfere constructively (add together) and where they interfere destructively (cancel out).



The nature of electrons as both particles and waves is known as wave–particle du
electrons as particles when, for instance, we talk about electrons being things in s
during chemical reactions. Trying to explain this with waves is much more compli
There is a limit to chemical understanding if the wave nature of electrons is ignor
be explored in the rest of this article.

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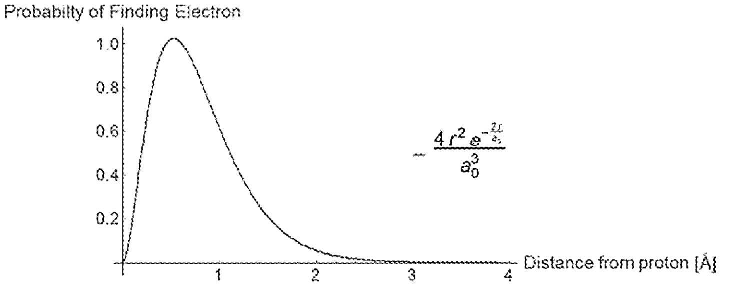
Orbitals

Because electrons are waves, the Bohr model of an atom with electrons orbiting a sufficient – waves cannot be described like this. Instead, electrons are described u pattern of an electron wave around the nucleus. The pattern is called the 'radial d shown below for a 1s orbital in a hydrogen atom. This pattern is the solution to a Schrodinger equation, and is an example of where the tools of mathematicians ar physicists and chemists to understand a theoretical concept. The solution is inclu



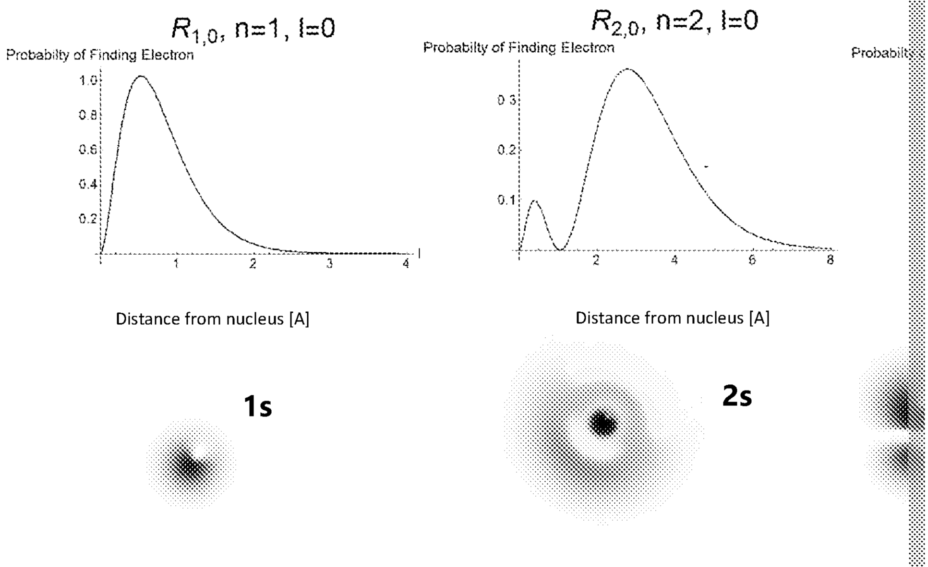
- The graph d electron wa
- The probabil Electrons ca with the par
- The graph is it approache This means t beyond whic in mind, an c 90 % of the e

This is the simplest orbital. To be able to distinguish between all orbitals, we need to use three quantum numbers, which describe the characteristics of the orbital an electron is in. These are:

- n, the principal quantum number. This tells us what shell an electron is in.
- l, which tells us the subshell (s, p, d, f)
- m_l which tells us the specific orbital

Comparing different orbitals

Each orbital has a different set of quantum numbers, and as a result has a slightly



Each orbital has the same general characteristics described above but varies in th electron density from the nucleus, and in the presence of 'nodes' where the proba Comparing 1s with the 2s and 2p orbitals, the 1s probability peaks at a shorter dis understanding of energy. 1s is the lowest energy orbital where the electrons are because the electron density is closest to the nucleus.

More interestingly, we see that the main peak for 2p is actually closer to the nucle filling orbitals, is 2s filled before 2p? The answer is because of the small peak in 2 means that when averaged out 2s experiences a stronger attraction to the nucleu average closer when taking into account this small inner peak. These inner peaks called shielding. By the time we get to 4s there are three of these small inner pea main peak of a 3d orbital. This electron density corresponding to these smaller p peak of 3d outside of it, meaning that 4s gets filled first (as in potassium) before 3

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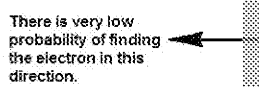
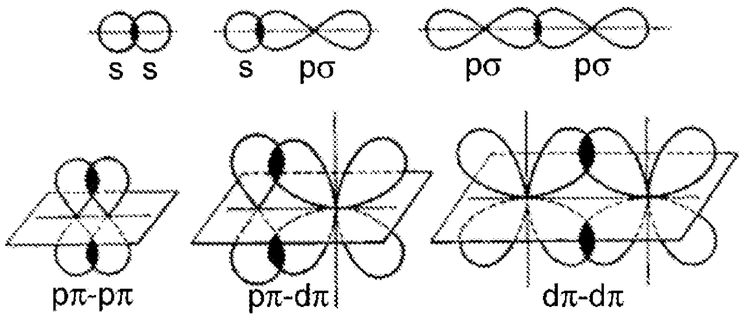
Orbitals and directionality

We can see that s orbitals are spherically symmetric.
This means that when s orbitals are involved in a reaction it doesn't matter what direction another atom or molecule approaches from – there is no steric effect. With p orbitals, d orbitals, f orbitals, etc. this is no longer true. For orbitals to overlap to form a bond, another orbital must approach these orbitals from the right angle – there is a steric requirement. It also means that it is also possible to form bonds head-on (sigma/σ bond) or side on (pi/π bond) or even form delta bonds.





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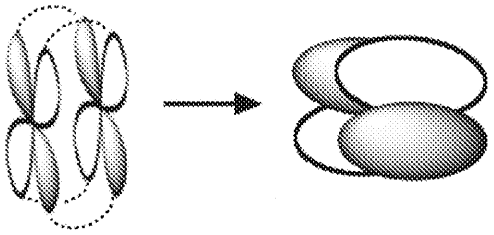

A delta bond involving two d orbitals

In carbon there are four electrons in the outer shell, but since 2s is lower than 2p, there would normally be two electrons in a spherical s orbital, two p orbitals each with an electron and an empty p orbital. How can carbon make four identical bor
By mixing these four orbitals together to form four identical 'hybrid' orbitals. These identical orbitals then give the characteristic tetrahedral shape. Since these four orbitals are made from an s and three p orbitals it is called an 'sp^3 hybrid'.

All of these orbitals can now be modelled using computer programs based on the original equations for these orbitals. By doing this we can also see what happens over time when molecules react, observing how the orbitals change shape as the electrons move from one molecule to another. This is a brand-new way to 'see' c them – not at the macro level on the bench in a lab, but on a computer screen, wa oscillate and alter as different species attract, repel and react. This is new territory future awaits for this 'computational chemistry'.

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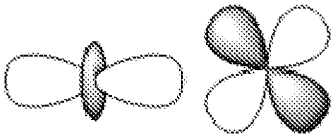
Comprehension questions

1. Define the following terms:
   a) Interference (of waves)
   b) Orbital
   c) Principal quantum number
   d) Radial distribution
   e) Hybridisation
   f) Node
2. In your own words, explain what is meant by wave–particle duality.
3. Write a set of bullet points to summarise the contribution of Thomson, Millik understanding of electrons.
4. In your own words, explain why treating electrons as if they were just particle explanations difficult.
5. Why do p orbitals have directionality but not s orbitals?
6. Why are 4s orbitals filled before 3d orbitals?

Application questions

7. Sketch the radial distribution of a 4s orbital. How many nodes does it have? you predict a 4d orbital would have?



8. The orbital on the left above is a d orbital. Draw the σ-bond formed betwee
9. To form a bond from two orbitals, the phases of the orbitals must match (thi the 'up' parts of a wave and the 'down' parts of a wave). Suggest why the d σ bond with an s orbital, but the d orbital on the right could not.
10. The orbital on the right above is also a d orbital. Of the three p orbitals in a could successfully form a bond with this d orbital. Draw diagrams to support

Taking it further

11. Research and write a three-quarters-of a-page summary on computational chem in different fields.
12. Research a bit more about the Schrodinger equation. Write a half-a-page su contains and how it is used (hard!).

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Boron – breaking the rules of

Like many areas of science, the concept of a 'chemical bond' is one that can be u person in the street all chemical bonds could be the same, whereas a school stud a few years will know, at least, that there are different types of bond, such as ionic This student may also be familiar with the idea that ionic bonding involves the 'tra covalent bonding involves the 'sharing' of pairs of electrons – and that elements d full/empty shells of electrons.

Boron, element number 5 in the periodic table, forces us to shift our understandin white view of ionic/covalent bonding. The chemistry of boron involves a mixing o consider electrons as waves rather than particles – opening up a whole new area o every rule of bonding that is taught in schools.

Electron deficiency

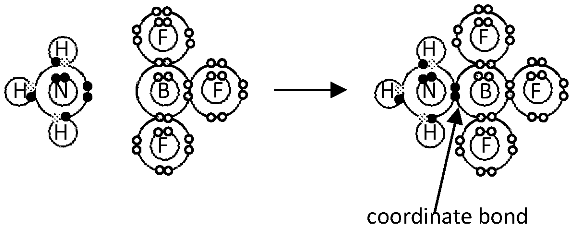
Because boron's outer electrons are only in the second shell, losing all three of th to form a B^{3+} ion is extremely unlikely, as a lot of energy would be needed to rem three electrons so close to the nucleus. Similarly, gaining five electrons to form B^{5-} would also take a lot of energy, meaning that boron does not form simple ioni compounds, and must rely on covalent bonding, at least in part.

- Boron has three electrons in its outer shell ($1s^2 2s^2 2p^1$).
- This means it can form three 'shared pairs' of electrons.
- Three shared pairs of electrons in its outer shell gives it six electrons; two sho of a 'complete octet'.

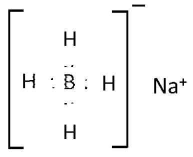
A compound such as boron trifluoride, with boron having only six electrons in the outer shell, breaks the 'octet rule' of elements having only full or empty shells in compounds. For this reason, we describe a compound such as BF_3 as 'electron-deficient'; if given the opportunity it would be more favourable for boron to have complete outer shell, and a compound like BF_3 is, therefore, going to be a compo that is reactive with electron-rich compounds.

Dative bonding

The obvious solution for a compound such as BF_3 is to form a 'dative covalent bo coordinate bond), where an atom, ion or molecule with a lone pair forms an extra electrons in the shared pair come from the other atom, ion or molecule.



In this example, a nitrogen atom in ammonia (NH_3) has a lone pair which it can use to form a coordinate bond. This forms the compound NH_3BF_3.



Lewis dot structure of $NaBH_4$

Here, an H^- ion dona BH_4^- ion, know

The second example above is a good example of where an electron-rich species, a an extra electron, bonds with an electron-deficient species like a BH_3 molecule. Th covalent bonds. You will meet the borohydride ion, BH_4^- ion, in organic chemistry to another compound in a reduction reaction (reduction is gain of electrons, and This transfer of H^- mimics the way reduction reactions often happen in nature, ma most important artificial reducing agents to organic chemists.

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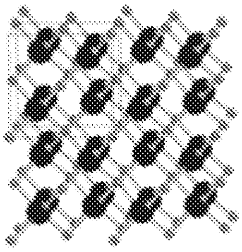
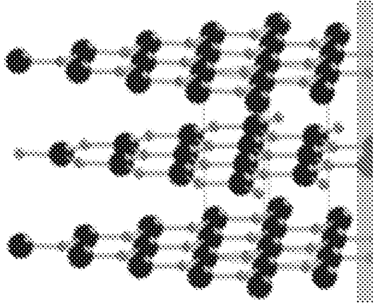
Scratching diamond?

When boron bonds to nitrogen, the result is a bit special because a boron and nit ***isoelectronic*** (3 outer electrons + 5 outer electrons) to two carbon atoms (2 × 4 therefore, the potential for boron/nitrogen compounds to be formed that are sim diamond and graphite.

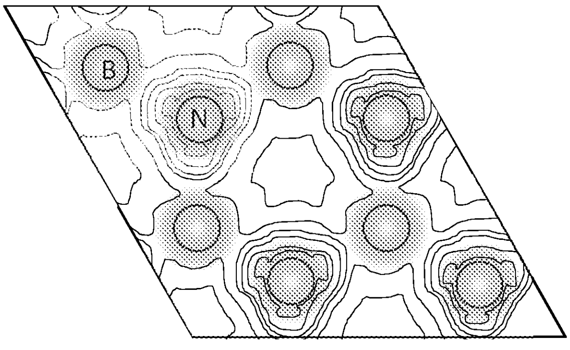

Cubic BN


Hexagonal BN

Every carbon atom in diamond or graphite is equivalent to every other carbon at contributes four electrons to form four shared pairs. The exciting thing is that in degree of ionic character as well, not just traditional covalent bonds. This is becau electronegative than boron, creating a dipole in the B–N bond and making the bo nitride alternately slightly positive (δ+) and slightly negative (δ-). Having covalen ionic (electrostatic) attraction can make a structure even stronger, and it has been diamond's structure), not diamond, is actually the hardest substance known to hu definitively proven, however, and is still a matter of scientific debate.

In addition, this means that hexagonal BN, which is similar to graphite, has graphi lubricant when layers slide over each other) but is much more stable at high temp 'ionic/electrostatic attraction' adding to the strength of the covalent bond. Where dipole–dipole forces between layers, the (δ+) boron atoms on one layer of BN ca on the next layer, strengthening the structure. Hexagonal BN is, therefore, the lub long-range rifle bores when the bullets are shot explosively out of the rifle.

Electrons as waves



An electron density map of hexagonal boron nitride

This mixing of ionic character i limitations of drawing a sharp be more useful to use the idea thinking of electrons as solid p density around every carbon is are identical. In the diagram a mapped in hexagonal BN, with around nitrogen (N) showing t density around the more elect

We can compare this to a situa almost all on one type of atom This situation we would call io between 'covalent bonding with ionic character' (as in the diagram above) and ionic electron density is on one type of atom) is ultimately slightly arbitrary. Covalent and examples at either end of the same spectrum of bonding!

Maps of electron density like this also show the limit of the idea of electrons bein electrons as waves allows us to think of electrons as spread over an area, with a h amplitude) in some areas than others. This is called wave–particle duality.

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Banana bonds

When we start to think of a bond between atoms as an area of overlapping electron density (as in the map above), we can start to challenge the assumption that a bond is only between two atoms. This is a radical challenge to our understanding – but the chemistry of boron forces us to do this!

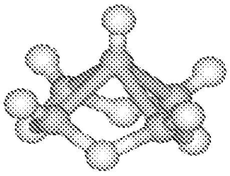
To recap so far, we have said that a simple molecule like BH_3 would leave boron with only six electrons in its outer shell (three from boron, one from each hydrogen in a covalent bond). The most common solution to this is for another atom or ion to donate a pair of electrons to form a coordinate bond.

In diborane, the two electrons come from a B–H covalent bond in another molecule of BH_3. This creates the situation where a pair of electrons is shared bet
covalent bond is a shared pair of electrons, this means that we have a covalent bo
This type of bond is called a 3-centre-2-electron (3c2e) bond. It is not possible fo
have the usual 109.5° bond angle in diborane, and instead the bonds form a shap

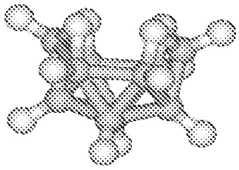
Unsurprisingly, it would be more stable if there were two covalent bonds, each wit
rather than the pair of electrons being shared across three atoms. Diborane is, the
catching fire in air – to the point that it is explosive. It was considered as a potenti
dangerous. Standard advice is for an evacuation area of one mile if there is a risk o

Far-fetched chemistry – boranes

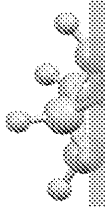
Once the idea of a covalent bond being a shared pair of electrons between two ato
wonderful molecules are possible. The limitation is that they will always be reactiv
bond would be more stable. The images below show molecules made from boron
multiple 3c2e bonds and truly stretch the models of chemistry used at school! The
own area of chemistry, and they have also found a use in a type of cancer treatmen



B_5H_9



$B_{10}H_{14}$



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Comprehension questions

1. Write definitions for the following in your own words:
    a) Electronegativity
    b) Isoelectronic
    c) Electron density
    d) 3-centre-2-electron bond
    e) Wave–particle duality
2. Ammonium fluoride (NH_4F) is an ionic compound containing covalent bonds explain what this means, and label any dative covalent bonds.
3. A single beryllium chloride ($BeCl_2$) molecule would be described as electron-
4. Explain in full why B–N is a polar bond and why it is isoelectronic to a Be–O b
5. Why does boron nitride have different properties from diamond and graphite
6. What is the link between the bond angles in diborane and its reactivity?
7. What is the link between an electron density map and the fact that electrons

Application questions

8. H^- is a particularly reactive ion, even though it has a full outer shell. Suggest stable with an extra electron (H^-) than any of the group 7 atoms that have fo
9. Describe an electron density map of graphite with its pattern, and its differen
10. Would a 3c2e compound be more likely to react with oxidising agents or redu

Taking it further

11. Research neutron capture therapy of cancer and draw a series of diagrams to

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Redox reactions in biolo

Despite often being taught as separate subjects at school, chemistry and biology
acids to adrenaline, DNA to dopamine, life depends on molecules and the chemic
Given how common redox reactions are in the lab, it is hardly surprising that they
In this article, you will meet new ideas that are relevant to redox reactions in gene
biological context. In doing so, you will discover how changes of oxidation state a
being mere arithmetic, sustain organisms across the globe.

Reduction potentials

When a sheet of zinc is left lying in copper(II) sulfate solution, the zinc reduces the

$$Cu^{2+}(aq) + Zn\ (s) \rightarrow Cu\ (s) + Zn^{2+}(aq)$$

When a copper sheet is left lying in zinc sulfate solution, nothing happens.

$$Zn^{2+}(aq) + Cu\ (s) \rightarrow \text{no reaction}$$

In your work on redox so far, questions have probably specified which direction a
above example does. If you weren't provided with this information, though, woul
direction? Yes, but we will need some new concepts if we are to do it. Firstly, red
two **half-equations**, one representing the reduction process in terms of electrons
the oxidation process similarly. When the half-equations are added together, the
For the reaction between copper ions and solid zinc, the half-equations are:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s)\ \text{(reduction)}$$
$$Zn\ (s) \rightarrow Zn^{2+}(aq) + 2e^-\ \text{(oxidation)}$$

Adding them together:

$$Cu^{2+} + Zn + \cancel{2e^-} \rightarrow Cu + Zn^{2+} + \cancel{2e^-}$$
$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

If we were interested in the oxidation of solid copper or the reduction of zinc ions
relevant half-equation.

The energetic favourability of a redox process is measured by a value called the **re**
and with units of volts. A positive redox potential indicates a favourable process,
the more favourable the process. In the same way that adding the half-equations
adding their redox potentials gives the redox potential for the overall reaction, E_r°

$$Cu^{2+} + 2e^- \rightarrow Cu\ E^\circ = +0.34\ V$$
$$Zn \rightarrow Zn^{2+} + 2e^-\ E^\circ = +0.76\ V$$

$$E_r^\circ = 0.34 + 0.76 = +1.10\ V$$

Since the reduction and oxidation processes are both favourable, it makes sense t
favourable as well.

Just as a half-equation for a redox process is flipped to show the reverse process,
flipped too. Thus, a process that is favourable in one direction will be unfavourab
the reaction between zinc ions and solid copper:

$$Cu \rightarrow Cu^{2+} + 2e^-\ E^\circ = -0.34\ V$$
$$Zn^{2+} + 2e^- \rightarrow Zn\ E^\circ = -0.76\ V$$

$$E_r^\circ = -0.34 + (-0.76) = -1.10\ V$$

The redox potential is negative, meaning that the reaction is unfavourable and do
When listing redox potentials, it is conventional to give the redox potential for th
whether the species is being reduced in the reaction being considered. As a result
as **reduction potentials**.

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Case study 1: superoxide dismutase

A paradox lies at the heart of human biology: the oxygen we need to survive has t our cells. Under extreme conditions, breathing pure oxygen can even be fatal. (F normal air is oxygen.) The culprits are **reactive oxygen species**, derivatives of ox components of the cell in an uncontrolled fashion.

One notable reactive oxygen species is the superoxide ion, O_2^-. Here, an oxygen molecule has gained an electron, and has been reduced. The ion is eliminated by a enzyme named superoxide dismutase (SOD), which contains Cu^{2+} ions. First, one superoxide ion is oxidised back to molecular oxygen, and a copper ion is reduced:

$$\mathrm{SOD.Cu^{2+}} + \mathrm{O_2^-} \rightarrow \mathrm{SOD.Cu^+} + \mathrm{O_2}$$

Then, another superoxide ion is combined with protons to form hydrogen peroxid Cu^{2+} in the process, ready to begin the cycle again:

$$\mathrm{SOD.Cu^+} + \mathrm{O_2^-} + 2\mathrm{H^+} \rightarrow \mathrm{SOD.Cu^{2+}} + \mathrm{H_2O_2}$$

The overall reaction is:

$$2\mathrm{O_2^-} + 2\mathrm{H^+} \rightarrow \mathrm{O_2} + \mathrm{H_2O_2}$$

(Hydrogen peroxide is itself a reactive oxygen species, and is removed by another The half-equations involved are shown below, along with some reduction potenti

$$\mathrm{O_2} + \mathrm{e^-} \rightarrow \mathrm{O_2^-} \quad E^\circ = \text{-}0.33\ \mathrm{V}$$
$$\mathrm{O_2^-} + 2\mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2O_2}\ E^\circ = +0.89\ \mathrm{V}$$
$$\mathrm{SOD.Cu^{2+}} + \mathrm{e^-} \rightarrow \mathrm{SOD.Cu^+}\ E^\circ = x$$

Though the reduction potential of the Cu^{2+} ion in superoxide dismutase has been documented, it is listed as x. This is because, as an exercise, we will try to place limits on the value using the data already given. We know that, for a reaction to be favourable, E_r° must be positive. For the first reaction, we change the sign of the O_2/O_2^- reduction potential and add it to the Cu^{2+}/Cu^+ reduction potential:

$$E_r^\circ > 0$$
$$x + (+0.33) > 0$$
$$x > \text{-}0.33\ \mathrm{V}$$

The overall combining opposite, enzy

E_r°

Yes, it v enzyme? T chemi energetical While t favo

For the second reaction, we change the sign of the Cu^{2+}/Cu^+ reduction potential a reduction potential:

$$E_r^\circ > 0$$
$$0.89 + (\text{-}x) > 0$$
$$x < 0.89\ \mathrm{V}$$

Taken together, these results tell us that x must be greater than -0.33 V and small dismutase is to perform both reactions. Does this fit with experimental observatio of the Cu^{2+} ion in superoxide dismutase has been recorded as between +0.12 V a

One of the remarkable features of enzymes is that they can carefully tune the red bound to them, controlling which reactions they will engage in. In other words, t varies from one enzyme to another. A simple way in which an enzyme might con ion is by placing a charged group next to it. For instance, placing a positive charg destabilising, due to electrostatic repulsion. Lowering the charge on copper woul reduction to Cu^+ more favourable.

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Oxidation states of carbon

Up until now, both in your lessons and in this article, you have focused on assignin **inorganic** compounds, defined by their lack of carbon atoms; the chemistry of life, overwhelmingly on **organic** molecules, which do contain carbon atoms. Thankfull we can use to establish the oxidation state of the carbon atoms in organic molecul

1. Carbon–carbon bonds, single or double, do not affect the oxidation state
2. Each carbon–hydrogen bond decreases the oxidation state by 1
3. Each carbon–oxygen single bond increases the oxidation state by 1
4. A carbon–oxygen double bond increases the oxidation state by 2

If the average oxidation state of the carbon atoms in a molecule increases, the molecule has been **oxidised**; if the average oxidation state decreases, the molecu has been **reduced**. As such, oxidation involves the loss of carbon–hydrogen bond and/or the formation of carbon–oxygen bonds, with the reverse true for reductio

Let's try these rules out, starting with ethane.

Each carbon atom forms one single bond to another carbon and three single bond a hydrogen atom, leaving it with an oxidation state of -3. Next, we'll consider ethe

Now, each carbon atom forms one double bond to another carbon and two single to a hydrogen atom, giving it an oxidation state of -2. Finally, we turn to ethanol.

The carbon atom on the left is identical to an ethane carbon, with an oxidation sta of -3. The other carbon atom forms one single bond to a carbon atom, two single bonds to a hydrogen atom and one single bond to an oxygen atom. As a result, i an oxidation state of -1, and the average oxidation state for a carbon atom in etha is -2.

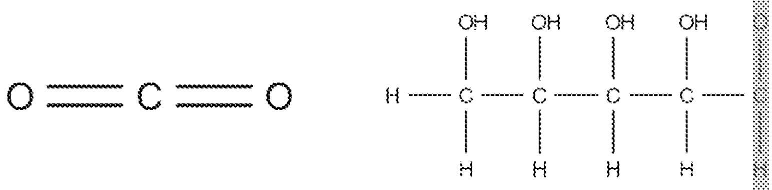
In summary, the conversion of ethene to ethane would be a reduction (-2 to -3; tw carbon–hydrogen bonds formed), and the conversion of ethane to ethanol would be an oxidation (-3 to -2; one carbon–hydrogen bond lost, one carbon–oxygen bond gained).

Case study 2: photosynthesis

Photosynthesis is carried out by plants, algae and some bacteria, and converts car glucose ($C_6H_{12}O_6$):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

While the biological importance of oxygen is well-known, glucose is equally signif the process of respiration. In terms of reactants and products, respiration is the re glucose and oxygen converted into carbon dioxide and water. However, animals c glucose, and it is only introduced to a food chain through animals that eat plants. photosynthetic organisms also regulate the greenhouse effect and, by extension, Before looking more closely at photosynthesis, let's establish whether carbon diox glucose. The structures of both molecules are shown below.



The structures of carbon dioxide (left) and glucose (right)

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The carbon atom in CO_2 forms two double bonds to oxygen, giving it an oxidatio middle four carbons have an oxidation state of 0, with the carbon–oxygen and ca cancelling each other out. The leftmost carbon forms two single bonds to hydro oxygen, and has an oxidation state of -1. The rightmost carbon has an oxidation bond to oxygen and one single bond to hydrogen. The average oxidation state o therefore, 0, and carbon dioxide is *reduced* to glucose. The corresponding half-e

$$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O \quad E^\circ = \text{-}0.4$$

The necessary electrons are obtained via the oxidation of H_2O to O_2:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\circ = \text{-}0.82\text{ V}$$

Using the redox potentials to calculate E_r°:

$$E_r^\circ = \text{-}0.42 + (-0.82) = \text{-}1.24\text{ V}$$

Hmm… the result is negative, suggesting that photosynthesis is not favourable, ye to breathe. What's going on? The key is that *unfavourable* does not mean *imposs* placing a ball at the top of a steep slope. Naturally, the ball will roll down the slo again, but you need to push it. Returning to redox reactions, electrons can be ma direction, if enough energy is supplied. In photosynthesis, this energy is provided that energy must be *taken in* for photosynthesis is consistent with the fact that en

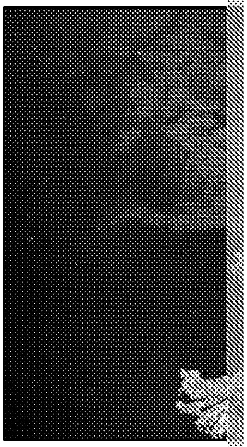
Dining in the dark

The deep ocean is home to many weird and wonderful creatures, including the a despite a total lack of sunlight. Clearly photosynthesis cannot take place under t the sugars necessary for life come from? In most cases, they fall from the upper waste matter and the remains of dead organisms. Surviving off these scraps is h much of the ocean floor. Scattered throughout this marine wasteland, though, a ecosystems thrive in comparison. These communities depend on **chemosynthe** carbon dioxide into sugars without light. They rely solely on chemical reactions

The reaction pathways used in chemosynthesis vary, but many involve oxidation of hydrogen sulfide, H_2S, to elemental sulfur. The overall equation for this class of reactions is given below.

$$6CO_2 + 24H_2S + 6O_2 \rightarrow C_6H_{12}O_6 + 24S + 18H_2O$$

Hydrogen sulfide is pumped into the water by geological formations known as hydrothermal vents, where water heated in Earth's crust bursts through the seabed. It is thought that life on Earth might have begun near these structures, with chemosynthesis supporting its development until photosynthesis evolved.



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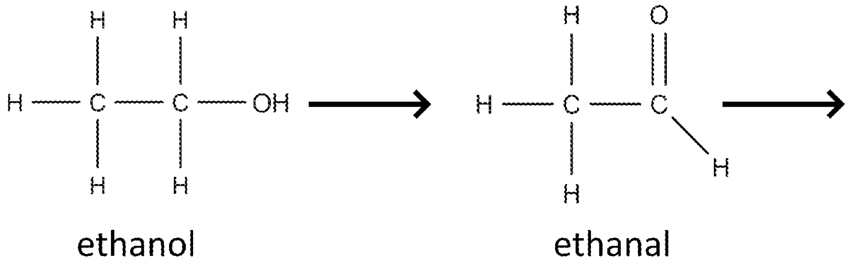
Comprehension questions

1. Explain the meaning of the following terms:
   a) reduction potential
   b) enzyme
   c) inorganic
   d) chemosynthesis
2. Haemoglobin (Hb) is a protein that transports oxygen around the body. Occ haemoglobin reacts with oxygen to form a superoxide ion. The relevant half potentials are given below.

$$\mathrm{Hb.Fe^{3+}} + e^- \rightarrow \mathrm{Hb.Fe^{2+}}\ E^\circ = +0.13\ \mathrm{V}$$
$$O_2 + e^- \rightarrow O_2^-\ E^\circ = +0.33\ \mathrm{V}$$

   a) Write the overall reaction equation.
   b) Which species is being reduced and which is being oxidised?
   c) Calculate E_r°. Is the reaction favourable?
3. During the metabolism of alcoholic drinks, ethanol is converted first into etha



Determine the average oxidation state of the carbon atoms in ethanal and et or reduced in the first reaction? What about ethanal in the second reaction?
4. Based on the change in the average oxidation state of carbon, explain why 2 following half-equation.

$$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$$

Application questions

5. There are several ions that contain only oxygen. By far the most common is oxygen has an oxidation state of -2. In the superoxide ion, O_2^-, oxygen has Deduce the oxidation state of oxygen in the following ions:
   a) peroxide ion, O_2^{2-}
   b) dioxygenyl ion, O_2^+
   c) ozonide ion, O_3^-
6. While calculating E_r° for photosynthesis, we did not multiply the potential of even though the half-equation was multiplied. Based on the fact that volts c coulomb, explain why. (Hint: coulomb is the SI unit for charge.)
7. In the article, you learned that unfavourable reactions can be carried out by s energy is often electrical.
   a) What name is given to the process of supplying electrical energy to driv reactions? (You might remember this from GCSE. If not, look it up.)

   One application of this process is isolating aluminium from its ore, bauxite.

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

   b) Write balanced half-equations for this reaction.

Taking it further

8. Research other redox reactions in biology. Choose **four** reactions and write one, including what type of organisms carry out the reaction, which species a the reaction is important.

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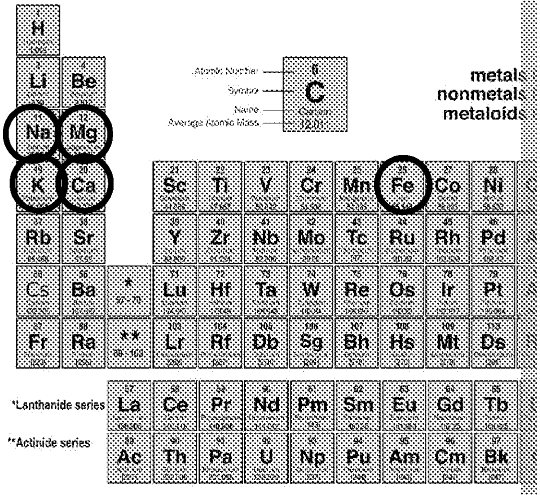
Magnesium – more than a sil

Among the elements most abundant in organic life, non-metals dominate, especi
nitrogen. Metallic elements do, however, play a key role in biological systems, inc
sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and iron (Fe^{3+}/Fe
Of these metals, however, only magnesium and iron find common use in other ar
You will probably be aware of iron's importance in steel – which holds up both ou
the end of a teaspoon. You may also be aware of the key role of iron ions at the c
carries oxygen to cells around the body, and carbon dioxide back to the lungs. M
as iron, but the variety of its roles in both organic and inorganic chemistry is impressive – and much of this relies on the principles you will cover in your study of group 2 at A Level.



The location of some metals in the periodic table

Magnesium and life

Magnesium is the eighth most abundant element in Earth's crust, being slightly le
sodium and calcium, and less than half as abundant as iron and aluminium. Desp
abundant metal across all cellular life. The reason for this is linked to the origin o
clearly had properties that made magnesium suited for incorporation into cells.

Staying in solution

Magnesium ions have a stronger electrostatic attraction to water molecules (and hydroxide ions) than the elements of group 2 below magnesium, which means they are more soluble. This is because magnesium ions are smaller, and can be thought of as having a 'more concentrated' 2+ charge, which attracts the partial negative charge (δ^-) on oxygen in water molecules more strongly.
Because calcium ions are less soluble than magnesium ions, they are more likely to form solid precipitates with other ions found in water, such as sulfate ions and carbonate ions. This explains why magnesium sulfate is soluble whereas the sulfates of group 2 below it are much less soluble (as you learn at A Level), and why calcium has a common role in living organisms as part of solids such as calcium carbonate (which makes up shells, coral and eggs) and a form of calcium phosphate which makes up bones.

Sodium ions and potassium ions are soluble, like magnesium ions, but form much
molecules due to their 1+ charge. The reason they are soluble in water, despite f
than the 2+ ions in group 2, is that the group 1 ions do not form comparably stro
other ions or molecules either, and, therefore, remain dissolved in water instead o

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Transport

The ability of magnesium to bind well to water molecules means it has the potential to be transported across membranes, a key trait in early cellular life. Sodium and potassium ions most commonly pass in and out of cells without contributing to any structures once inside the cell – they just pass out again (movement that is key to nerve transmissions). However, because magnesium can form stronger electrostatic attractions, magnesium ions can then bind to other substances containing electronegative oxygen or nitrogen atoms. This means transported magnesium ions can be incorporated into important structures inside the cells, such as chlorophyll in plants, or bind to substances to allow them to carry out their role; for example, binding to ATP (our 'energy currency') in many organisms.

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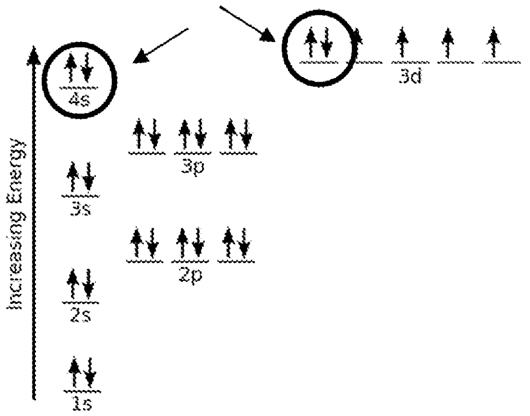
withc

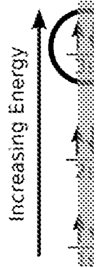
Fe vs Mg

Iron 2+ ions (Fe^{2+}) behave in a similar way to magnesium ions – they form relatively strong bonds with water, and can then also form new electrostatic attractions with other molecules containing nitrogen or oxygen atoms inside a cell. Both Fe and Mg are essential in many forms of life. Two key differences between the two are:

1) their size – magnesium's outer electrons are in a 2p subshell, whereas
2) and iron's ability to be oxidised into other ions, mainly Fe^{3+}. This change involves Fe^{2+} losing an electron to form Fe^{3+}, which it often regains to form F



Iron electronic structure – the 4s electrons are lost easily, but a 3d electron may also be lost and regained, meaning iron forms both Fe^{3+} and Fe^{2+} commonly



Magnesium electr
are lost easily, bu
held r

The extra electron that Fe^{2+} loses when it forms Fe^{3+} can allow other chemical rea
than they would have done otherwise, meaning that Fe^{2+} ions can play a role as a
oxidation and reduction. Mg^{2+} does not lose or gain electrons easily – the 3s elec
to form Mg^{2+} as they are further away and not held strongly, but losing subseque
very difficult due to their proximity to the nucleus. This means that Mg^{2+} ions are
magnesium metal is very reactive). There are many examples of biological molec
chemically if they are to perform their function (e.g. the backbone of DNA and the
and, therefore, Mg^{2+} is much more suited in these situations than Fe^{2+}.

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Magnesium as a metal

Most people associate magnesium metal with the strips that get burned in Chemi
white light (while the teacher tells the class not to look directly at it!). It also gets
tubes of hydrochloric acid, watching it bubble and lighting the gas to produce a s
hydrogen. Not many people think of magnesium as being a metal that is useful i
to a metal that has a very important set of properties.

Density

The metals in the top left of the periodic table have in common a high reactivity, b
low molecular weight. Magnesium is the least reactive of the metals in groups 1 a
beryllium, which is quite different from the other elements), and is by far the most
alloys, partly due to its lower reactivity. Only iron and aluminium are more comm
and structures, and magnesium is normally used to form an alloy with these meta
magnesium with these metals is that its low density allows for lower-density alloy
in construction, transport, electronics and many other areas of technology where

Elektron

The risk with using magnesium in alloys is that the metal itself is very reactive, bur
vigorous reaction. This is very rarely a problem in alloys, as shown by the fact tha
magnesium – has been used to make engines for the aerospace and car industry,
Elektron Ltd company having produced the alloy in Manchester since 1936.

On two occasions, however, the flammability of the magnesium has meant that
Elektron has hit the headlines. Firstly, in World War II, when the low-density Elekt
was used to make bomb casings. The lighter-weight bombs could be transportec
dropped in higher numbers, and when they exploded on landing the burning
magnesium burned through metal, reacted with any water poured on it, and cont
to react for over 15 minutes. In the 1955 Le Mans race the same effect was obser
with horrifying consequences when a car with an Elektron engine crashed and its
tank exploded, causing the Elektron engine to subsequently explode and shower
crowd in burning magnesium. Unwitting stewards attempted to put out the fires
water, making them much worse and creating flames which burned for several ho
Sadly 85 spectators were killed, as well as the driver of the car.

Modern research continues to work on developing magnesium alloys that are resi
safe to use by varying the amount of magnesium in the alloy, and including other
likelihood that magnesium will react with oxygen.

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Comprehension questions

1. Explain what the following terms mean:
   a) Electronegative
   b) Partial charge
   c) Precipitate
   d) Molecular weight
   e) Alloy
2. Why are barium ions (Ba^{2+}) less soluble in water than the ions of the element
3. Summarise the key properties of a) Mg^{2+} ions and b) Magnesium metal ment
4. Summarise the key reasons why Mg^{2+} ions are the most common metal ion i
   not being the most common metal on Earth.

Application questions

5. Enthalpy of hydration is the energy released when one mole of a gaseous me
   The enthalpies of hydration of K^+, Mg^{2+} and Na^+ are, from largest to smallest

   $-1926\ kJ\ mol^{-1}$, $-406\ kJ\ mol^{-1}$, $-320\ kJ\ mol^{-1}$

   Match the values to the metal ions, explaining your reasoning.
6. Suggest the benefits and risks of using lithium in alloys compared to magnes
7. Suggest the main environmental advantage of using magnesium in engines a
   from the centre of the periodic table.
8. Mg^{2+} ions can act as catalysts, but often in a different way to Fe^{2+}/Fe^{3+} ions.
   ions acting as a **cofactor**. Find out what this means, and write an explanatio
   out a biological example of when this is important.
9. Magnesium ions can act as **Lewis acids**, which allow pH to be lowered in a g
   cells, rather than by releasing lots of H^+ ions like Bronsted–Lowry acids which
   a Lewis acid is, and explain why a Lewis acid (such as Mg^{2+}) would slightly lo

Taking it further

10. Copper ions are also important to life. Research some of the key roles that c
    what the key properties of copper ions are that allow it to perform its role we

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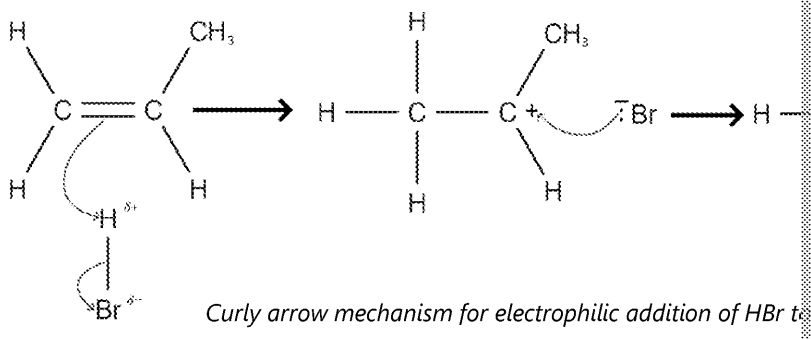
Expanding the chemistry of

The reaction most commonly associated with alkenes is electrophilic addition. Yo and hydrogen halide molecules as the electrophile, but there are many possible a reaction very versatile, and its use in industry is widespread. Hopefully, you are co mechanism, outlined below.



Curly arrow mechanism for electrophilic addition of HBr t

To begin with, the electron-rich carbon–carbon double bond acts as a nucleophile by donating a pair of electrons to the electron-deficient hydrogen atom in hydrogen bromide. A carbocation forms, and the H–Br bond breaks to produce a Br$^-$ ion. The Br$^-$ ions acts as the nucleophile in the second step, donating a pair of electrons to the electrophilic carbocation. The hydrogen atom is preferentially added to the less substituted carbon, i.e. the one with fewer alkyl groups attached to it. This is Markovnikov's rule, named after Vladimir Markovnikov, who published a paper on the phenomenon in 1870. Unlike the Russian chemist, we know the reason for the observation: carbocations form on more substituted carbon atoms, where they are more stable, so the hydrogen atom is left to add to the other, less substituted carbon.

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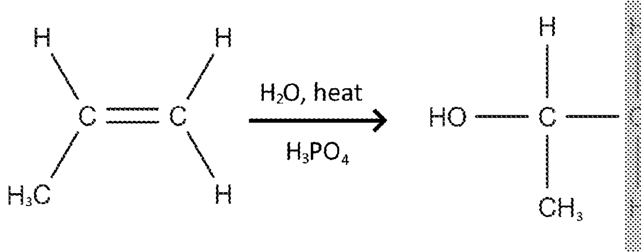
For all its importance, this type of electrophilic addition is far from the only chemi alkenes. In this article, we will explore three further aspects of their chemistry, eac come to expect.

Alkenes as nucleophiles

Electrophilic addition can be employed to convert propene into its corresponding



Overview of hydration of propene

A hydrogen atom has been added to one of the carbon atoms in the double bond the other. However, the hydrogen atom did not come from the water molecule, a Instead, it was provided by the phosphoric(V) acid catalyst. Once the carbocation nucleophile in the second step, and the acid is regenerated by picking off a proto Markovnikov's rule, the major product is propan-2-ol.

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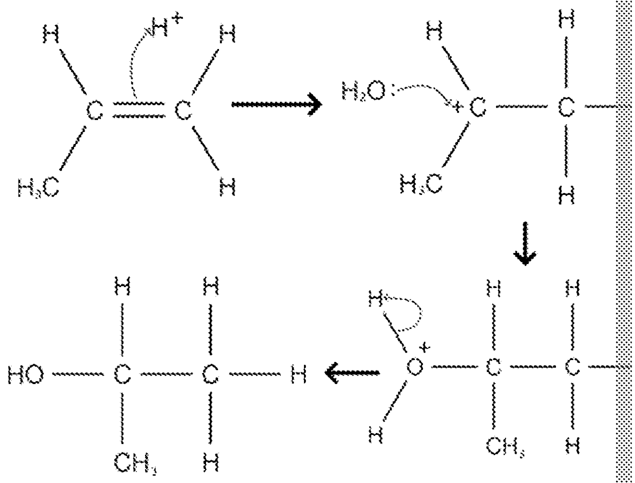
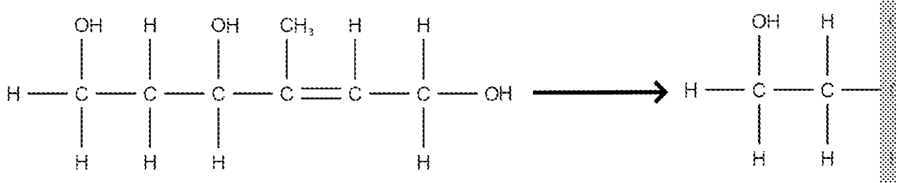


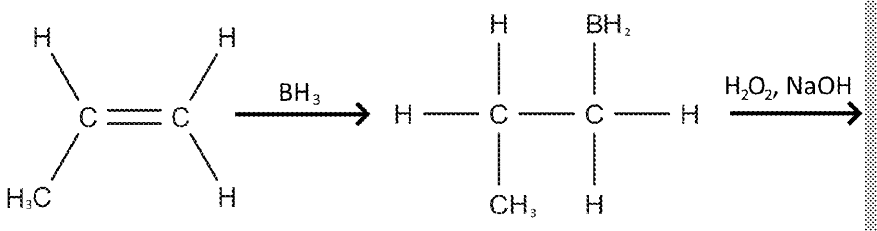
Curly arrow mechanism for hydration of propene

What if chemists want to add an OH group to the *less* substituted carbon? For ex of a synthesis for a compound with anti-tumour activity:



A step in the synthesis of a promising anti-tumour compou

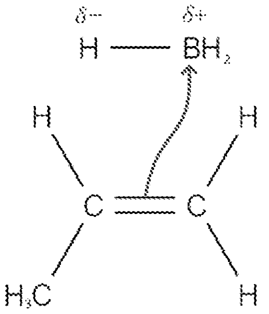
In that case, they turn to the **hydroboration–oxidation** reaction. This name mak two steps involved in the process.



Overview of hydroboration–oxidation reaction

During the first step, a hydrogen atom is added to one carbon in the double bond added to the other (boration). Next, the BH_2 group is replaced by an OH group (o article, we'll focus on the hydroboration step, as this is where the **anti-Markovnik**

As in the two previous mechanisms, the electron-rich double bond acts as the init donating a lone pair of electrons to a hydrogen atom, it attacks the boron atom. halogens, boron is *less* electronegative than hydrogen, bearing a partial positive c accommodate the lone pair because it only has six electrons in its outer shell, two



First step in the curly arrow mechanism for hydroboration of pr

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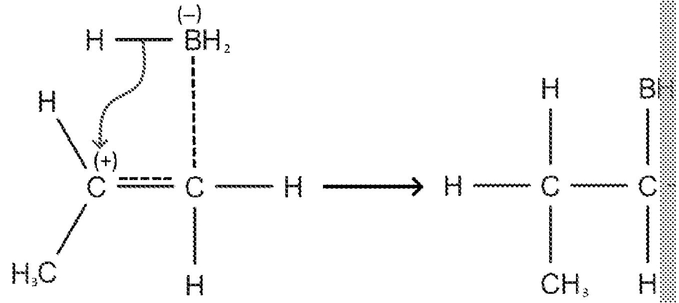
While this transfer of electrons takes place, a negative charge develops on the bo electron density without giving any up. Meanwhile, a positive charge develops on double bond. Again, it is more stable on the more substituted carbon. However, formed, the electron-deficient carbon is attacked by an electrophile. Despite havi boron atom has no lone pairs, while the solvent molecules are too far away. Wha You might find the answer surprising: the electron pair comes one of the B–H bor electrophile as being an H^-, or hydride, ion. Once more, this is possible because than boron, allowing the lighter element to draw the electrons in the bond towar

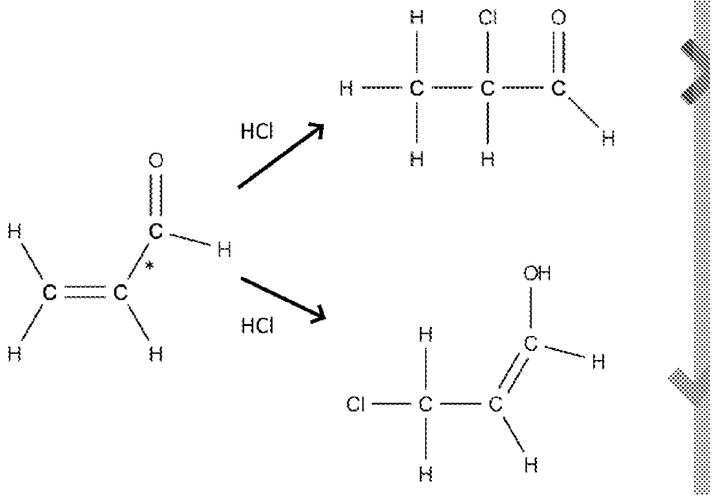


Second step in the curly arrow mechanism for hydroboration of propene; dashed line the case of the C–B bond) or breaking (in the case of the C–C π-bond); plus/minus sig charges above) or disappearing

With now only three bonds, the boron is neutral again, giving the expected produ

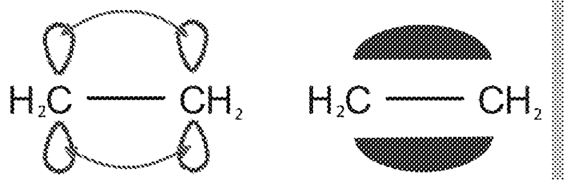
Alkenes as electrophiles

The molecule on the left-hand side of the diagram below is called acrolein. If you of the reaction between acrolein and HCl, you would, very reasonably, produce so the right-hand side. In reality, the product is the bottom molecule.



Reaction of acrolein with HCl; the top product assumes the alkene is nucl bottom product assumes it is electrophilic

If that wasn't enough, the length of the bond marked with a star is *between* those bond and a typical carbon–carbon double bond. What's going on? As you might to do with the C=O bond, which is probably unfamiliar. Before we get to that, th ourselves of the bonding in ethene, the simplest alkene.



Orbital overlap involved in carbon–carbon π-bond (left) and the distribution of electr

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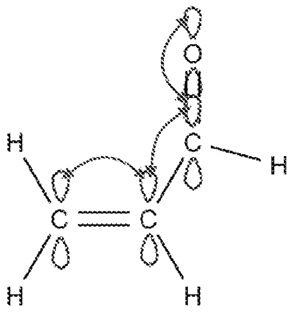
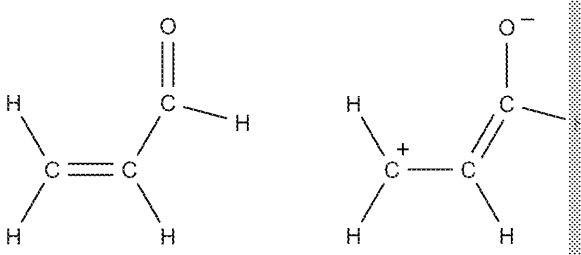
Both carbon atoms have a p orbital, which contains one electron. The two p orbit π-bond with electron density above and below the plane of the molecule. The sa bond, so acrolein has two of these systems connected by a carbon–carbon single and, rather than two, separate π-bonds, there is now a single π-*system*, containin



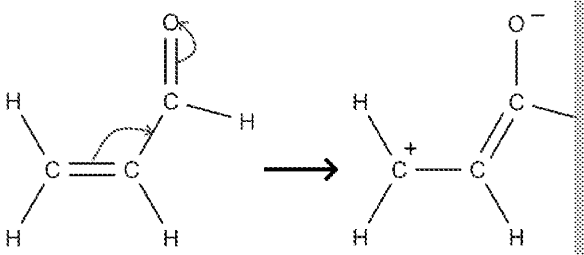
Overlap involved in π-system of acrolein
(For clarity, arrows only show overlap between top lobe of each p orbital; bottom lobe

The electrons in the π-system are no longer restricted to just one bond, and are s be distributed across the π system in several ways. For instance, in acrolein:



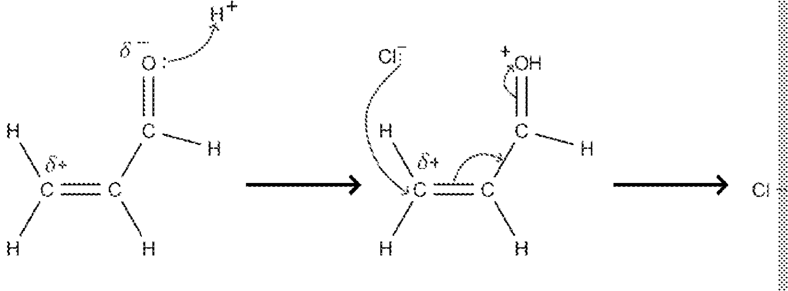
Two resonance structures of acrolein

Each of these representations is called a **resonance structure**, and can be unders



Relationship between the two resonance structures, shown usin

Even so, it is important to understand that these are *not* two different species, int electrons. Actually, neither of them exists as shown. From experimental observat that real acrolein molecules are somewhere between these two forms – a combin properties correspond more closely to those of the neutral structure, it is the con species that interest us. Firstly, the carbon–carbon bond marked with a star was s has some double bond character. Secondly, the alkene acted as an electrophile i electron density was reduced by the C=O group, giving one of its carbon atoms a



Curly arrow mechanism for the addition of HCl to acrole

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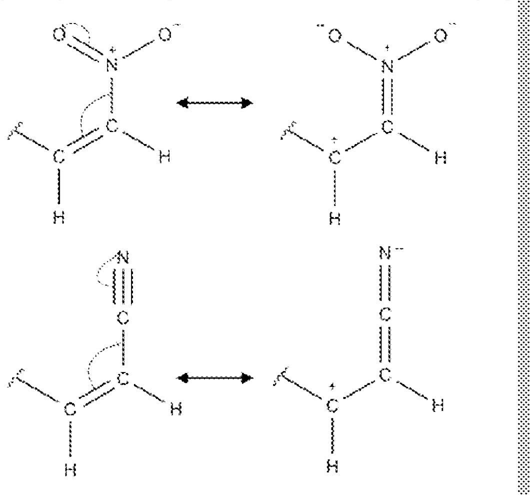
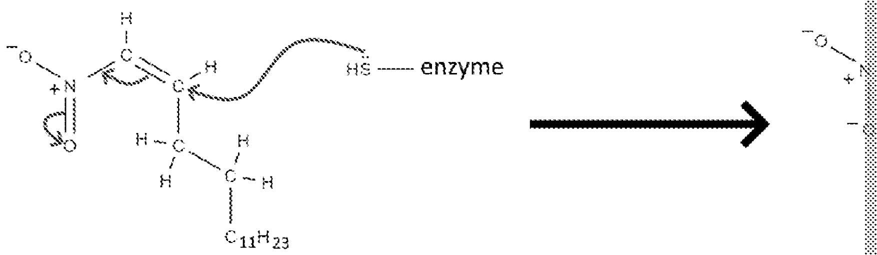
Other examples of electron-withdrawing groups include the nitro group, NO_2, and
the double bonds can be separated by only one single bond; this is called **conjug**



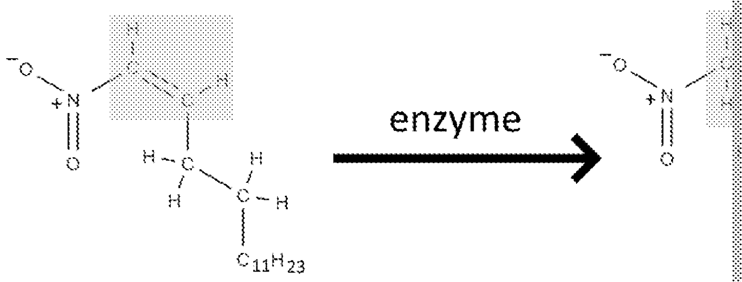
Resonance structures for an alkene conjugated to a nitro group (top) and a nitrile gr
double-headed arrows are used to link resonance structures of the sa

Besides appearing in the syntheses of countless pharmaceuticals, this type of reac
As an example, some termite species poison ants, their main predators, by secreti
1-nitropentadec-1-ene. The molecule wreaks havoc by reacting with various com
including proteins and DNA. Many important enzymes depend on a thiol group, S
In the reaction below, the thiol group is inactivated, preventing the enzyme from



Curly arrow mechanism for the inactivation of a thiol-containing enzyme by

To avoid accidentally injuring themselves, the termites produce an enzyme that hy
ene to 1-nitropentadecane, rendering it harmless.



Overview of the reduction of 1-nitropentadec-1-ene to 1-nitropentadecane (sit

Alkenes as… neither?

Practically all of the reactions that you will meet during your Chemistry A Level ca
electron-rich species (the nucleophile) donating a lone pair of electrons to an elec
electrophile). Often, the mechanism will have multiple steps, and will involve char
exceptions are the halogenation of alkanes and, for some exam boards, the deple
these are radical reactions, featuring the transfer of single electrons from one spe
initiation step, a termination step, and various propagation steps. Alkenes are oft
class of reactions: pericyclic reactions. An example is presented on the next page.

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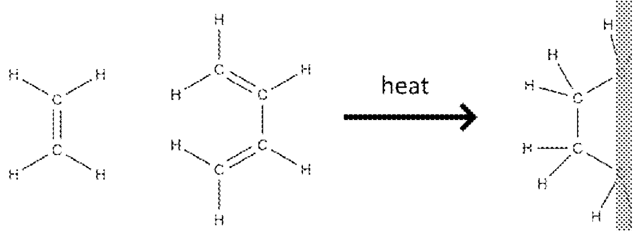
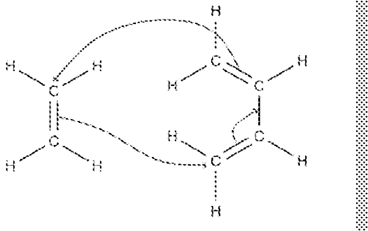
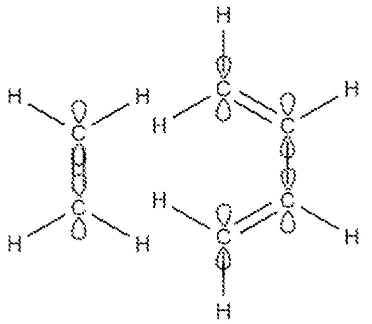


Curly arrow mechanism:



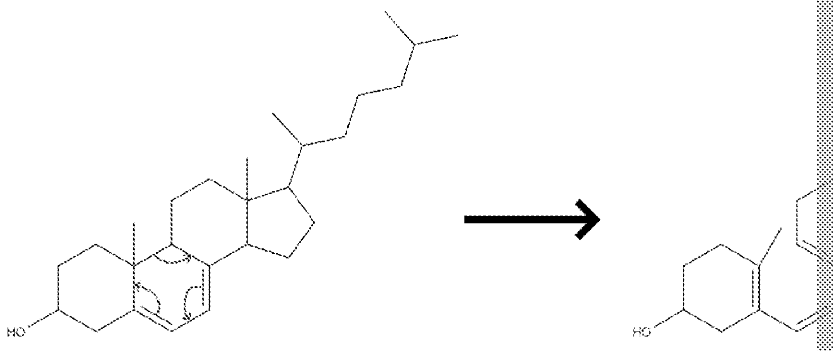
An overview of, and curly arrow mechanism for, a cycloaddition reaction betw

This particular type of pericyclic reaction is called a cycloaddition, as two molecule
cyclic product. Unlike polar and radical reactions, we do not have one molecule d
another accepting it; instead, both molecules are simultaneously donating *and* ac
It would be equally valid to draw the mechanism with the directions of the arrows
pericyclic reactions. Other defining characteristics are that bond formation and b
time, leading directly to the product, and that the p orbitals involved are arranged
occur when the reactants are exposed to certain wavelengths of light.



The layout of the p orbitals in the cycloaddition reaction sho

Although pericyclic reactions are not mentioned at A Level, they are by no means
essential to human health. Vitamin D promotes the absorption of calcium in the i
development. In the autumn and winter months in the UK, most people rely on f
their main source of the vitamin. In spring and summer, however, all the vitamin
our own skin cells. Why the seasonal variation? One of the key steps in the prod
reaction, and ultraviolet light from the Sun supplies the energy required for it to t
reaction is known as an electrocyclic ring-opening.



Curly arrow mechanism for an electrocyclic ring-opening reaction involved in the
(Due to the size of the molecule, skeletal formulae have been

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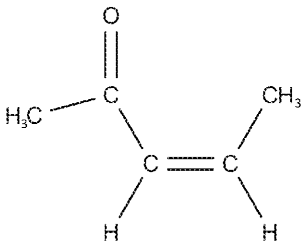
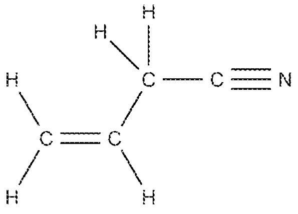
Comprehension questions

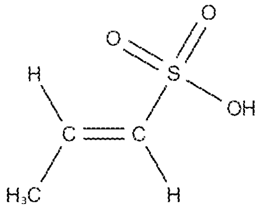
1. Explain what the following terms mean:
    a) Hydroboration
    b) Anti-Markovnikov addition
    c) Hydride ion
    d) Delocalised electrons
2. Explain how the properties of boron are important to hydroboration reaction
3. Predict the product of the reaction between HBr and the molecule below.



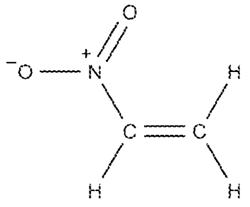
4. How many of the following molecules contain an electrophilic carbon–carbo



A



B

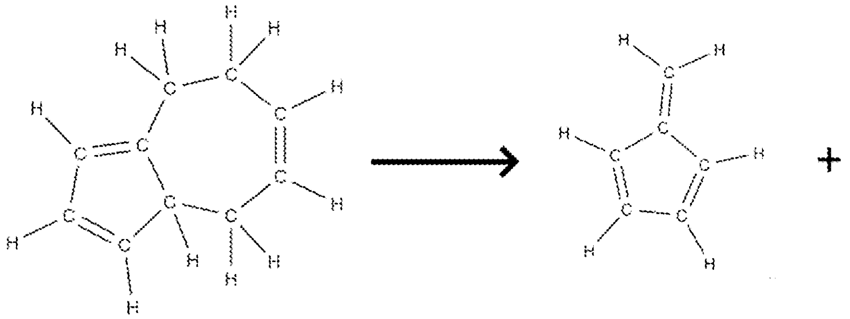


C

5. How many hydrogen atoms does the vitamin D precursor in the last section

Application questions

6. Look back at the product given for the reaction between HCl and acrolein. T bond in this molecule is *more* nucleophilic than the one in ethene. Suggest your answer. (Hint: one of oxygen atom's lone pair is in a p orbital.)
7. Suggest a curly arrow mechanism for the pericyclic reaction below.



(Hint: this is a cycloreversion reaction, the reverse of a cycloaddition reaction

Taking it further

8. Alkynes are hydrocarbons that contain a carbon–carbon triple bond. Write 3 including a comparison of their chemistry with that of alkenes.

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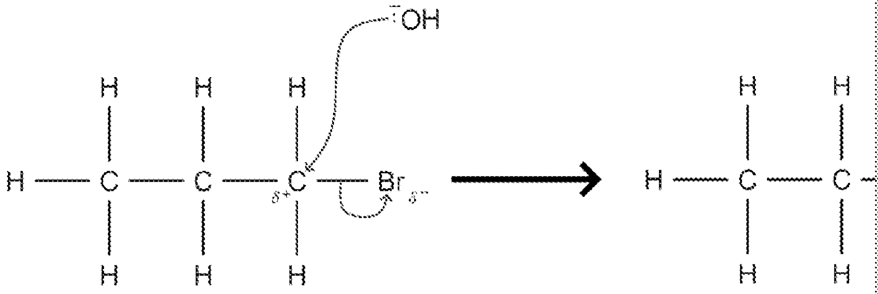
A closer look at nucleophilic su

While learning about halogenoalkanes (otherwise known as haloalkanes), you wi
nucleophilic substitution reaction. An example is presented below.

$$CH_3CH_2CH_2Br + {}^{-}OH \rightarrow CH_3CH_2CH_2OH + Br^{-}$$

In this type of reaction, an electron-rich **nucleophile** (^{-}OH) donates a lone pair o
carbon atom (the C–Br carbon), forming a bond to it and causing it to expel an at
'**leaving group**' (Br^{-}). The overall transformation is the substitution of the nucle
electrophilic carbon. You may also have covered a curly arrow mechanism for the



Curly arrow mechanism for a nucleophilic substitution reaction

The arrows represent visually the flow of electrons described above. The leaving g
electrophilic carbon atom cannot form five covalent bonds. (Note the partial posi
which arises from the electronegativity difference between carbon and bromine. T
atom being electron-deficient.)

A diversion into kinetics

In addition to an overall equation, a reaction can be represented as a series of ele
steps reflects a chemical interaction, detailing which species react with each other
curly arrow mechanism is essentially an elementary step. Where the overall equati
the elementary steps describe how it happens.

Among the elementary steps is a **rate-determining step**. This is the slowest step,
acts as a bottleneck for the whole reaction. As an analogy, imagine that you are m
a large fruit cake. Collecting the ingredients from the cupboard, weighing the
ingredients, mixing the ingredients, leaving the mixture in the oven and decoratin
cake would all be elementary steps. If the mixture needs to be left in the oven for
hours, this will be the rate-determining step. Regardless of how quickly you comp
preceding steps, and how quickly you can decorate the cake, you will always be sl
down in between. Only by changing the oven's temperature can you drastically sp
the process. Similarly, the rate of a chemical reaction is dictated by the species in
in the rate-determining step.

In our nucleophilic substitution mechanism, there is only one step, so it must be t
It involves two species: the nucleophile and the molecule containing the leaving g
paragraph, we would expect the rate of substitution to be determined by the natu
exactly right. Experimentally, we observe that some nucleophiles are 'good', resul
and others are 'bad', resulting in slow substitution reactions. The same is true for
molecule containing the leaving group.

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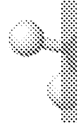
Factors affecting the rate of substitution

Let's start with what makes a good nucleophile. This is a slightly tricky question, s will focus on some rules of thumb. Firstly, nucleophiles donating their lone pair fr are better nucleophiles (e.g. NH_3 is better than H_2O). Hopefully, this sounds reaso lone pair less tightly will donate it more readily. Secondly, deprotonated species a equivalent protonated species (e.g. ^{-}OH is better than H_2O and $^{-}NH_2$ is better th

We turn next to the molecule containing the leaving group, where we will conside

1. The leaving group – since you have only encountered nucleophilic substituti halogenoalkanes, we will limit ourselves to halide leaving groups, which sho radius of the halogen atoms increases down the group, the strength of their making them better leaving groups. Hence, alkyl iodides undergo substituti alkyl chlorides.
2. The number of alkyl groups attached to the same carbon atom as the halogen atom – due to the molecular orbitals involved in the interaction, the nucleophile must attack the electrophilic carbon from behind the leaving group. In an effect known as **steric hindrance**, the other groups bound to the carbon obstruct the approach of the nucleophile. Although the steric hindrance caused by small hydrogen atoms is insignificant, it is more pronounced with alkyl groups. As the number of alkyl groups attached to the electrophilic carbon increases from zero to three, the amount of steric hindrance increases, and the rate decreases.



At this point, we have developed a simple framework to explain the rates of nucleophilic substitution reactions. However, the reaction below seems to pose a problem.

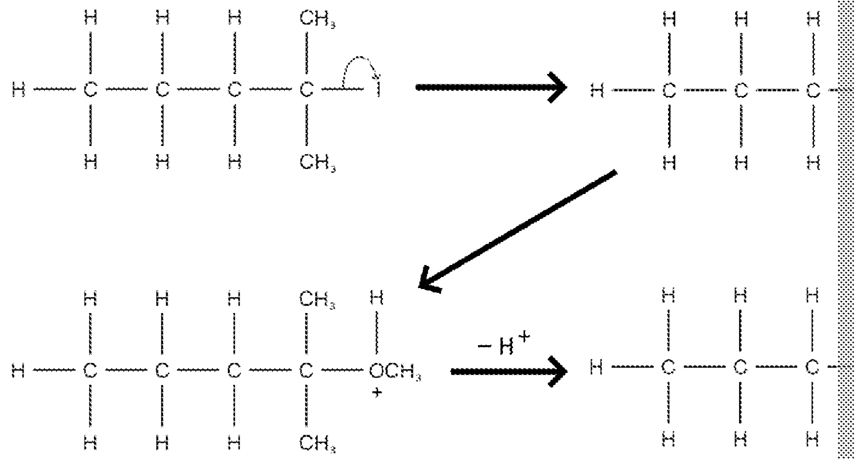
The
illust

$$CH_3CH_2C(CH_3)_2I + CH_3OH \rightarrow CH_3CH_2C(CH_3)_2OCH_3 + I^-$$

There are three alkyl groups attached to the same carbon as the iodide, severely hind nucleophile. Furthermore, the nucleophile is neutral, with the lone pair belonging to a How does substitution take place at a reasonable rate under these conditions?

The two mechanisms of nucleophilic substituti

The answer is that there is another mechanism by which nucleophilic substitutio that we have been discussing so far is referred to as **S_N2**. This is because it describ attack by a nucleophile, with two species involved in the rate-determining step. methanol, this mechanism would be incredibly slow, for the reasons outlined. Yet, **S_N1** mechanism is much faster. Here, while there is again a substitution reaction only one species appears in the rate-determining step. This becomes clearer with t



Curly arrow mechanism for the S_N1 mechanism

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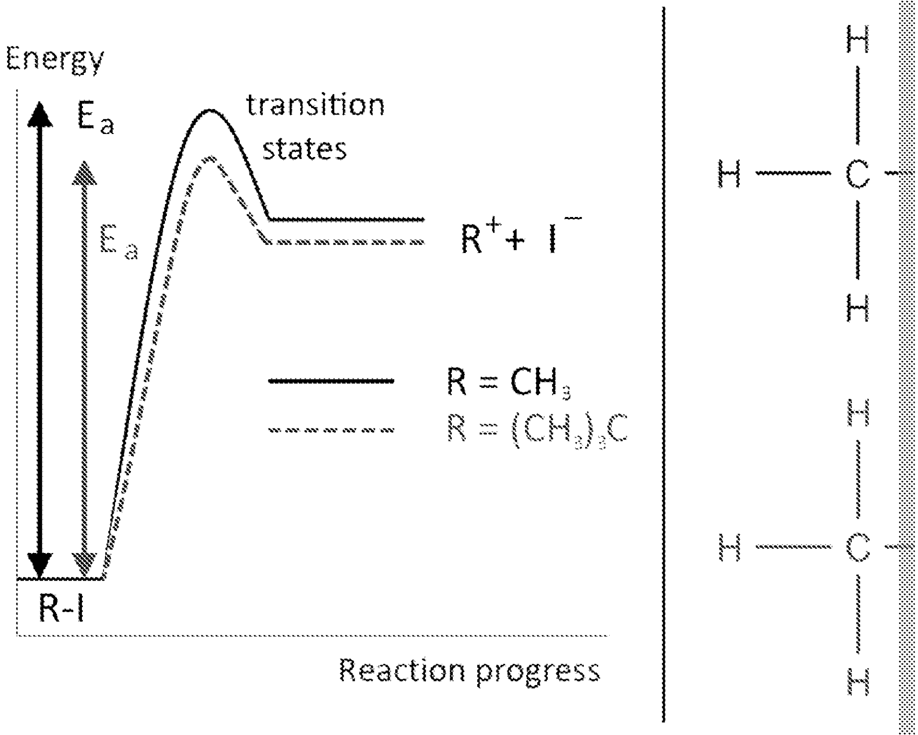
Immediately, we can see that there are two main steps, so assigning the rate-dete before. In the first step, the bond between the carbon and the leaving group brea intermediate. (These are also formed during electrophilic addition to an alkene.) I nucleophile donates a lone pair to electrophilic carbocation, forming a new bond. proton is removed, either by a solvent molecule or by iodide, to form the final pro first step must be rate-determining, as it is the only one that involves just one spe chemical sense too: a bond is being broken, leading to a high activation energy a

The fact that the molecule containing the leaving group is the only species in the perhaps surprisingly, the identity of the nucleophile is now unimportant. The carb as opposed to a partial positive charge, making it very electrophilic. As a result, v donate a lone pair to it, including neutral solvent molecules.

Moreover, we need to re-examine what is a good structure for the molecule conta S_N1 mechanism, the rate of substitution *increases* as the number of alkyl groups a leaving group increases. As you discovered while studying alkenes, alkyl groups a stabilise carbocations. The more alkyl groups there are connected to the same ca the more stable the carbocation will be as it develops in the transition state of the transition state is more stable, the activation energy will be lower, and the rate wil



left: reaction profiles for the first step of the S_N1 mechanism with CH_3I (solid li
right: transition state for reaction with CH_3I (top) and $(CH_3)_3CI$ (bottom); long, dotted
of breaking; charges in brackets represent developing charges; arrow heads on b

What about steric hindrance, which impedes S_N2 reactions at carbons that are cro reactions, the effect plays a much smaller role in determining the overall rate. Wi lone pairs, carbocations have a trigonal planar geometry, i.e. they are flat. Compa seen in S_N2 reactions, this makes the electrophilic carbon considerably more acce minimising steric hindrance.

One factor that is key to the rate of S_N1 *and* S_N2 reactions is the identity of the lea involved in the rate-determining step of both reactions.

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Closing comments

A common misconception is that, for a given set of conditions, a nucleophilic sub through only one of the two mechanisms. In reality, both are possible, and what r When a textbook or website says that a reaction takes place through an S_N1 mech mechanism is significantly faster than the S_N2 mechanism, and that most molecul

It should also be pointed out that, as with ionic and covalent bonding, S_N1 and S_N spectrum of mechanisms for nucleophilic substitution reactions. Cases where bon are perfectly synchronised are rare; equally, it is uncommon to see bond formatio leaving group is completely broken.

Finally, you might be wondering why it matters which mechanism a nucleophilic s After all, though the intermediate steps differ, the S_N1 and S_N2 mechanisms appea In fact, this is not true but, to understand why, you'll need to look at optical isome covered at A2 level. Controlling this type of stereoisomerism is often a crucial asp especially in the pharmaceutical industry, where the optical isomer of a drug mole actively toxic.

Comprehension questions

1. Explain what the following terms mean:
    a) Nucleophile
    b) Rate-determining step
    c) Carbocation
    d) Activation energy
2. Using a table with the headings 'S_N1' and 'S_N2', compare the features of the t number of species in the rate-determining step, quality of the nucleophile, q how the rate depends on the number of alkyl groups attached to the same c
3. Would you expect PH_3 and H_2S to be better or worse nucleophiles than NH_3
4. Explain why it is rare for alkyl fluorides to undergo nucleophilic substitution r

Application questions

5. Draw the transition state for an S_N2 nucleophilic substitution reaction betwe (Note: a bond in the process of forming is represented in the same way as a b and a charge disappearing is represented in the same way as a charge develo
6. N_3^- is a much better nucleophile than $[(CH_3)_2CH]_2N^-$, despite both species b an electron pair from a nitrogen atom. Suggest why. (Hint: what shape is N_3
7. $(CH_3)_2(CF_3)CBr$ undergoes S_N1 nucleophilic substitution more slowly than (CH
8. When $(CH_3)_3CCH_2I$ is reacted with NaOH, both nucleophilic substitution mech Suggest why. (Hint: sketch the molecule.)

Taking it further

9. Like nucleophilic substitution reactions, elimination reactions can proceed by mechanisms, E1 and E2. Research the mechanisms, then write 300 words co

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The chemistry of visio

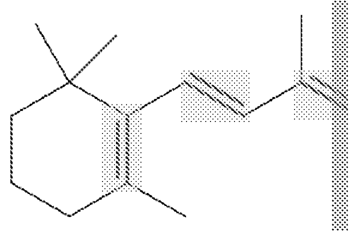
Sight is a fundamental part of life for most people. Whether crossing the street, admi
reading an article like this one, we are constantly being fed visual information. For mi
sought to unravel the nature of this remarkable sense. In ancient Greece, many philos
out beams of some kind, and that, when these beams fell on an object, an image of it
By the eleventh century, the Arabic scientist Alhazen had determined that visual perce
the eye. Yet, it was only in the 1950s and 1960s that, thanks to advances in technolo
sight were unveiled. In this article, we will explore these processes, including the vital

A refresher on E–Z isomerism

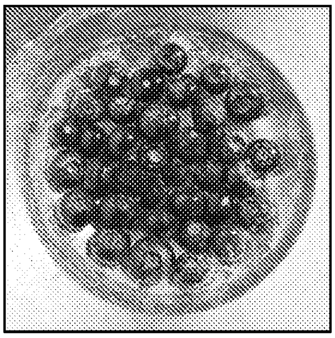
E–Z isomerism occurs when molecules containing a carbon–carbon double bond
attached to *both* carbon atoms in the bond. The groups can be single atoms or c
two groups on the same carbon atom, one is said to have a higher 'priority' than t
whichever one has the heavier atom bound directly to the carbon, e.g. OH has a h
oxygen has a higher atomic mass than carbon. If the atoms bound to the carbon
directly to *those* atoms are considered. This continues until the atoms differ. In Z
groups are on the same side of the double bond; in E isomers, they are on differe
Carbon–carbon double bonds cannot rotate under normal conditions, preventing
isomers. In short, this is because rotation reduces the sideways overlap between t
component of the bond. This requires the input of more energy than is available

The visual cycle

As you may already know, sight in humans depends on light from our surroundings striking a thin layer of tissue at the back of our eye called the **retina**. The retina contains photoreceptor cells that respond to incoming light by transmitting electrical signals to the brain, which processes the signals to produce what we experience as vision. How do these photoreceptor cells work, though? What 'switch' does light flick to trigger the electrical signals? The answer lies in a molecule called **retinal**, the key to the so-called 'visual cycle'.

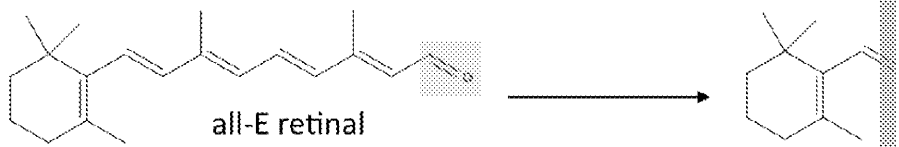


The skeletal formula of retina
highlighted in yellow an



In the diagram above, you can see that retinal conta
bonds. Here, the molecule is shown in its usual for
each double bond is separated from the next by exa
bond. This alternating single bond / double bond p
'conjugation', and molecules that exhibit it often ab
visible regions of the electromagnetic spectrum. Th
distinctively coloured. Examples from nature includ
compounds to which blueberries owe their name, a
in plants that was mentioned in the article on magn

Notice, too, that there is an aldehyde group at one end of the retinal's carbon cha
you learned that an aldehyde results from the partial oxidation of a primary alcoh
imagine that the chemistry of life is somehow different from the reactions you ha
relationships between functional groups are exactly the same! In fact, the first ste
reverse of the process described above: the aldehyde group in retinal is reduced t



Conversion of all–E retinal to all–E retinol (site of change highli

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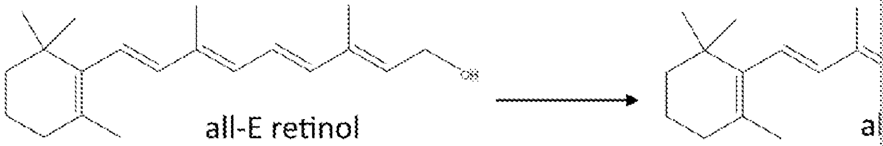
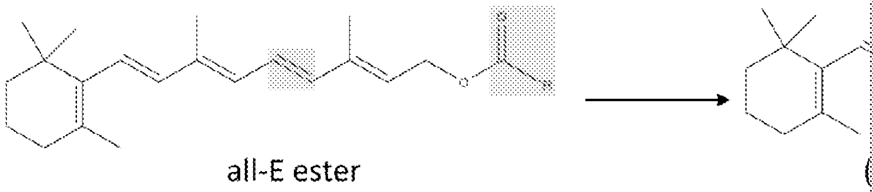
Admittedly, the reagents and conditions in nature *are* different. During your A2 s would accomplish this reduction using sodium borohydride, $NaBH_4$. In the aqueo reagent would react violently with the water, and our bodies instead perform the of protein that catalyses chemical reactions.

The alcohol, retinol, is then reacted with a carboxylic acid to form an ester – a fun proton in a carboxylic acid is replaced by the alkyl group from an alcohol.



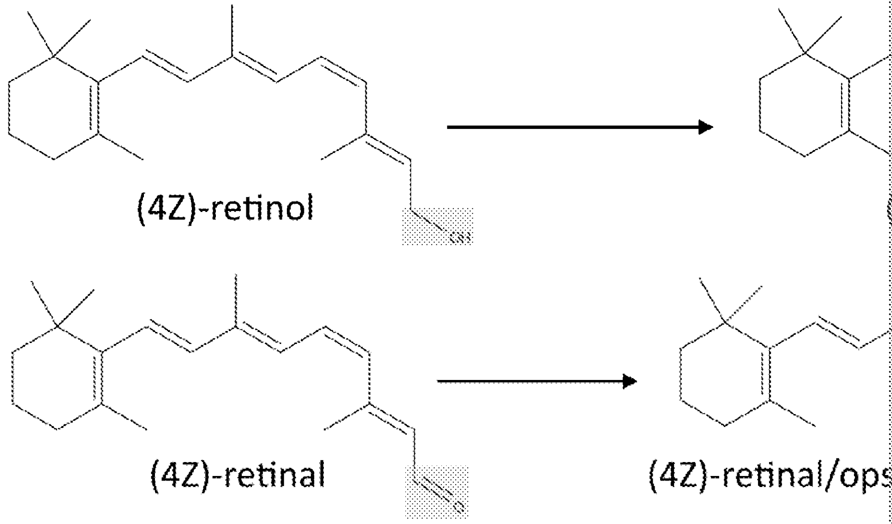
Conversion of all–E retinol to an all–E ester (site of change highlighted); the lor carboxylic acid has been abbreviated to R

In the very next step, an enzyme breaks the ester down into an alcohol and a carb initially seem pointless. However, as part of the reaction, the stereochemistry of c is changed from E to Z. This will be important later.



Conversion of all–E ester to (4Z)-retinol (sites of changes highlighted); the long car carboxylic acid has been abbreviated to R

Once (4Z)-retinol is oxidised enzymatically to (4Z)-retinal, only one step remains. conjugated molecules often absorbed ultraviolet or visible light? By itself, retinal For the molecule to absorb visible light, as we are expecting, it must be attached t The link is formed through the aldehyde group, and involves the smaller molecule the protein, referred to as the binding site. The structure of the binding site has e accommodate (4Z)-retinal, and fit is very tight.



Conversion of (4Z)-retinol to (4Z)-retinal, followed by conversion of (4Z)-retinal to (sites of changes highlighted)

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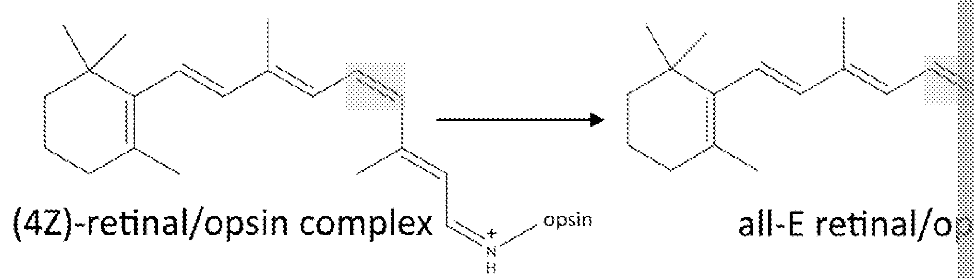
Finally, we have our molecular switch. Now what? When a photon (a particle of li
enough energy to break the C4–C5 π bond, leaving the molecule free to rotate ba
Since the binding pocket is arranged to specifically fit the (4Z)-retinal, it must alte
the new isomer. This leads to changes in the overall conformation of the protein,
the photoreceptor cell that leads electric impulses to fire in the nervous system.

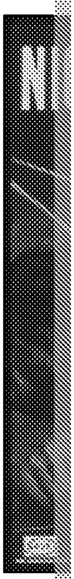


Conversion of (4Z)-retinal/opsin complex to all–E retinal/opsin comple

Afterwards, all–E retinal is released from the opsin binding site to begin the cycle
regenerate (4Z)-retinal accounts for the dark splotches that appear in your field o
bright light. With the retina flooded with photons, a large fraction of the retinal m
isomerised at once and, until they are replaced, your ability to see is impaired.

Examining an old wives' tale

Were you ever told that carrots would give you night vision? It may have sounded like a trick to make you eat your vegetables, but there is some truth behind it. Interestingly, despite our reliance on it, humans cannot produce retinal. Instead, we must obtain it from our diet. As a matter of fact, retinol and retinal are more commonly known as vitamin A.
Carrots derive their striking orange colour from a conjugated molecule called beta-carotene. (The same compound is found in pumpkins and sweet potatoes.) With the help of yet another enzyme, our bodies can split this molecule into two molecules of retinal, ready to enter the visual cycle! That said, foods such as carrots only contribute to the maintenance of regular vision, and do not grant superhuman vision or the ability to see in complete darkness.



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A likely explanation for this myth lies in propaganda from the Second World War. Carrots were heavily promoted to the British public, both to ensure that people were able to see during blackouts and because the vegetables could be grown domestically. Allegedly, the Air Ministry even attributed the success of their pilots to carrots, in order to distract German intelligence from the RAF's new aircraft-mounted radar systems. Before the war had ended, carrots were being endorsed by the United States government too. Over the years, these various campaigns probably gave rise to the exaggerated claims circulating today.

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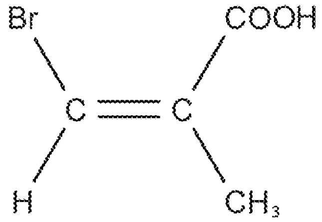
Comprehension questions

1. Explain what the following terms mean:
   a) Isomer
   b) Conjugation
   c) Ester
   d) Photon
2. Write the molecular formula of retinal.
3. Determine whether the molecule shown below is an E isomer or a Z isomer.



4. Explain why E and Z isomers cannot be directly interconverted without the ap

Application questions

5. Retinal and its derivatives have to be ferried around the cell by retinoid-bindi
6. Describe the reagents and conditions used in a lab to oxidise primary alcoho reasons that these would not be suitable in a biological setting, such as in th
7. By considering the relative concentrations of the retinal/opsin complex and s molecules, suggest why our eyes, once adapted to the dark, are more sensitiv

Taking it further

8. This article covered the well-established molecular mechanisms behind sight underpinning olfaction (sense of smell) are less certain. Research the two lea docking theory and vibration theory, and write 150 words on each of them.
9. The retinal/opsin complex is an example of a 'photoswitch', a molecule that u structural change when exposed to light. Research other photoswitches, nat of their applications.

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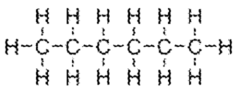
Solvents – making solut

When trying to improve or invent a chemical reaction a chemist will normally thin
the actual chemicals that are reacting. These are the catalyst, the conditions and t
area of study, and different examples of catalysts, such as metal catalysts and enz
The effect of conditions is an even more common area of study at school level – w
alter the rate of reaction introduced to students at an early stage, and pH and pre
stage. The last of the three is often overlooked, and barely gets a mention in A Le
make the difference between a reaction happening and not happening. Whereas
solvents are the norm, organic chemistry features a much wider selection of optio
which one to choose?

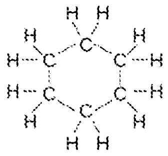
The basics

In order to be an effective solvent, a substance needs to be able to dissolve the rea
form during the reaction. If this doesn't happen, a reactant will simply clump toget
to encounter and react with other reactants. In organic chemistry solvents can be c

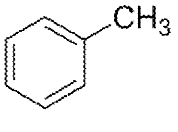
Polar solvents vs non-polar solvents – this refers to how much of a



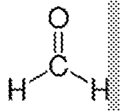
Hexane



Cyclohexane



Methylbenzene



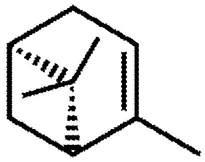
Methanal (formalde

Non-polar solvents
Solvents that are made entirely from carbon and hydrogen are non-polar, as there is not a sufficient electronegativity difference between the atoms to create a meaningful dipole. The principle forces between molecules are temporary dipole–dipole forces.

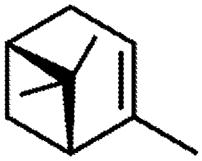
P
Solvents that have el
or halogens bound t
so long as the molec
dipoles don't cancel
Permanent dipole–di
molecules, which are
dipole–dipole forces.

This difference is very useful in liquid chromatography. Molecules with long carb
better in a solvent like hexane, whereas a molecule with lots of oxygen atoms and
carbon will dissolve better in propanone (acetone).

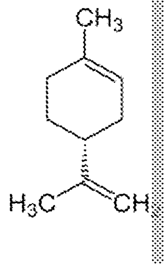
This also partly explains why oil-based foods and fatty foods often are very flavou
Many flavour molecules are carbon-based, and often have quite similar structures
below are found in pine trees, rosemary and eucalyptus oil, whereas one of the li
orange flavour, and the other a subtle lemon flavour. These molecules cannot for
interactions (or hydrogen bonds) with polar solvents, and so become concentrate



(+)-α-pinene



(−)-α-pinene



***R*-limonene**

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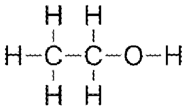
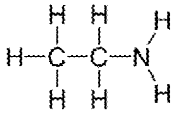
Protic polar solvents vs non-protic polar solvents – this refers to w
can also form hydrogen bonds.

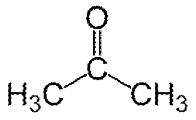
The most well-known protic solvent is, of course, water, but alcohols such as etha
important examples. O–H and N–H bonds are extremely polar and the hydrogen
bonds are extremely strong. This means that a molecule that doesn't have an O–H
to break apart the hydrogen bonds and dissolve. This explains why most organic
water unless they contain enough O–H or N–H bonds for their size. The larger th
bonds it needs to dissolve in water.



Ethanol (an alcohol)



Ethylamine (an amine)



Propanone (aka aceton

Protic polar solvents
These solvents contain N–H or O–H bonds and can form hydrogen bonds to molecules, or can form strong interactions with ions.

Non-protic
These solvents are po
dissolve a wider range
that don't contain O–

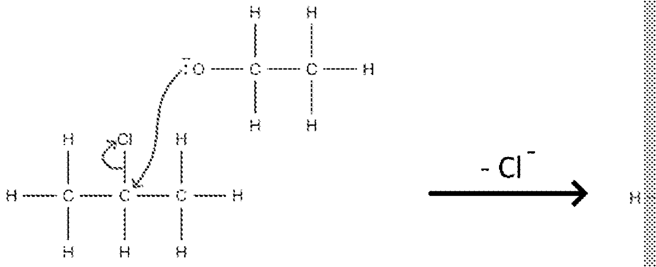
Caffeine is a well-known molecule that is present in tea and coffee, and has a stimulating effect on the body which is often unwanted – hence the desire for decaffeinated tea and coffee. The presence of lots of nitrogen atoms means that caffeine is polar – and it can just about dissolve in water. However, caffeine dissolves in polar non-protic solvents much more successfully. If tea is dissolved in water, and then a polar solvent is added such as dichloromethane, then the caffeine will pass into the dichloromethane, leaving the rest of the tea in the water. The water and dichloromethane can be easily separated afterwards, as they do not mix with each other (as shown in the separating funnel to the right.) This is the basis for the traditional decaffeination process – although food scientists have had to be careful not to use solvents that are harmful if they get into the tea.

The lig
dichloromet
water, so it sin

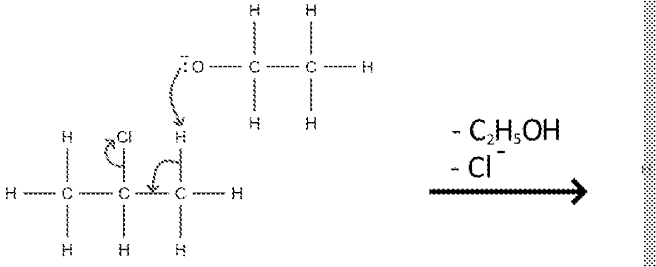
Effect of solvents on reactions

Consider the reaction between $CH_3CHClCH_3$ and $CH_3CH_2O^-Na^+$. The $CH_3CH_2O^-$ io
strong base, and will carry out either an S_N2 or elimination (E2) reaction:

S_N2



E2



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In a polar protic solvent, $CH_3CH_2O^-$ will be constantly surrounded by solvent mole
hydrogen bonds. The solvent 'shell' effectively increases the size of the ion. As di
nucleophilic substitution, this makes the ion less nucleophilic, and disfavours S_N2.
case of E2, as the ion only needs to pick off a hydrogen atom, rather than attackin
In summary, a polar protic solvent increases the amount of the alkene product rec

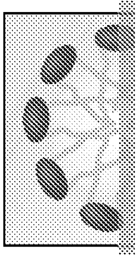
Ions, being charged, dissolve better the more polar a solvent is. In a non-polar so
negative $CH_3CH_2O^-$ ions are less likely to separate, and so the $CH_3CH_2O^-$ ion will s
base. This will inhibit *both* reactions.

Amphiphiles

The use of organic solvents such as hexane, chloroform ($CHCl_3$), dichloromethane
has been the norm in organic chemistry for decades. They work well, but there is
the organic solvents ultimately derive from the processing of crude oil, which is n
contaminated solvents must then be taken away for disposal after a reaction (as m
human health). It is not unheard of for a chemistry laboratory to be the biggest p
city! Over recent years, therefore, chemists have been seriously looking for altern
from non-renewable sources.

Decan
as the
the c

One innovative answer is the use of amphiphiles. An amphiphile (from the Greek words amphi – meaning both, phile – meaning like) is a molecule that has a polar protic part that dissolves in water and a non-protic or apolar part that does not dissolve in water. In water these molecules form globules called micelles (spheres) with the part that dissolves in water (hydrophilic) pointing out, and the rest of the molecule on the inside.



Diagra

If the amphiphile, the organic reactants and the right choice of catalyst are added to water then the amphiphiles will form micelles, trapping the organic reactants inside with the catalyst. Once that happens, the reactants can then react in the usual way in the middle of the micelles to form products. Once the water is removed, the products can then be separated from the amphiphiles, and purified. The amphiphiles could even be reused. From a sustainability point of view this offers a much more realistic way forward for organic chemistry than the waste of gallons of solvent, and is the sort of chemistry that can win people Nobel Prizes!

Like many of science's great ideas, the concept of trapping chemical in a micelle
using amphiphiles has actually been copied from nature. The idea of a biological
cell is to create an environment for organic reactions to happen that would not
happen in the aqueous environment outside of a cell. Many cells do this by havin
a bilayer of amphiphiles surrounding a cell. It's not yet totally clear how the first c
formed, but it is a tantalising idea that amphiphiles (e.g. fatty acids and
phospholipids) formed micelles in the aqueous environment of the ocean.
Once they formed, they could have trapped simple organic molecules on the
inside, and once they were supplied with some energy (e.g. from a thermal vent
under the ocean) this could have created the environment for the first
reactions that led to protein synthesis and life.

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Comprehension questions

1. Explain what the following terms mean in your own words:
   a) Protic and aprotic
   b) Hydrophilic and hydrophobic
   c) Amphiphile
   d) Micelle
2. Why doesn't a substance bound together with hydrogen bonding mix well w dipole–dipole reactions?
3. Why can't many Bronsted–Lowry acids and bases act very well as acids or bas
4. A chemist used an acid to catalyse an organic reaction, then added aqueous neutralise the acid. Explain how a separating funnel can be used to remove a
5. Nail-varnish remover contains propanone (CH_3COCH_3). Suggest what this im nail varnish.

Application questions

6. Br⁻ can act as a nucleophile in organic chemistry, and can be used in the form does not act as a very good nucleophile if the solvent is either a) non-polar o cannot act well as a nucleophile in these examples.
7. A chemist wanted to separate some different halogenoalkanes using chroma that contained the ether functional group, $CH_3CH_2OCH_2CH_3$, mixed with hexa choice for separating halogenoalkanes, and suggest why using pure hexane w
8. If using amphiphiles to allow reactions to occur in an aqueous solvent, the siz the reactions happen as well as in an organic solvent. Suggest what factors c the size of the micelles.

Taking it further

9. Research current theories on the role of bilayers, vesicles and micelles in the write a one-page summary.
10. The article contained one example of the sort of reaction that a solvent can i can you research? Explain the importance of the solvent in your own words.

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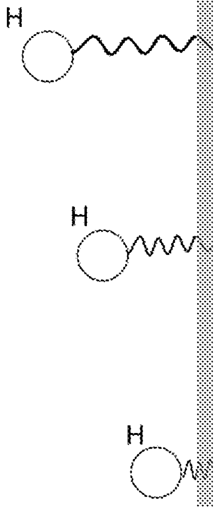
Springing into action – the the
infrared spectroscopy

Infrared (IR) spectroscopy is a useful analytical tool, commonly employed in both
Despite providing less information about molecular structure than other popular t
and versatile. By now, you will have learned that IR spectroscopy relies on the abs
bonds, the vibrations of which in turn become more pronounced. Further details
A Level syllabus, partly because of the complicated spectra generated by most org
will consider simpler molecules to uncover the principles behind molecular vibrati
why the spectra of larger, organic molecules are so difficult to interpret complete

Diatomic molecules

Diatomic molecules are those that contain just two atoms, such as hydrogen chloride (HCl) and carbon monoxide (CO). Despite the difference in scale, these molecules can be modelled quite effectively by treating them like two balls connected by a stiff spring. Like a spring, the bond connecting the atoms has a resting, equilibrium length, from which it can be compressed or stretched. In fact, the bond is constantly shifting between its maximum and minimum lengths; this is molecular vibration.



Representat
when it is ex

A molecule can exist in one of several different vibrational energy levels, each denoted by a vibrational quantum number *v*. The value of *v* must be a non-negative whole number (0, 1, 2, 3, etc.). The higher the energy level, the further the bond can be compressed or stretched away from its equilibrium length, i.e. the greater the range of lengths. As with electrons in shells around an atom, the vibrational energy of a molecule cannot lie between energy levels, and the molecule can only move to another energy level by gaining or losing an amount of energy exactly equal to the transition energy. This occurs through the adsorption or emission of a photon. There is another restriction, too: molecules can only move to adjacent energy levels. Combining this with the fact that the separation between energy
levels is much larger than the thermal energy available to molecules at room tem
in the $v = 0$ level, the main transition in any IR spectrum is the $v = 0 \rightarrow v = 1$ trans
sometimes called the fundamental transition.

The vibrational energy of energy level *v* of a diatomic molecule is given, in waven

$$E = \left(v + \frac{1}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$$

Some of these terms will be unfamiliar, so let's take a closer look. *c* is the speed o
called the force constant and is a measure of the bond strength or, continuing the
the spring. It is measured in newtons per metre (N m^{-1}), indicating the force that
bond length by a given amount. k_F is approximately 2290 N m^{-1} for N≡N, 1130 N
F–F. Finally, μ is the reduced mass, measured in kilograms. This is essentially a m
make calculations simpler. For two atoms A and B, of mass m_A and m_B respective

$$\mu = \frac{m_A \times m_B}{m_A + m_B}$$

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With definitions out of the way, we can now derive a formula for the energy of a fundamental transition:

$$E_{0\to 1} = E_1 - E_0 = \left(1+\frac{1}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}} - \left(0+\frac{1}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$$
$$= \left(\frac{3}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}} - \left(\frac{1}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$$
$$= \frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$$

This allows us to work out, for example, the energy of the fundamental transition for a $^{14}N^{16}O$ molecule, whose bond has a force constant of 1595 N m^{-1}. First, we will need to calculate the reduced mass of the molecule, remembering that 1 atomic mass unit equals 1.66×10^{-27} kg.

$$\mu = \frac{(14 \times 1.66 \times 10^{-27}) \times (16 \times 1.66 \times 10^{-27})}{(14 \times 1.66 \times 10^{-27}) + (16 \times 1.66 \times 10^{-27})}$$
$$= 1.2 \times 10^{-26} \text{ kg}$$

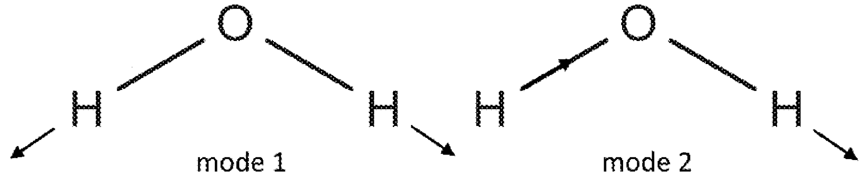
Then,

$$E_{0\to 1} = \frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$$
$$= \frac{1}{2\pi \times 3 \times 10^{10}}\sqrt{\frac{1595}{1.2 \times 10^{-26}}}$$
$$= 1900 \text{ cm}^{-1}$$

Sure enough, there is a peak at this wavenumber in the experimental IR spectrum of NO!

Polyatomic molecules

In molecules with more than two atoms, there are multiple bonds, which can vibrate in various combinations. Chemists and spectroscopists refer to these combinations as normal modes. Normal modes can be divided into stretching modes, which involve only changes in bond length, and bending modes, which involve only changes in bond angle. A molecule containing N atoms possesses 3N – 6 normal modes, unless it is linear, in which case it has 3N – 5. This is consistent with our previous examples of HCl and NO: they are linear and contain two atoms, giving only one normal mode, which we saw is a stretching mode. Meanwhile, a water molecule is non-linear and contains three atoms, so it displays three normal modes, represented below.



The normal modes of water

Modern ar

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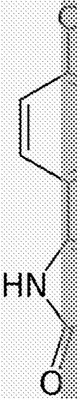

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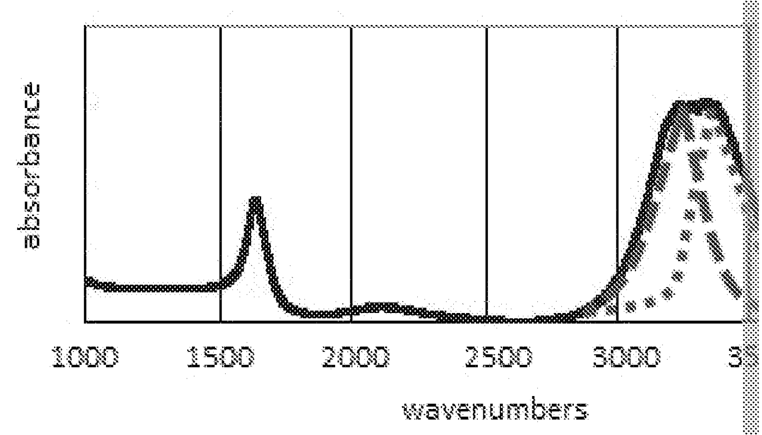
The first two modes are stretching modes. Mode 1 is called a symmetric stretch,
stretched and compressed at the same time; mode 2 is called an asymmetric stret
stretched while the other is compressed, and vice versa. Mode 3 is a bending mo
fluctuating about its equilibrium value of 104.5°.

Each mode has its own value of *v* and, although the equation from the previous s
calculate transition energies, we observe in spectra that each mode absorbs at a



*An IR spectrum of water (the two stretching modes have similar transition energies, and ove
how this happens, a dashed line and a dotted line have been added to represent the two in*

What about the larger, organic molecules that you are used to seeing analysed th
Applying the 3N – 6 formula, we discover that even a simple example like ethanoi
Among those that contribute to the IR spectrum, several will have similar transitio
region), causing them to overlap, and making it difficult to assign a given peak to
themselves also become harder to visualise as the complexity of the molecule inc

Limitations of IR spectroscopy

Not all normal modes can be excited by IR radiation, making it hard to identify so
molecules where both atoms are the same have no IR-active modes. Think about
atmosphere: H_2O, CO_2, CH_4, but not N_2 or O_2!

Fortunately, normal modes that are not IR-active may show up in spectra collecte
vibrational spectroscopy called Raman spectroscopy. Whereas IR spectroscopy re
higher vibrational energy levels through the *absorption* of photons, Raman spectr
of photons, which lose energy in the process. The incoming photons usually belo
regions of the electromagnetic spectrum. While IR and Raman spectroscopy diffe
the transition energies for a given molecule, and the rules governing the transitio

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Comprehension questions

1. Explain what the following terms mean:
   a) Fundamental transition
   b) Force constant
   c) Normal mode
   d) Fingerprint region
2. Would you expect the energy of the fundamental transition in $^{1}H^{37}Cl$ to be la same as in $^{1}H^{35}Cl$? Explain your answer.
3. How many vibrational modes does butan-1-ol have?
4. Suggest why water cannot be used be used as a solvent when collecting IR s

Application questions

5. Would you expect the bond in carbon monoxide (CO) to have a higher or lo Explain your answer. (Hint: think about filling octets to work out the nature c
6. Using the reduced mass and energy level transition formulae, explain why O- higher wavenumbers in an IR spectrum than other bonds found in organic m fundamental transition energies are higher.
7. Derive a formula for the energy of the transition between v = n and v = (n+1 energy level and the one directly above it. What do you notice about your re
8. How many stretching modes does CO_2 have? Sketch them.

Taking it further

9. Each vibrational energy level has associated rotational energy levels, describe quantum number, *J*. Transitions between vibrational energy level are often a between rotational energy levels. The finely spaced peaks that result from th high-resolution IR and Raman spectra. Research rotational–vibrational spect following: how the spacing between rotational energy levels compares to the energy levels; the values that *J* can take; which transitions between rotational and Raman spectroscopy; how rotational–vibrational spectroscopy can be us diatomic molecule; the P-branch and the R-branch.
10. Raman scattering is described as 'inelastic' because the energies of the photo the process. On the other hand, Rayleigh scattering is 'elastic', with the energ remaining the same. Write 200 words, and including diagrams, explaining wh
    i) the daytime sky to look blue
    ii) the Sun to look yellow
    iii) sunsets to look red

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Rates of reaction – how not to mathematical model

Being able to understand and control the rates of chemical reactions is essential r swathes of industry and biology. In the body, understanding the rates of metabol fundamental – as is understanding the impact of conditions such as concentration engineers designing ignition systems in car engines, which would cause the car to finest gastronomy in France and the bridge designers working out how often thei from the elements, people are thinking about how to make reactions faster and sl

In the school chemistry lab, simple experiments might be done to show that an ex higher temperature, or that chopping up food to increase surface area allows a re real world, however, scientists of all forms are rarely dealing with a single factor su must be considered if the scientists are to seize control of the exact rate of reactio temperature, pressure and concentration for starters.

The rate constant

In Year 13 Chemistry, you'll meet equations that look like this:

$A + B \rightarrow P$ Rate = k[A][B]

What this means is that for the reaction on the left, where A and B react together calculated by multiplying

- k, a 'rate constant'
- [A] and [B], the concentrations of A and B. (Square brackets mea

These equations look slightly different for different reactions, especially when the but the rate is always worked out by multiplying or dividing a constant, k, by conc tells us that for a given step in a simple reaction, if we increase the concentrations happen faster. It also shows us that concentration is not the only thing that affect

The interesting part of this equation is the rate constant, k. It is a different numbe change depending on the conditions of the reaction. An enormous value of k (e.g for a reaction taking place in a rocket engine) means an exceptionally fast reaction value of k (e.g. 1 × 10^{-10} dm^3 mol^{-1} s^{-1} or smaller for steps in rusting) means a tort actually is the rate constant? Well, that's where the maths comes in.

An expression

In a university textbook you may see an expression for the rate constant for a gas

$$k \propto P\,\sigma\sqrt{\frac{T}{M}}\,e^{\frac{-E_a}{RT}}$$

The aim here is not to be intimidated. What this equation is saying should be und A Level student!

The first thing is to remember that an α (Greek letter alpha) sign means 'proportio that the rate constant, k, is proportional to a series of factors. If you make them la increase and the reaction will get faster.

To understand what those factors are, a helpful trick with a complicated equation

So: $k \propto P\,\sigma\sqrt{\frac{T}{M}}\,e^{\frac{-E_a}{RT}}$ becomes $k \propto P \times \sigma\sqrt{\frac{T}{M}} \times e^{\frac{-E_a}{RT}}$

The way this has now been split up hopefully makes clear that the equation is say the rate constant is proportional to. These are:

- $e^{\frac{-E_a}{RT}}$ – an energy requirement
- $\sigma\sqrt{\frac{T}{M}}$ – a collision requirement
- P – a steric requirement

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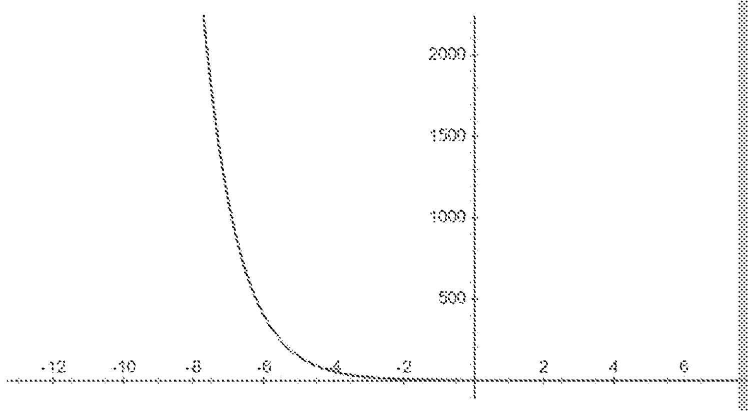
The energy requirement

In the expression $e^{\frac{-E_a}{RT}}$, 'e' is an exponential. An exponential is a particular kind of
that means as one thing increases something else increases by increasing amount
exponential of a negative number, which is the opposite (it decreases by decreasi
it approaches 0, but never reaches 0).



A graph of e^{-X}. The curve gets closer and closer to 0 as x incre

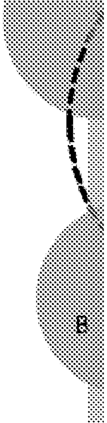
$e^{\frac{-E_a}{RT}}$ therefore means the negative exponential of E_a – which is the activation ener
the gas constant) and T, temperature. Does this make sense? Activation energy i
a reaction to occur. As it increases, and there is a larger energy barrier to the reac
slower. In this expression, as E_a increases our negative exponential is going to get
does make sense. The bigger E_a is for a reaction, the smaller the rate constant for

How is the activation energy overcome in a reaction? By increasing the temperatu
GCSE. This also fits with the equation because T is dividing E_a. As T increases $\frac{E_a}{RT}$ g
negative exponential k will increase. In simple terms, the higher the temperature
This portion of the equation also captures the impact of a catalyst on the rate of a
an alternative route for a reaction with a lower activation energy. The presence of
the value of the rate constant k for a reaction – further reassurance that the intimi
experiences in Chemistry lessons!

The collision requirement

For a reaction to occur, particles must collide with enough energy. The expressio
temperature, as a higher temperature means that particles are moving faster and,
interact. It also includes M, which is a term in the expression that takes account o
Heavier particles will move more slowly at a given temperature, so M is in the den
sign matter? No – due to the fact that higher temperatures increase the rate cons
heavier particles will have a lower rate constant.

That leaves the curious σ (Greek letter sigma), which means the 'collision cross section'. This captures how easy it is for two reactant particles to hit each other – the 'target area'. The diagram to the right shows how σ can be represented mathematically, by looking down the path of a particle labelled A as it travels through a group of particles labelled B. Particle A has a radius of r_A and each particle B has a radius of r_B. If the distance between the centre of particle A and the centre of a particle B is less than or equal to ($r_A + r_B$), the particles will collide.
In other words, any particle B whose centre lies within the dashed circle will collide with A. The area of this circle is σ and, if we designate ($r_A + r_B$) as r, is equal to πr^2. This makes sense intuitively, with a larger molecule colliding more frequently than a small molecule travelling at the same speed, because it carves out a greater path.



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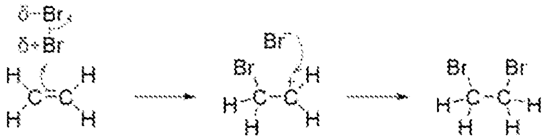
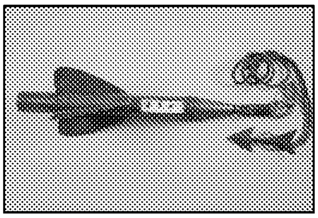
The steric requirement

The problem with the model of the collision cross section σ is that it is based on p course in nearly all cases they are not, and this is where the maths breaks down. C that takes account of the orientation of reactants is largely beyond the scope of c fortunately the age-old solution of doing experiments provides a way out.



The example reaction above from organic chemistry provides an example of this. T approach the alkene from the right direction. If it approached from the side (as dr happen. The collision cross section would, therefore, not be a circle. However, this rate of reaction at a given temperature and at given concentrations can be predict $k\ \alpha\ \sigma\sqrt{\frac{T}{M}}\ e^{\frac{-E_a}{RT}}$. If we use these equations to predict the rate, we find it doesn't mat is used to calculate the unknown steric factor, given the letter P, so if the experime expected we would add in P to the equation for k: $k\ \alpha\ P\ \sigma\sqrt{\frac{T}{M}}\ e^{\frac{-E_a}{RT}}$, and we would h



By doing this, we find that, unsurprisingly, P is much l reactions are slower than expected because molecul way to react. In a fantastic example of mind-blowing discovered that P was above 1 for a few reactions, su and Br_2. This means that in some cases, atoms or ion What is going on? How is this possible? The explan harpoon mechanism. Potassium, K, is so keen to lose passing bromine molecule like a harpoon. This makes K^+ and Br_2^-, which immedia together and react (hence the name 'harpoon' – the K atom fires the electron, the

The harpoon mechanism really captures how chemistry draws together mathemat experimental results and creativity of thought to come up with interesting explana world around us. Turns out the equations we started with are not so boring after a

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Comprehension questions

1. Explain what the following mean in your own words:
   a) Rate equation
   b) α (in a mathematical context)
   c) Exponential
2. In your own words, explain why reactions have:
   a) a collision requirement
   b) an energy requirement
   c) a steric requirement
3. Using what you have learned in the article, explain why increasing the tempe
   increase the reaction rate.
4. Draw an illustration of the harpoon mechanism in the reaction between pota

Application questions

5. Enzymes are often large molecules which have a specific binding site that ca
   allow them to react via a route with a lower activation energy. Suggest what
   energy requirement and the steric requirement for a reaction.
6. A chemist increases the temperature of a reaction by 100 Kelvin and notices
   factor of 1.5. Explain why increasing the temperature by another 100 Kelvin
   a different amount.
7. The principles discussed throughout apply to gas-phase reactions. In solutio
   need to be taken into account as a result of the solvent. Suggest reasons wh
   solvent would have an impact on reaction kinetics.

Taking it further

8. Choose a real-life application of chemistry that interests you (e.g. in an indus
   medical or everyday setting) and research and write three quarters of a page
   kinetics has been applied to that area.

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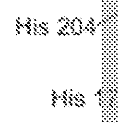
Haemoglobin – winning the equili

Haemoglobin is a protein that carries the oxygen in the blood and allows it to be cells all around the body. Haemoglobin is actually made of four units, called haem ion that can carry an oxygen molecule. The success of haemoglobin can be judge almost all vertebrates (apart from some fish), and, therefore, clearly iron's ability to something that was made use of a long time ago in the history of life's evolution.

In some invertebrates, such as lobsters, different molecules are used, such as haemocyanin – a copper-based molecule that gives lobster blood its famous blue colour – but these creatures are much smaller and haemocyanin does not bind to blood in the same way as haemoglobin. The fact that Fe^{2+} ions can be oxidised to Fe^{3+} fairly easily is important to haemoglobin's success in being used across the majority of vertebrates, but other relatively common transition metal ions can also move quite easily between oxidation states, so what makes haemoglobin special? The answer is the way it manipulates equilibrium.



Haemocya
the o

Haemoglobin and Le Chatelier

Haemoglobin, Hb, binding to an oxygen molecule to form oxyhaemoglobin, Hb(O can be represented as:

$$Hb + O_2 \leftrightarrows Hb(O_2)$$

The first way that Le Chatelier's principle is used is making use of the different oxyg the body (called partial pressures because oxygen is not the only gas dissolved in t pressure affects the position of equilibrium is essentially the same as concentration pressure is high, which pushes the equilibrium to the right, forming oxyhaemoglob reaches the muscles, away from the lungs, the oxygen partial pressure is much low by the muscles for respiration. This causes the position of equilibrium to shift back that had been bound and freeing up the haemoglobin. The oxygen can then be us haemoglobin is free to return to the lungs, carrying some carbon dioxide with it at

Le Chatelier's principle also explains why substances such as carbon monoxide are more strongly to haemoglobin than oxygen does. If carbon monoxide is inhaled i carboxyhaemoglobin. The position of equilibrium for this reaction is far to the rig equilibrium is to the right, the concentration of free haemoglobin (Hb) is significa the oxyhaemoglobin equation:

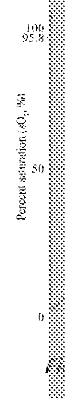
$$Hb + O_2 \leftrightarrows Hb(O_2)$$

the equilibrium shifts to the left as haemoglobin is removed, meaning that not en cells do not get enough oxygen for respiration, and a person is likely to die unless to push the position of equilibrium back to the right to form enough oxyhaemogl

The oxygen dissociation curve

The change in how much haemoglobin is bound to oxygen can be represented by an 'oxygen dissociation curve'. The values plotted in this curve are measured by experiment.

Towards the left of the diagram, where oxygen partial pressure is low (such as in the muscles) it is the situation where the equilibrium has shifted to the left and most haemoglobin is free (low saturation). Conversely, on the right-hand side, oxygen partial pressure is high and most haemoglobin is bound to oxygen (high saturation).



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The experiment that is used to plot the dissociation curve can be carried out at di temperature or pH, in people with different health conditions or in different anim we can find out that the shape of this curve is changed by different factors, which altered by different factors.

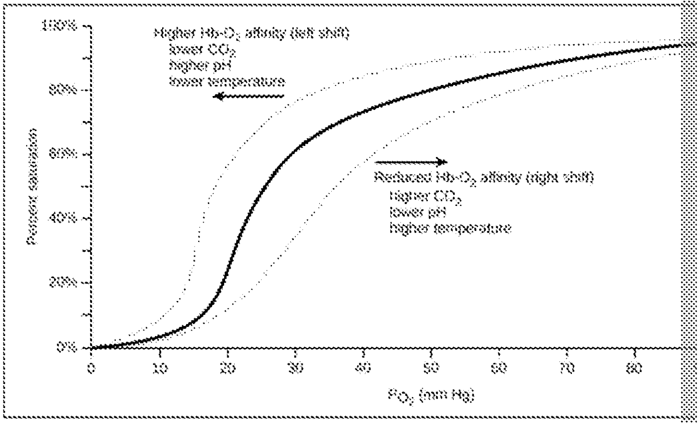

***Figure 2**: The effect of a change of conditions on the oxygen disso*

The shape of the curve for higher pH and lower temperature shows that haemogl more easily in these conditions. Look at the values at a 20 mmHg partial pressure The curve for lower temperature / higher pH has a much higher saturation of hae is able to carry oxygen and the position of equilibrium is shifted to the right in ou such as sharks, which live in cold temperatures and have a higher blood pH. This sharks can carry just as much oxygen in their blood, even though the oxygen pres

This curve also shows the risk to marine life of increased CO_2 levels and global wa sea and contributes to global warming, which raises sea temperatures. This risks 'acidosis' in fish, whereby the shape of the oxygen dissociation curve is flattened. are needed to saturate the haemoglobin, and it is harder for equilibrium to be sh our lungs. Fish blood (and all blood) contains **buffers** which help minimise the ch the sea becomes more acidic. However, these buffers only work up to a certain p have to adapt to the lowering of sea pH or risk extinction as the haemoglobin in t oxygen to their muscles.

Why is it even a curve? The cleverest bit of all...

What the shape of the curve tells us is that once some oxygen is bound to haemo easier to add a lot more (the curve becomes steeper). The reason for this is becau of haemoglobin binding to oxygen – relaxed (HbR) and tensed (HbT).

- Relaxed haemoglobin binds to one oxygen molecule and becomes tensed h (Position of equilibrium more to the left.)
- Tensed haemoglobin then easily binds to three more oxygen molecules. (Po the right.)

Haemoglob
hae

This is a phenomenon called **cooperative binding**. A haemoglobin molecule has four binding sites containing Fe^{2+}. Once the first Fe^{2+} binds to oxygen, a pull is exerted on the rest of the haemoglobin molecule (making it tensed), and moving the other three Fe^{2+} sites into a position where they bind more easily.

This is a fantastic manipulation of equilibrium – taking a situation where the position of equilibrium lies too much to one side (like the binding of O_2 to HbR, with the equilibrium further to the left meaning little oxygen can be transported) and changing the situation to one where the position of equilibrium lies more in the desired direction (more O_2 can bind – as with HbT).

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So why not just have HbT all the time if it makes it easier to bind all four oxygen m the oxygen needs to be released again at the muscles. In Figure 2, oxygen releas to left, and the degree of saturation of Hb (y-axis) decreases. It is much harder to curve with a high Hb-O_2 affinity – the partial pressure of O_2 (x-axis) has to drop to oxygen to be freed. If HbT turns back into HbR, however, HbR has a flatter curve, right to left, that the oxygen is released at an earlier stage.

This is incredibly clever! The conversion between tensed haemoglobin and relaxe binding and easy release of oxygen – equilibrium is truly being manipulated! Nat relationship over millions of years, and makes use of the different shapes of curve more oxygen or less oxygen needs to be absorbed, or when an animal's environm pH. This ability to adapt is the basis of natural selection, and it is, therefore, not a the position of equilibrium in different reactions has played a central role in evolu

Comprehension questions

1. Define the following terms:
   a) Haem group
   b) Partial pressure
   c) Dissociation
   d) Le Chatelier's principle
   e) Buffer
   f) Cooperative binding
2. Draw a flow diagram to illustrate what happens at each stage of the oxygen of O_2 and release of O_2.
3. Explain how acidosis can cause fish to suffocate, using the oxygen dissociati
4. Write a series of bullet points to explain how haemoglobin/blood exemplifie
5. Why is the ability of iron to form multiple stable oxidation states important f

Application questions

6. Sketch and annotate an oxygen dissociation curve to explain the phenomen opposite of acidosis).
7. How would the oxygen dissociation curve appear different if there was no co this would be a problem.
8. How would you expect the equilibrium between HbR(O_2) and HbT(O_2) to be aff

Taking it further

9. Research the different oxidation states of iron and how they link to iron's orb of why iron has multiple different oxidation states.
10. What other examples of equilibrium reactions can you find in the human bo conditions in the human body or natural world affect the position of equilibr least half a page on your chosen example(s).

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Answers

What are orbitals?

Comprehension questions

1. a) The result of waves overlapping and either adding together ‘constructiv
   ‘destructively’. The result is an interference pattern.
   b) An area of space that can hold up to two electrons.
   c) The quantum number that determines the energy level of an electron.
   d) The pattern which describes how an electron / an electron’s probability
   outwards from the centre of an atom.
   e) The mixing together of orbitals to form new ‘hybrid’ orbitals which have
   original orbitals.
   f) A point where the probability of an electron existing is zero / the electro

2. Own words, but should convey the idea that, for example, light or electrons (or a
   waves and particles, and have properties of both. Treating them as just waves or
   explain phenomena such as interference (a wave property) or having discrete en

3. See article.

4. See article, but should acknowledge issues with explaining the fact that elect
   of space, rather than just being in one place at a particular time like a particle

5. Because s orbitals are spherical, and are, therefore, identical in every directio
   distributed in a direction along one axis.

6. Because electrons in 4s orbitals are overall lower energy than in 3d orbitals.
   in the distribution of the 4s orbitals, which the 3d orbitals lack, and, therefore

Application questions

7. 4s should have four increasing peaks, with the outer peak comfortably the la
   peak should be further away than the 2s and 1s orbitals in the article. 4d wo

8. Two of the orbitals next to each other, with the right-hand lobe (white) of on
   lobe (also white) of the other.

9. The large lobes of the d orbital on the left are in a particular phase (they are
   nodes, so the whole orbital is in the same phase. If the d orbital overlapped
   (unshaded) then a σ bond could form. However, if the d orbital on the right
   orbital would overlap with a shaded part and an unshaded part. These would

10. Only one p orbital could form a bond as the p orbital perpendicular to the pa
    d orbital at all, and the p orbital going left-to-right has the same phase prob
    previous question.

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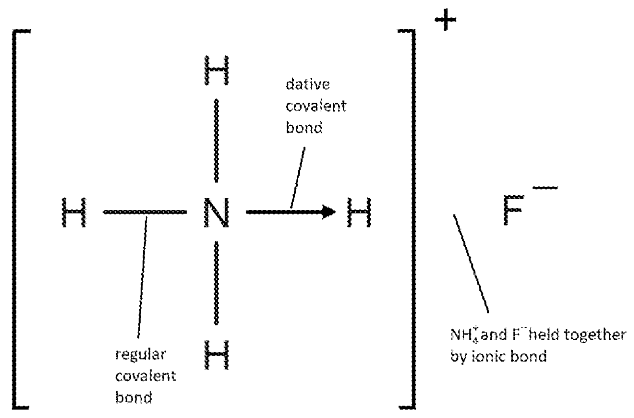
Boron – breaking the rules of bonding

Comprehension questions

1. a) The ability of an element to attract a pair of electrons in a covalent bond
   b) Atoms and ions that have the same electronic configuration.
   c) The probability of finding an electron in a particular area of space.
   d) When the orbitals of three atoms overlap to form a bond that still only c
   e) The idea that, for example, light and electrons have both properties of w

2. 

3. Because the beryllium atom would have used both its electrons to form cova however, it would still only have four electrons in its outer shell. It would nee second shell; therefore, it is electron-deficient.

4. Nitrogen is more electronegative than boron, and, therefore, has a greater attr bond. The result is that the electrons are more attracted to the nitrogen, maki boron slightly positive (δ+). Boron has three outer electrons and nitrogen has which makes it isoelectronic to Be–O as beryllium has two outer electrons and

5. There can be a degree of ionic attraction between slightly negative charges c charges on boron. This increases the strength of the bonding compared to a theoretically make cubic boron nitride harder than diamond. The attractions less soft than graphite, as the layers cannot easily slide over each other due t the charges.

6. The bond angles in diborane are smaller than 109.5°, which is the bond angle four bonds round boron. This 'strain' leads to higher reactivity.

7. It wouldn't be possible to plot a map of electron density if an electron was ju one place at a particular time, whereas waves are spread out over a region of density map.

Application questions

8. The first electron shell is much smaller than the second, third shell, etc., which H^- would repel each other a lot more, making H^- more unstable and more re

9. Same as hexagonal BN (in article) but with the electron density around all the

10. Reducing agent – a 3c2e bond is electron-deficient as the atoms have a lowe would in a normal bond (two electrons between two atoms). Therefore, a red electrons would be able to react with a 3c2e bond.

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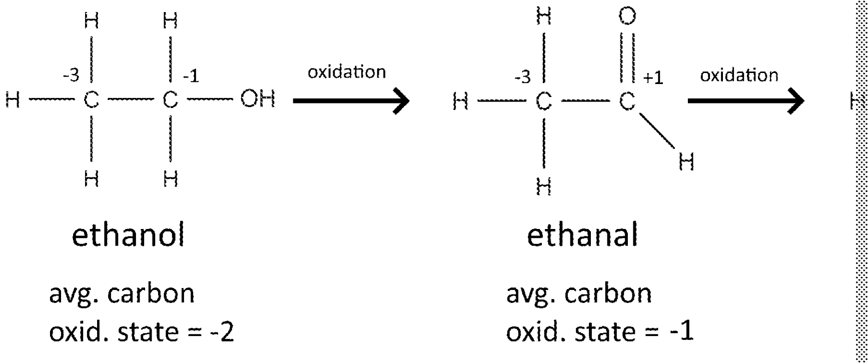
Redox reactions in biology

Comprehension questions

1. a) a measure of how energetically favourable a reduction process is; b) a la
speeds up chemical reactions; c) applies to compounds that do not cont
production of glucose from carbon dioxide using chemical reactions as t

2. a) $\mathrm{Hb.Fe^{2+} + O_2 \rightarrow Hb.Fe^{3+} + O_2^-}$
   b) Hb.Fe^{2+} is being oxidised and O_2 is being reduced
   c) $E^\circ_r = 0.33 + (-0.13) = +0.20\ \mathrm{V}$; $E^\circ_r > 0$, so the reaction is favourable

3.



4. As explained in the article, the change in the average oxidation state of the c
carbon atoms in glucose, giving an overall change in oxidation state of -24.

Application questions

5. a) -1; b) +$\frac{1}{2}$; c) -$\frac{1}{3}$

6. Each electron has a fixed charge, so $E°$ can be thought of as the energy taken
a given number of electrons in a reaction. This does not depend on the num
example of an **intensive** property. Another example is density. The density o
volume, and does not vary with amount of the material present.

7. a) electrolysis
   b) $\mathrm{Al^{3+} + 3e^- \rightarrow Al}$ (reduction), $\mathrm{2O^{2-} \rightarrow O_2 + 4e^-}$ or $\mathrm{O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-}$ (oxida

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Magnesium – more than a silver ribbon

Comprehension questions

1. a) The ability to attract a pair of electrons in a covalent bond.
   b) The increase or decrease in electron density as a result of a difference in dipole in a bond.
   c) A solid formed from the mixing of two solutions.
   d) The sum of the relative atomic masses of the atoms in a molecule.
   e) A mixture of metals, usually with distinctive properties.

2. Because barium ions are larger than the ions of the elements above AND larg attractions to the partial negative charges on water.

3. Mg^{2+} ions:
   - soluble in water
   - experiences strong electrostatic attraction to oxygen and nitrogen atom
   - relatively small
   - chemically stable, being hard to reduce or oxidise

   Magnesium metal:
   - very reactive, but less so than the other group 1 and group 2 metals
   - reacts very exothermically with oxygen
   - low density
4. Mg^{2+} ions are soluble in water, the main constituent of cells, which also allow cell membranes. The reasons for their solubility are their high charge and sm experience strong electrostatic attraction to water molecules. The ions exper attraction to other molecules with oxygen and nitrogen atoms too, making th into many important biological substances.

Application questions

5. -1926 kJ mol^{-1} is Mg^{2+} as the 2+ charge gives rise to stronger electrostatic at
   -320 kJ mol^{-1} is K^+ as it is the largest ion (has an extra shell of electrons) mea weakest (as the extra shielding outweighs the extra protons in K^+).
   -406 kJ mol^{-1} is Na^+ as it only has a 1+ charge but has fewer shells than K^+, a

6. e.g. Lithium is less dense but lithium is also more reactive.

7. e.g. Low density means that the engines are lighter, meaning less fuel is need transport the engine.

8. A cofactor is an atom, molecule or ion that binds to an enzyme and allows th substrate. (e.g. Magnesium is a cofactor for DNA polymerase.)

9. A Lewis acid is an electron pair acceptor. By accepting an electron pair from magnesium ion draws electron density away from the oxygen atom, which in the O–H bonds, weakening them. This makes it more likely that an O–H bon which would lower the pH.

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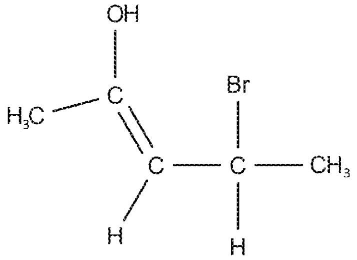
Expanding the chemistry of alkenes

Comprehension questions

1. a) The addition of a hydrogen atom to one side of a carbon–carbon bond
   b) Addition to a carbon–carbon double bond where the hydrogen atom bon
   c) An H⁻ ion.
   d) Electrons that are not restricted to one bond (and/or atom).

2. The fact that boron has a lower electronegativity than hydrogen means that t on the boron atom, causing it to be attacked by the nucleophilic alkene. It is because it only has six electrons in its outer shell. The electronegativity differ hydrogen then allows the B–H bond to act as a nucleophile.

3.

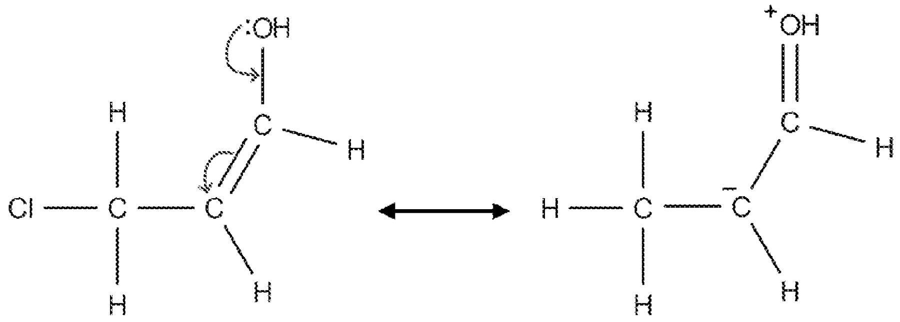


4. Two; A is not electrophilic, because the carbon–nitrogen triple bond is separa bonds, i.e. the π-bonds are not conjugated; B is electrophilic, because the alk oxygen π-bond; C is electrophilic; D is not electrophilic, because there are no

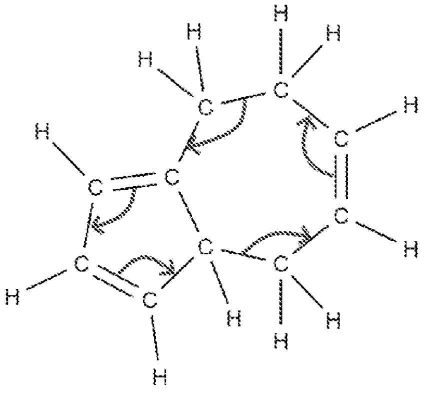
5. 44

Application questions

6. The oxygen lone pair is fed into the double bond as part of a delocalised π-s from the oxygen will have a partial negative charge.



7.



(or with every arrow the opposite way round)

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A closer look at nucleophilic substitution

Comprehension questions

1. a) An electron-rich species that donates a lone pair of electrons to an elect
   b) The slowest of the elementary steps that make up a reaction.
   c) A species with a positive charge on a carbon.
   d) The difference in energy between the reactants and the transition state.

2.

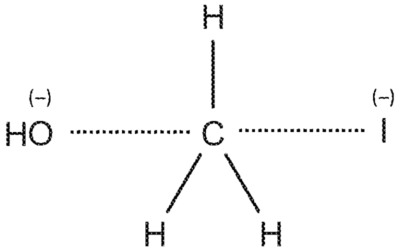
	S_N1	
Number of species in the rate-determining step	one	
Quality of nucleophile	good or bad	
Quality of leaving group	good	
How rate depends on number of alkyl groups attached to same carbon as leaving group	rate decreases as number of alkyl groups decreases	rat

3. PH_3 and H_2S should be better nucleophiles than NH_3 and H_2O, because phos electronegative, on account of being further down their respective groups.

4. C–F bonds are strong, making F^- a bad leaving group.

Application questions

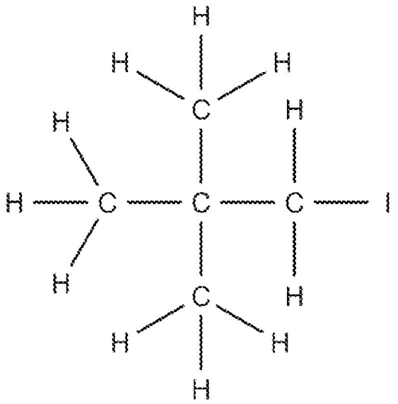
5.



6. $[(CH_3)_2CH]_2N^-$ has two bulky alkyl groups attached to the nitrogen atom, so a lot of steric hindrance. Meanwhile, N_3^- has a sleek, linear shape, minimisin

7. Due to their high electronegativity, the fluorine atoms in the CF_3 group remo donating it. This destabilises the developing positive charge in the transition activation energy, and a slower rate.

8. S_N1 is slow because there is only one alkyl group attached to the same carbo little stabilisation of the developing positive charge in the transition state. S_N groups on the adjacent carbon to the leaving group lie along its path of attac



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The chemistry of vision

Comprehension questions

1. a) One of multiple molecules with the same molecular formula but a differe
   b) The presence of alternating single and double bonds in a molecule.
   c) A class of molecules containing the RCO_2R' functional group.
   d) A single particle of light.

2. $C_{20}H_{28}O$

3. Z isomer. The first atom in each group attached to the right-hand carbon is what is bonded to those carbons. Oxygen has a higher atomic mass than hy priority group. It is on the same side as the bromine.

4. Carbon–carbon double bonds contain a π component formed by sideways o 2p orbitals. In order to switch between geometric isomers, one of these orbi to the other. At the point where the orbitals are perpendicular, there is no o bond breaks. This requires the input of more energy than is available at roo

Application questions

5. Most of the retinal molecule is composed of carbon and hydrogen, rendering insoluble in the water that compromises much of a cell's interior. This proble to water-soluble proteins.
6. Oxidation of alcohols is carried out by heating them with acidified potassium problem is that high temperature and low pH could damage cells; by denatu Secondly, the dichromate(VI) ion is toxic and carcinogenic.

7. In daylight, photoreceptors are constantly being struck by photons, meaning is inactive at any given time. Thus, the probability of any given photon that e retinal/opsin complex is lowered. In the dark, there are far fewer photons, ar contain retinal/opsin complexes. When a photon enters the eye, the likeliho complexes is higher.

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Solvents – making solutions!

Comprehension questions

1. a) Own words but protic = a solvent that can form hydrogen bonds, aproti hydrogen bonds.
   b) Attracted to / repelled by water.
   c) A molecule with hydrophilic and hydrophobic parts.
   d) A sphere formed when amphiphilic molecules group together, creating hydrophobic interior.

2. Hydrogen bonds are stronger than dipole–dipole interactions. In order for t bonding would be broken and replaced with dipole–dipole interactions, whic hydrogen bonds are stronger.

3. In a non-polar solvent, ions cannot mix well with the solvent, and, therefore, H^+ ions cannot be released easily by acids).

4. The organic products are most likely to dissolve better in an organic solvent water. If the chemist pours the reaction into a separating funnel at the end a end, the aqueous base will form one layer and the organic solvent with the p After shaking/inverting and allowing the layers to separate, the tap in the sep collect the bottom layer, leaving the other layer (usually the organic layer) in

5. They are polar and aprotic.

Application questions

6. a) NaBr cannot easily separate to form ions.
   b) The protic solvent forms strong attractions to the Br^- ion charge, meanin cannot easily get to another molecule to act as a nucleophile.

7. The ether is polar, due to the oxygen, but is not protic as there is no O–H bo halogenoalkanes, which are also polar and aprotic.

8. Lots of answers, including size and shape of the hydrophilic and hydrophobic how polar the hydrophilic parts are (which will affect the strength of attractio therefore, how tightly they pack together). External factors include temperat the molecules, and pH, which will affect how attracted the hydrophilic parts a Concentration will also be important as micelle formation can be an equilibri

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Springing into action – the theory behind infrared spectrosco

Comprehension questions

1. a) the transition between v = 0 and v = 1; b) a measure of the strength of force required to extend or compress by a given amount; c) the simultan combination of bonds in a molecule; d) a complicated region of an IR sp 1500 cm^{-1}, with large numbers of overlapping peaks that are difficult to

2. The reduced mass of $^{1}H^{37}Cl$ is higher than that of $^{1}H^{35}Cl$. As the energy of th proportional to $\frac{1}{\sqrt{\mu}}$, it would be smaller for $^{1}H^{37}Cl$.

3. Butan-1-ol has 15 atoms and is non-linear; (3 × 15) – 6 = 39 normal modes

4. Water strongly absorbs IR radiation, meaning that it would appear in an IR sp obscure peaks from the molecule under study, complicating analysis.

Application questions

5. O_2 has a double bond, while CO has a triple bond. A triple bond is stronger t higher for CO.

6. $E_{n \to n+1} = \frac{1}{2\pi c}\sqrt{\frac{k_F}{\mu}}$

   The expression is independent of n, i.e. all vibrational energy levels are evenl expect all transitions to appear on top of each another in a spectrum.

7. When m_A is much bigger than m_B (as in the case of N or O bonded to H),

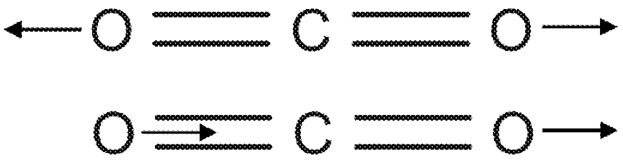
   $m_A + m_B \approx m_A$ (≈ means 'is approximately equal to')

   $\mu \approx \frac{m_A \times m_B}{m_A}$

   $= m_B$

   Since m_B is small, μ is small. This leads to a high vibrational transition energy

8. Two (a symmetric stretch and an asymmetric stretch)



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Rates of reaction – how not to be scared of mathematical mod

Comprehension questions

1. a) Own words, but should convey the sense of an equation that describes ho of the concentrations of the reactants, raised to the power of their coeffic
   b) Own words, but essentially 'proportional to'.
   c) Own words, but should convey the sense that an exponential increases a

2. a) Reactants must collide in order to react (except in the harpoon reactions
   b) Reactants must collide with enough energy to break chemical bonds.
   c) Most reactions require reactants to collide with at least one of them in a
3. Increasing temperature increases reaction rate partly because it causes reacta frequently (see collision requirement), but mainly because it increases the pro meet the energy requirement.

4. Open to interpretation, but should show the electron moving from K to Br_2 o

Application questions

5. Lowers the energy requirement as the E_a term decreases, meaning $e^{\frac{-Ea}{RT}}$ incre Raises the steric requirement; therefore, the steric factor decreases, reducing k

6. Own words but should convey the sense that the relationship with the collisio additive, and that the relationship with the energy factor is exponential, not a

7. Would affect the energy requirement as the reactants need to break the bon affecting the activation energy. The collision frequency would also be affecte the way, meaning that the rate of diffusion through the solvent becomes imp

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Haemoglobin – winning the equilibrium game

Comprehension questions

1. a) An iron-containing giant molecule. There are four of them in the protei
   b) The pressure exerted by one gas in a mixture of gases.
   c) Splitting apart or separation of a molecule.
   d) Own words, but the idea that a reaction in dynamic equilibrium will resp change to the equilibrium.
   e) A solution that minimises the change in pH when small amounts of acid
   f) When the binding of one molecule by a protein makes it easier for othe

2. See article for the information that should be included.

3. A lower pH causes the oxygen dissociation curve to shift to the right. This m oxygen is required in order to saturate the haemoglobin, meaning it is more oxygen required to its muscles.

4.
   - When oxygen partial pressure is high (e.g. in the lungs), equilibrium shif and forming oxyhaemoglobin.
   - When oxygen partial pressure is low (e.g. in the muscles), equilibrium sh and haemoglobin from oxyhaemoglobin.
   - Carbon monoxide binds strongly to haemoglobin, reducing its concentr shifts to the left to restore haemoglobin concentration.
   - Buffering in the blood relies on the equilibrium $H_2CO_3 \leftrightarrows HCO_3^- + H^+$.
     If the sea becomes more acidic, the concentration of H^+ in fishes' blood equilibrium will shift to the left to reduce H^+ concentration, minimising t

5. When iron binds to oxygen it is oxidised, and when the oxygen dissociates th can easily have different oxidation states it is easy for the iron in haemoglobi different points in the body.

Application questions

6. Diagram should be of curve shifted to the left, showing that although oxygen the oxygen to then dissociate from the haemoglobin in the muscles.

7. The curve would be closer to a flat straight line. This would mean higher par needed in order for the same amount of oxygen to bind, so it would be hard the muscles.

8. As the partial pressure of O_2 increases, the equilibrium $HbR(O_2) + 3O_2 \leftrightarrows HbT$

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