Storyline: answers to assignments

1 a 10 000 ppm (by volume)

- **b i** $1.8 \times 10^{-6} \text{ dm}^3 (0.0018 \text{ cm}^3)$
 - **ii** 0.00018% (Students should be aware that the percentage composition of a gas by volume is the same as its percentage molar composition.)
- **c** CO₂: combustion of hydrocarbon fuels (eg in power stations); deforestation
 - CH₄: rice paddy fields; cattle; rubbish tips
 - N₂O: fertilised soils
 - NO_x : combustion of hydrocarbon fuels (eg from car exhausts)
 - CO: incomplete combustion of hydrocarbons (eg from car exhausts).
- 2 a Highest death rate occurs at lower latitudes where there are more sunlight hours on average, and where the sunlight is more intense. (Also, sunlight passes through the atmosphere more obliquely at higher latitudes, and so contains less ultraviolet radiation.)
 - **b** There appears to be a greater risk of skin melanomas occurring with pale skins, occasionally exposed to intense sunlight (eg office workers sunbathing on holiday), than with the skins of people who work outdoors and tan gradually.
- 3 a molecules, atoms (eg noble gases) radicalsb molecules, atoms, radicals
 - $\boldsymbol{c}~$ ions, electrons (but also radicals, atoms, molecules)
 - **a** 8.3×10^{-19} J molecule⁻¹
 - **b** $v = 1.3 \times 10^{15} \text{ Hz}$
 - **c** Higher frequency radiation has more energy associated with it, so could also break the bond. (But you may wish to point out that the correct answer is not as simple as this. Many compounds do not absorb energy of just the right frequency to cause bond fission, so you can only use bond enthalpies to predict a *minimum* frequency required. You would need to know the absorption spectrum of the compound to be more precise.)
- **5 a** Reactions 4 and 5
 - **b** Reactions 1 and 5
 - **c** Reactions 2, 3 and 4
 - **d** In both pairs of reactions, the two reactions are the reverse of each other but energy is absorbed and liberated in different forms in the forward and back reactions.
 - **e** O_2 and O_3 molecules both absorb the Sun's ultraviolet radiation in the stratosphere and undergo photodissociation (reactions 1 and 5). These reactions take place in reverse (reactions 3 and 2) and energy is liberated to the surroundings in the form of heat. The reaction between O_3 and O radicals (reaction 4) is also exothermic – so, overall, the series of reactions have the effect of converting the Sun's ultraviolet radiation into thermal energy.

The Sun's radiation is most intense at the top of the stratosphere, and the photodissociation reactions take place there most readily.

6 The concentrations of the gases involved in the reactions. (An increase in concentration will increase the rate of the reaction.)

The intensity of radiation. (If the reaction involves radiation, an increase in intensity of appropriate

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radiation will increase the rate of the reaction.) The temperature. (For many reactions, a rise in temperature increases the rate of the reaction.)

- 7 Overall reaction: $O + O_3 \rightarrow O_2 + O_2$ Cl atom behaves as a catalyst in the reaction.
- 8 **a** $O + H_2O \rightarrow 2OH$ **b** $NO + O_3 \rightarrow O_2 + NO_2$ $\frac{NO_2 + O \rightarrow NO + O_2}{O + O_3 \rightarrow O_2 + O_2}$ Overall reaction
- **9 a** To find out the rate at which CFCs were accumulating in the troposphere, so that they could calculate whether significant quantities would be transported to the stratosphere.
 - **b** The calculated ozone loss was so large, they wanted to check their results very carefully.
 - **c** Rowland and Molina's work (like many great discoveries) arose from purely academic findings, which at the time had no practical application.
- **10 a** By measuring the ultraviolet absorption spectra of samples of air. Ozone absorbs ultraviolet radiation at a characteristic frequency, so the concentration of ozone in the air sample can be calculated from the intensity of the absorption at this frequency.
 - **b** The NASA computers were programmed to ignore data outside certain 'reasonable' limits. Very low measurements were thought to be inaccurate and were disregarded.
 - **c** They wanted to repeat their measurements and check they were correct.
 - **d** They stay in the atmosphere for a very long time and, when they do eventually break down, they form very reactive species.

¹¹ a

| | Bond broken | Bond formed | ∆ H/kJ mol ⁻¹ |
|-------------|-------------|-------------|---------------------------------|
| Reaction 8 | C–H | H–Cl | +4 |
| Reaction 9 | - | CI–CI | -242 |
| Reaction 10 | CI–CI | CI–CI | 0 |

b Reactions 8 and 9.

- **c** In reaction 8, a C–H bond in CH₄ must be broken and the atoms and electrons must rearrange to form a new bond in HCl. In reaction 9, no bond must be broken; simple recombination of atoms, so no activation enthalpy.
- **d** $[CH_4] >> [Cl]$ in the stratosphere. Note that this is the reverse effect to the one described in the Storyline which compares the effects of O and Cl atoms on the removal of ozone. In the case of CH_4 and Cl atoms, the concentration difference is very large and this is the dominating factor.

(One of the problems with reaction 9 is that the pairs of Cl atoms which collide have enough energy to fly apart again, and many do not go on to form Cl_2 . For the reaction to occur, the two chlorine atoms must be stabilised by losing some of their energy to a 'third body', M:

$Cl + Cl + M \rightarrow Cl_2 + M$

This involves a collision between three particles, which is comparatively rare, particularly at the low pressures found in the stratosphere.)

ACTIVITIES: NOTES AND ANSWERS TO QUESTIONS

- 12 a No
 - **b** Yes, in the region 0.39×10^{14} Hz– 0.46×10^{14} Hz
 - **c i** Presence of CH₄ reduces amount of low frequency radiation which is radiated out to space.
 - ii Temperature increases.
- **13** a $H_2O(g) > CO_2 > CH_4 > N_2O > CCl_2F_2 > CCl_3F$
 - $(O_2; N_2; Ar negligible effect)$
 - **b** H_2O ; CO_2 ; CCl_3F ; CCl_2F_2 ; O_3 ; CH_4 ; N_2O
 - $\mathbf{c} \operatorname{CO}_2$
 - **d** The amount of water vapour in the atmosphere depends on the temperature and is controlled naturally by the evaporation/condensation processes in the water cycle.
- **14 a** As the temperature rises, the amount of water vapour in the atmosphere will increase.
 - **b** Global warming will increase as a result.
 - **c** Warming brought about by other greenhouse gases, increases evaporation and this allows the atmosphere to hold more water. This, in turn, enhances the original warming effect.
- **15 a** The peaks correspond to the winter months and the troughs to the summer months. (This illustrates the relatively slow mixing of atmospheric gases, since summer in the Northern Hemisphere corresponds to winter in the Southern Hemisphere.)
 - **b** CO₂ levels fall to a minimum in summer because greatest photosynthetic activity occurs at this time, withdrawing CO₂ from the air.
 - **c** About 15% increase.
 - **d** Area of high population, so levels of CO₂ will be affected locally by traffic, industry, etc.

- **c** 4.6%
- **d** 1.7%
- **e** The observed increase is much less than the calculated increase.
- **17 a** Position of equilibrium will move towards the right and more carbon dioxide will dissolve in the water.
 - **b** Position of equilibrium of this reaction will also move towards the right, and more CO₂(aq) will react with water to form ions.
 - **c** As the concentration of carbon dioxide in the atmosphere increases, more CO₂(g) will dissolve in the oceans. This reduces the effect of the initial rise in concentration, ie to some extent, oceans can 'soak up' carbon dioxide from the air.
 - **d** The carbon dioxide concentrations will never really be in equilibrium. The presence of living organisms and human activities mean that levels are constantly changing and there will be local variations. Mixing is slow because of the vast sizes of the atmosphere and the oceans.
- **18 a i** 205 Gt **ii** 202 Gt **iii** +3 Gt
 - **b** More CO₂ released from increased burning of fossil fuels and from wood burning as a result of increased deforestation. Less CO₂ absorbed as more forests cut down.
 - c Photosynthesis of land plants.
 - d i 3.7 years ii 4.9 years iii 0.07 years

Many land-based plants have relatively long lives or are eaten by animals with long lives. Ocean life is mostly made up of small organisms such as phytoplankton or bacteria with much shorter lifetimes and carbon is 'turned over' very rapidly.

The 'turn over' of carbon in the atmosphere is quite slow; increased emissions of CO_2 will cause long-term effects.

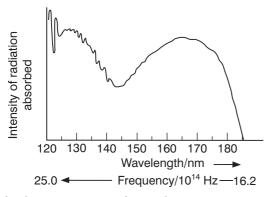
16 a 121 Gt **b** 2771 Gt

Activities: notes and answers to questions

A2.1 What substances can act as sunscreens?

This is a short exercise on the ultraviolet absorbing characteristics of substances.

Depending on the group, you may wish to show students an example of an absorption spectrum. These are usually plotted to show the intensity of radiation absorbed at each wavelength rather than frequency. The ultraviolet absorption spectrum of water is shown below:



The absorption spectrum of water above 120 nm

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- **a** No. Water does not cut out the u.v. radiation present in sunlight.
- **b** You do not tan through glass since it absorbs the u.v. radiation responsible for tanning.
- **c** Main absorption in visible and near u.v. Only limited absorption of the most harmful ultraviolet radiation, so not a very good sunscreen.
- **d** Good sunscreen.

A2.2 Investigating sunscreens

Safety note Students must not look directly at any u.v. source. They must follow the recommended precautions concerning eye protection.

Ultraviolet radiation

Ultraviolet radiation from the Sun between 9.3×10^{14} Hz and 10.7×10^{14} Hz (320 nm–280 nm) is known as mid-u.v. or u.v. B radiation. It is known to cause both skin-tanning and skin cancer. However, there is also evidence that over-exposure to near-u.v. or u.v. A radiation in the range 7.5×10^{14} Hz to 9.3×10^{14} Hz (400 nm–320 nm) can also be harmful.

(You may wish to refer students back to Chemical

Ideas 4.2 where the relationship between bond

enthalpy and bond length was discussed for

carbon-carbon bonds.)

Comments

A simple combination of equipment could be used, such as: u.v. source (eg sunlamp), sunscreen thinly smeared on a Perspex sheet or on cling film, and detergent or washed white fabric, etc as a detector. Students should be aware from **Activity A2.1** that lenses and mirrors made of glass will eliminate the u.v.

It is important that the sunscreen layer is as uniform as possible and the same thickness in each case.

The room will need to be well blacked out, but complete darkness is not necessary. With care, the detector should fluoresce more strongly when low factor sunscreens are used than with high factor products.

Alternatively, an effective result can be obtained using u.v. sensitive paper, covered with cling film on which the sunscreens are smeared. This gives good sensitivity to different sunscreens when exposed to sunlight (outdoors, of course).

A2.3 What is the effect of the atmosphere on the Sun's radiation?

This is a short exercise to reveal the importance of ozone as an absorber of the Sun's ultraviolet radiation.

Note

The spectrum of the Sun's radiation in space is best drawn with a linear wavelength scale, rather than with a linear frequency scale. At this stage in the course, students will be more familiar with the electromagnetic spectrum in terms of frequencies, but, as the course develops, they will need to become familiar with both frequency and wavelength scales and the relation between them.

In this exercise, absorption ranges for the gases are given in both frequency and wavelength units, but students will find it easier to draw in the wavelength ranges on the spectrum.

Comments

a and **b** Oxygen, ozone and sulphur dioxide absorb solar radiation in the ultraviolet region. Oxygen is the most abundant of the three gases and absorbs most of the high energy radiation below 241 nm (above 12.4×10^{14} Hz). Ozone absorbs strongly in the 296 nm to 214 nm (10.1 × 10¹⁴ Hz to 14.0 × 10¹⁴ Hz) region. Sulphur dioxide is only a minor trace gas in the atmosphere, and its role is small by comparison.

The solar radiation reaching the surface of the Earth consists of infrared, visible and some near ultraviolet $(2 \times 10^{14} \text{ Hz to } 11 \times 10^{14} \text{ Hz})$, with most energy being radiated in the visible.

A3.1 More about ozone

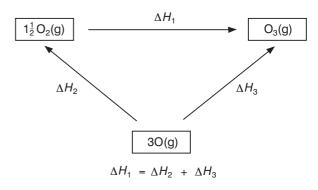
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| a | Substance | Length O–O bond /nm | Bond enthalpy O–O bond/kJ mol ^{–1} |
|---|-------------------------------|------------------------|--|
| | 0, | 0.121 | +498 |
| | H ₂ O ₂ | 0.148 | +144 |
| | 03 | 0.128 | +302 |

b The lengths and bond enthalpies of the two oxygen–oxygen bonds in ozone are identical and intermediate between single and double bonds.

с

i



- **ii** $\Delta H_1 = \Delta H_f^{\circ}(O_3)$ $\Delta H_2 = \text{enthalpy change when bonds are broken}$ $= \frac{3}{2} \times E(O = O) = +747 \text{ kJ mol}^{-1}$ $\Delta H_3 = \text{enthalpy change when bonds are made}$ $= -2 \times E (O = O) (\text{in ozone}) = -604 \text{ kJ mol}^{-1}$ $\Delta H_f^{\circ}(O_3) = +747 \text{ kJ mol}^{-1} - 604 \text{ kJ mol}^{-1}$ $= +143 \text{ kJ mol}^{-1}$
- d O₂ is energetically more stable than O₃; the conversion of O₂ to O₃ is an endothermic reaction.
 (Enthalpy change is only an approximate guide to energetic stability, but as 'a rule of thumb' it is adequate for our present purposes.)
- **e** An endothermic substance is one formed from its elements in an endothermic reaction under standard conditions.
- **f** O_3 is energetically unstable with respect to O_2 . It is also much more reactive than O_2 . (Now would be a good time to point out to students the difference between energetic stability and kinetic stability. Predictions, like the one they have just made about the reactivity of O_3 , do not always give the correct answer, eg diamond is energetically less stable than graphite, but diamond is not more reactive than graphite. In this case, the two allotropes are solids and the activation enthalpy for the conversion of diamond to graphite is very large. Hence, the conversion of diamond to graphite does not take place under normal conditions.)

A3.2 The photodissociation of bromine (optional teacher demonstration)

Safety note Information about hazardous chemicals is given on the activity sheet. Bromine must always be handled in a fume cupboard. Eye protection and gloves must be worn. If skin contact occurs, the affected area must be kept immersed in sodium thiosulphate solution (approximately 1 mol dm⁻³). Hexane is highly flammable and harmful (Heptane is less harmful and can be substituted for hexane.) If a u.v. source is used students must not look directly at it.

The experiment works well in sunlight, or you could use a strong lamp or hold the tubes next to a fluorescent light tube. Another possibility is to put the tubes in beakers on top of an overhead projector.

- a The bromine only decolorises in the presence of light (tube 1 and near the surface in tube 3). (It is reasonable to conclude that it must be Br₂ which undergoes photodissociation rather than hexane, since Br₂ is a coloured liquid and absorbs visible light, though this might not be obvious to students at this stage.)
- **b** Students should be able to conclude that the weaker Br–Br bond should break more readily than the C–H bond in hexane by absorption of visible radiation. $\mathbf{i} + 3.20 \times 10^{-19}$ J; 4.83×10^{14} Hz (visible) $\mathbf{ii} + 6.86 \times 10^{-19}$ J; 10.3×10^{14} Hz (ultraviolet)
- **c** Hexane

(An additional experiment might be to expose a tube containing a drop of Br_2 (or a drop of Br_2 in $2 \text{ cm}^3 \text{ H}_2\text{O}$) to light for 5–10 min. Photodissociation of Br_2 still takes place, but the Br atoms simply recombine. Decolorisation only occurs if there is something for the Br atoms to react with.)

- **d** HBr (acid gas which fumes in moist air and gives white fumes with ammonia).
- **e** $\text{HBr}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Br}(s)$

A3.3 Investigating the reaction between bromine and bexane

Safety note Information about hazardous chemicals is given on the activity sheet. Bromine must always be handled in a fume cupboard. Eye protection and gloves must be worn. If skin contact occurs, the affected area must be kept immersed in sodium thiosulphate solution (approximately 1 mol dm⁻³).

Measuring bromine in a pipette is difficult because the liquid is so volatile. Teachers may prefer to do this for students.

Hexane is highly flammable and harmful. (Heptane is less harmful and can be substituted for hexane.) The quantities used here are best measured out in a fume cupboard.

The bromohexane products are flammable. Their vapours are harmful and can be lachrymatory. The reaction mixtures should be collected in a residue bottle in the fume cupboard. The aqueous layer may then be flushed down the fume cupboard sink with plenty of water. Large volumes of the organic residues should be kept for collection. Smaller volumes can be emulsified with liquid detergent before diluting with water (at least × 10), and running to waste with plenty of water.

This activity provides a further opportunity for students to practise and develop their skills in evaluating their evidence and procedures. Alternatively, it could be used for *assessment* (see **OCR Teacher Support: Coursework Guidance for Chemistry (Salters)**).

Comments

If too much bromine is added, the decolorisation will take too long. It is best if the titration can be done on the same day and not left to the following lesson.

h $C_6H_{14} + Br_2 \rightarrow C_6H_{13}Br + HBr$

- i Substitution reaction.
- **j** To dissolve the HBr gas.
- **k** Organic layer.

A4.1 How do balogenoalkanes differ in reactivity?

Safety note Information about hazardous chemicals is given on the activity sheet. Ethanol, 1-chlorobutane, 1-bromobutane and 1-iodobutane are highly flammable. If possible, hot water from a tap or an electric kettle should be used for the water bath. If a flame is used to heat the water bath, it should be extinguished before these chemicals are used. They also have harmful vapours and should be handled with care and in the specified quantities.

Activity A4.1 is divided into two parts, a planning exercise and some laboratory work.

Activity A4.1a can be used to give students a further opportunity to practise producing a written plan, risk assessment and list of sources consulted. The student plans will need to be checked for safety before they embark on the experiment. This will be an opportunity to review the quality of their written plan and risk assessment against the current assessment criteria.

If you do not wish to use the activity to practise planning skills, or their plan is not appropriate, students can be given **Activity A4.1b**.

- **a** Ease of hydrolysis increases from the chloro- to the iodo-compound.
- **b** Relative rates of these reactions depend on the ease with which the C–Hal bond breaks. The reactivity follows the pattern of bond strengths.
- **c** Suggests 1-fluorobutane would be less reactive than 1-chlorobutane.
- **d** Halogenomethanes are gases (except CH₃I which is a volatile liquid).
- e Suggests that fluoroalkanes and chloroalkanes would be the most stable (but, of course, this experiment only provides evidence about their reactivity to attack by water in a nucleophilic substitution reaction).

A4.2 Making a balogenoalkane

Safety note Information about hazardous chemicals is given on the activity sheet. This activity will give students experience at working safely with flammable, harmful and corrosive substances.

The experiment uses a relatively large quantity of concentrated hydrochloric acid which is shaken in a stoppered separating funnel.

The constant shaking may cause a problem, with a buildup of pressure. The shakings must be very gentle and the pressure must be released *between each shaking*.

The procedure should be explained carefully and demonstrated prior to the experiment being done.

When purifying the product, sodium hydrogencarbonate solution is added. As there will be some acid in the funnel, there can be a marked build-up of gas pressure. Again the shakings must be very gentle and the pressure released *between each shaking*.

The vapours produced during the activity can be harmful. Students should work in a well-ventilated laboratory and avoid inhaling the fumes.

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Advance preparation

The melting point of 2-methylpropan-2-ol (*t*-butyl alcohol) is 25.5 °C. If kept in a cold store, it will take some time to melt.

$$a \rightarrow OH + HCI \rightarrow -CI + H_2O$$

- **b** This question could be used, if felt desirable, to introduce the idea of the alcohol being protonated.
- **c** The starting materials.
- **d** Hydrochloric acid.
- **e** Carbon dioxide gas is produced.
- **f** Less alkaline and thus will not tend to react with the halogenoalkane:

$$\begin{array}{cccc} \mathsf{CH}_3 & \mathsf{CH}_3 \\ \mathsf{H}_3\mathsf{C} & -\!\!\!\!\! & \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_3\mathsf{C} & -\!\!\!\! & \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_3 & \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_3 & \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_3 \end{array} + \begin{array}{c} \mathsf{CH}_3 \\ \mathsf{C} \\ \mathsf{C}$$

- **g** Went clear from cloudy. Traces of water absorbed by the anhydrous sudium sulphate
- **h** For example, anhydrous magnesium sulphate.
- i Boiling points are a characteristic property of a substance and are affected by the presence of impurities. Pure liquids boil over a narrow range.

| j | Solubility | Acidity | Volatility |
|---|---------------------|---------|---------------|
| | H ₂ O | HCl | methylpropene |
| | 2-methylpropan-2-ol | | |

k Mass of 2-methylpropan-2-ol used = xgMass of 2-chloro-2-methylpropane made = γg

$$i C_{4}H_{9}OH + HCl \rightarrow C_{4}H_{9}Cl + H_{2}O$$

$$74g \qquad 92.5g$$

$$xg \qquad -92.5 \times x$$

$$74$$

$$g$$

$$ii 92.5 \times x$$

$$74$$

$$g$$

$$iii 92.5 \times x$$

$$74$$

$$g$$

$$iii Yield = \frac{yg \times 100}{92.5 \times x}$$

$$g$$

- **1** Formation of other products, eg methylpropene; some product lost during extraction and purification.
- **m** (Nucleophilic) substitution.
- Consider the problems involved in moving the chemicals from one container to another, mixing the chemicals thoroughly, heating and cooling, as well as the choice of materials to make the apparatus. Safety precautions would be necessary for handling large quantities of concentrated acids and volatile organic compounds.

Note

After such a long practical, students might find it helpful to summarise the various stages in the form of a flow chart.

A4.3 Designing refrigerants

Part A: Properties of refrigerants

- **a** A refrigerant needs to be non-toxic, non-flammable and not too expensive. It should also be relatively unreactive and have no adverse effects on the environment.
- **b** The advantages and disadvantages of compounds containing H, Cl and F atoms should be apparent from

the table, and students should be able to predict that a chlorofluorocarbon (such as CCl_2CF_2) has an optimum set of properties for a refrigerant. The drawbacks are the environmental effects of CFCs (ozone depletion and global warming) which Midgeley was unaware of.

Midgeley selected halogenoalkanes, which did not contain H atoms because of their unreactivity, insolubility and volatility. He may have chosen CCl_2CF_2 (CFC-12) because of its particular boiling point and its relative ease of manufacture.

Part B: Replacing CFCs

- **c i** Fully halogenated CFCs have high ODPs as they are stable in the troposphere and so get into the stratosphere where the C–Cl bond is broken releasing Cl radicals.
 - ii Presence of hydrogen atoms in a halogenoalkane lowers the ODP. Alkanes and ethers have low ODPs. These compounds all have short atmospheric lifetimes. The presence of H atoms makes them much more reactive. They are oxidised in the troposphere and do not reach the stratosphere.
- d i CCl₃F (CFC 11) can be replaced as a blowing agent by HCFC 123. (Toxicity is low; it is not flammable.) It does cause ozone depletion but only to ¹/₅₀th of the extent of CFC 11.
 - ii CCl₂F₂ (CFC 12) can be replaced as a refrigerant by HFC 134a, which has similar properties and a zero ODP. (Toxicity is low; it is not flammable.) However, HFC 134a is considerably more expensive.
 - iii There is as yet no satisfactory alternative to CCl₂FCClF₂ (CFC 113) as a cleaning solvent. Some use is being made of methanol propelled by HCFC 22. (Toxicity is low; it is not flammable.)

More details about toxicity and reactivity. In particular, information about its lifetime and reactions in the atmosphere, and the toxicity of breakdown products. Whether the replacement compounds will contribute significantly to global warming.

Availability of the compounds (or time required to develop manufacturing techniques if not yet available). Interactions of refrigerants with fridge materials and lubricants.

Pressure at which refrigerants need to be used.

Note: naming CFCs

Students might be interested to learn how the number code for CFCs works. It was devised by some industrial chemists so that it would not be obvious to an eavesdropper what compounds they were discussing in their research.

- The first digit gives the number of C atoms minus 1, and is omitted if zero.
- The second digit gives the number of H atoms plus 1.
- The third digit gives the number of F atoms. If the compound has isomers, then it is assumed to be the symmetrical isomer if there is no letter, *a* represents the slightly asymmetric isomer, and *b* represents a more asymmetric isomer. (Halons are named more simply; the digits represent the numbers of C, F, Cl and Br atoms, respectively.)

Part C: International agreements

This part of the activity allows students to practise IT and communication skills. The **Salters Advanced Chemistry Web Site** contains some useful references.



A6 Which are the greenhouse gases?

The spectrum of the radiation emitted by the Earth is best drawn with a linear wavelength scale, rather than with a linear frequency scale. At this stage in the course, students will be more familiar with the electromagnetic spectrum in terms of frequencies, but, as the course develops, they will need to become familiar with both frequency and wavelength scales and the relation between them.

In this exercise, absorption ranges for the gases are given in both frequency and wavelength units, but students will find it easier to use the wavelength ranges when drawing in the absorption ranges.

- **b** H_2O and CO_2
- c Above 17 000 nm (up to 0.18×10^{14} Hz); 12 500 nm to 6950 nm (0.24×10^{14} Hz to 0.43×10^{14} Hz) and below 4670 nm (above 0.64×10^{14} Hz).
- **e** CH_4 , N_2O , CCl_3F and O_3 are all greenhouse gases and absorb in the 'window' left by CO_2 and H_2O the natural greenhouse gases. (CO_2 acts differently more of it simply increases its effect. H_2O is an effective greenhouse gas, but its concentration in the atmosphere is fixed as long as the temperature remains fairly constant.)
- **f** The contribution of a gas to the greenhouse effect will depend on its concentration and on its effectiveness as an i.r. absorber. *Greenhouse factors* are assigned to gases to denote their effect relative to the same concentration of CO₂, which is given a greenhouse factor of 1.

A8.1 The effect of concentration changes on chemical equilibria

Safety note Information about hazardous chemicals is given on the activity sheet. Chromates(VI) irritate the skin and are suspected carcinogens. Avoid all skin contact. Any spillage should be washed off at once.

Equilibrium 1

| Change | Observation | Cause | What has happened to the position of equilibrium? |
|---|-------------------------------------|---|--|
| Concentration H ⁺ (aq) increased | Yellow solution became orange | Concentration Cr ₂ O ₇ ^{2–} (aq) increased | Position of equilibrium has shifted to right |
| Concentration H ⁺ (aq) decreased | Orange solution became yellow | Concentration $CrO_4^{2-}(aq)$ increased | Position of equilibrium has shifted to left |

a $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ Acid–base reaction

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Equilibrium 2

| Change | Observation | Cause | What has happened to the position of equilibrium? |
|---|-----------------------------------|--|--|
| Concentration Fe ³⁺ (aq) increased | Solution turned darker red | Concentration $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ increased | Position of equilibrium has shifted to right |
| Concentration SCN ⁻ (aq) increased | Solution turned darker red | $\begin{array}{l} \text{Concentration} \\ [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}(\text{aq}) \\ \text{increased} \end{array}$ | Position of equilibrium has shifted to right |
| Concentration Fe ³⁺ (aq) decreased | Solution turned lighter red | $\begin{array}{l} \text{Concentration} \\ [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}(\text{aq}) \\ \text{decreased} \end{array}$ | Position of equilibrium has shifted to left |

b Position of equilibrium would shift to left.

Summary

c When the concentration of one of the substances in an equilibrium mixture is changed, the system is no longer in equilibrium. The concentrations of all the substances change until a new position of equilibrium is reached.

When the concentration of one of the reactants on the left is increased, the position of equilibrium shifts to the right and the concentrations of the products on the right increase. Conversely, when the concentration of one of the products on the right is increased, the position of equilibrium shifts to the left and the concentrations of the reactants increase.

A8.2 Measuring the concentration of carbon dioxide in air samples

It is not intended that the students should be taken very far into the ideas of chemical equilibrium at this point. They use a calibration graph to work out their results.

(The plot of lg $[CO_2 \text{ concentration/mol dm}^{-3}]$ against pH gives a straight line. This is because the relationship for the two equilibrium constants can be combined:

$$CO_{2}(g) \rightleftharpoons CO_{2}(aq)$$

and
$$CO_{2}(aq) + H_{2}O(l) \rightleftharpoons HCO_{3}^{-}(aq) + H^{+}(aq)$$

$$K_{1} = \frac{[HCO_{3}^{-}(aq)][H^{+}(aq)]}{[CO_{2}(aq)]}$$

and
$$K_{2} = \frac{[CO_{2}(aq)]}{[CO_{2}(g)]}$$

Hence, $\lg [CO_2(g)] = -pH + \lg [HCO_3^{-}(aq)] - \lg K_1K_2$

If the air contains very low levels of CO₂, the assumptions made in the calculation are no longer valid. For example, we can no longer assume that all the $H^+(aq)$ ions come from the reaction of CO₂(aq) with H₂O, and must take into account the $H^+(aq)$ ions present from the dissociation of HCO₃⁻(aq) ions and from the dissociation of H₂O.

The graph then curves asymptotically to pH = 9.53 without CO_2 .)

- **a** Outdoor air: $1.3 \times 10^{-5} \text{ mol dm}^{-3}$ Indoor air: $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ Carbon dioxide: $3.5 \times 10^{-2} \text{ mol dm}^{-3}$
- **b** The uncertainty associated with each pH reading is \pm 0.05. The percentage errors will depend on the volumes used.

- **c** $0.9/2.5 \times 100 = 36\%$
- **d** The method is sensitive enough to detect the difference between normal air and CO_2 gas. In most cases, it will also detect a difference between air outside and inside the laboratory, though, of course, this depends on how similar the concentrations are.
- e One of the limitations of the method is that small differences in pH correspond to large differences in concentration. The method is not suitable for accurate measurement of atmospheric CO₂ concentrations, for which infrared intensity measurements are used.

A9 Controlling carbon dioxide

The aim of this activity is to provide students with practice at carrying out an 'open book' exercise. They will need guidance in finding suitable additional sources, referencing correctly and writing their abstract.

Although students should be encouraged to use other sources of information, it is worth pointing out that the information given in the activity itself should provide the main basis of their report. **a** $C + O_2 \rightarrow CO_2$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$ $2H_2 + O_2 \rightarrow 2H_2O$

| b | Fuel | Amount CO_2 given out per kJ of energy released by fuel/mol kJ ⁻¹ |
|---|---|---|
| | coal natural gas gasoline hydrogen | $\begin{array}{c} 2.54 \times 10^{-3} \\ 1.1 \times 10^{-3} \\ 1.5 \times 10^{-3} \\ \text{none} \end{array}$ |

c Coal releases more CO₂ per kJ of energy generated than natural gas and gasoline (roughly twice as much). Methane, which has a high hydrogen content, releases the least CO₂ of these three fuels per kJ of energy generated. Combustion of hydrogen does not generate carbon dioxide.

A note about organic chemistry in the Salters Advanced Chemistry course

By the end of this teaching unit, students will have met some of the basics of organic chemistry: the idea of homologous series, structural isomerism and simple reaction mechanisms. They will have studied the alkanes and halogenoalkanes in some detail and met briefly other types of compounds (alkenes, arenes, alcohols and ethers). They have learned to write structural and skeletal formulae and should practise drawing these at every opportunity.

Their knowledge of organic chemistry will be extended further in the AS course (in units PR and WM) and in the A2 course (in units DP, EP, AA, CD and MD). In the final unit, **Medicines by Design**, students bring all this knowledge and understanding together in the context of the synthesis of medicines. They build up a 'toolkit' to help them carry out synthetic steps (**Activities MD 3.1, 3.2** and **3.3**).

Now is a good time to start building up this toolkit. Students should be encouraged to draw spider diagrams (of the type shown in **Chemical Ideas Section 14.2**) to summarise their work at each stage, giving the reaction conditions and type of reaction or mechanism involved, where appropriate.

AS LEVEL