Storyline: answers to assignments

- **1 a** Delocalised electrons are not shared between two particular atoms but are 'spread out' among a number of atoms.
 - **b** Since the molecule is flat, it has a plane of symmetry and its mirror image is identical with the original molecule.
 - **c** Substitution of bromine into an aromatic ring can be achieved using Br₂(l) and a catalyst such as FeBr₃.
- **a** 1.72 moles of positive charge**b** 1.72 moles of negative chargeOverall the charges must balance.
- **3 a i** 34810 mg
 - **ii** A typical value might be 400 mg.
 - **b** The most abundant anion in mineral water will be HCO₃⁻, with far less SO₄²⁻ and Cl⁻. The situation is reversed in sea water which has a much greater mass of Cl⁻ than any other ion.

The relative amounts of Group 2 to Group 1 cations are also different for the two water samples. Mineral water contains more Mg^{2+} and Ca^{2+} than Na^+ and K^+ ; in sea water Na^+ is by far the most abundant cation. The large quantities of Na^+ , Cl^- and Br^- in sea water cannot be explained in terms of run-off from the land.

4 The oceans are in a steady state in which the rates of supply of ions from the various sources are balanced by their rates of removal.

Some combinations of anions and cations reach saturation, and insoluble salts precipitate out forming sediments. Some ions enter biological cycles. Some are lost into the atmosphere in spray from breaking waves. Salts are also removed as 'evaporite deposits'. These form when areas of the sea become cut off by land, are evaporated totally to dryness and then often become part of the rock structure. The Cheshire salt deposits are thought to have formed in this way.

- 5 **a** Surface area = 360×10^6 km²; average depth = 3.7 km Volume of the oceans = 1.33×10^9 km³
 - **b** 1 km = 10^4 dm; therefore 1 km³ = 10^{12} dm³ Volume of the oceans = 1.33×10^{21} dm³
 - **c** 1.33×10^{10} g or 13.3×10^{3} t
 - \mathbf{d} 2.22 g each
 - e i £17.85 (approximately)
 - ii You would have to pay something towards the cost of the equipment, processing costs, salaries of crew, etc, administration costs, and so on. It is likely that this would exceed &17.85 per person on the Earth.

$$\begin{array}{cccc} 6 & a & H & H \\ & & 1 & 1 \\ & H - C - S - C - H \\ & 1 & 1 \\ H & H \end{array}$$

Dimethyl sulphide is a bent molecule; the four electron pairs around sulphur (two bonding pairs and two lone pairs) adopt a tetrahedral arrangement.



A2 LEVEL

The C–S–C bond angle is close to 109°.

- **b i** Ethers
- ii The molecules interact by permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces which are relatively weak. Hydrogen bonding is not possible. (Students should realise that dimethyl sulphide is not a linear molecule and so does possess a dipole.) The attractive forces between molecules are easily broken and the liquid is volatile.
- **c** In both cases the sulphur atom has gained oxygen.
- 7 In summer, evaporation of sea water and cloud cover cool Victoria and St John's; no such cooling is possible in Winnipeg. In winter, currents of sea water and moist air keep the climates of Victoria and St John's relatively mild, particularly Victoria which is favoured by warm water currents.
- 8 **a** $(36 \times 10^{15} \text{ kg}) \times (2260 \text{ kJ kg}^{-1}) = 8.1 \times 10^{19} \text{ kJ of energy}$ released annually.
 - **b** $(8.1 \times 10^{19} \text{ kJ}) \div (6 \times 10^{13} \text{ kJ}) = 1.4 \times 10^{6} \text{ power}$ stations. In other words, well over 1 million power stations.
- 9 **a** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
 - **b** 4.4 times more soluble.
 - **c** The CO₂ bubbling out of the water made it seem that the lake was simmering.
 - **d** Piping fizzy water would cause the gas to escape more rapidly from solution, and gas 'locks' would form in the pipes. Also any reduction in pressure as the liquid came to the surface would cause CO₂ to be released. These problems are avoided by piping gas and water separately.
- **10** On a clothes line, water vapour next to the washing is blown away by the breeze, causing more water to evaporate.

As carbon dioxide diffuses out of the open can, more gas comes out of the beer to take its place.

- **11 a** $\Delta H_{\rm f}^{\,\circ}$ values are: CaCO₃(s) = -1207 kJ mol⁻¹ Ca²⁺(aq) = -543 kJ mol⁻¹ CO₃²⁻(aq) = -675 kJ mol⁻¹ $\Delta H_{\rm r}^{\,\circ}$ = -11 kJ mol⁻¹
 - **b** If the equilibrium

 $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

moves to the left to produce more calcium carbonate, the concentration of $\text{CO}_3^{2-}(\text{aq})$ will decrease. This in turn will cause equilibrium

$$\begin{aligned} &\text{HCO}_3^{-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \\ &\text{and equilibrium} \\ &\text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^{-}(aq) \end{aligned}$$

to move to the right,

(or, using the overall equation, the equilibrium

 $CO_2(aq) + H_2O(l) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$

will move to the right).

The resulting decrease in the concentration of $CO_2(aq)$ will cause equilibrium

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

to move to the right and more carbon dioxide will dissolve.

- 12 Aqueous calcium ions are strongly hydrated. Arranging water molecules around the Ca²⁺ ions, rather than leaving them moving randomly in the liquid, corresponds to an entropy decrease.
- **13 a** The equilibrium in reaction 6 is displaced further to the right-hand side by an increased CO₂ concentration.
 - **b** Precipitation is mainly caused by the fall in the concentration of gaseous CO_2 , which is 10 to 40 times lower in the cave than in the soil. The high CO_2 concentration in the soil displaces the equilibrium in reaction 6 to the right as explained in **a**. The lower CO_2 concentration in the cave displaces the equilibrium back to the left-hand side, forming solid CaCO₃.
 - **c** On a planet without life, there would be no photosynthesis, respiration, decaying organisms, etc, on which the levels of CO₂ depend. Calcium carbonate rock would probably not exist on such a planet. Also, there would not be the different concentrations of gaseous CO₂ which are needed to make the process occur.

14 a Sulphur is clearly reduced from oxidation state +6 to -2. There must be a corresponding oxidation, making the process redox. (Note that it is difficult to assign oxidation states to atoms in organic compounds.)

d Far more energy is released in aerobic respiration which is a much more efficient process.

Activities: notes and answers to questions _

General note

Since this teaching unit comes near the end of the course, the activities have been designed differently from those in most other units. Students may appreciate the opportunity to practise structured questions of the type found on the examination papers, perhaps more than they feel the need to practise skills which are more relevant to the coursework, which they may already have done. Also, there will probably be no future occasions for developing and applying many of the concepts covered in the **Chemical Ideas** relating to bonding, intermolecular forces, enthalpy and entropy changes and chemical equilibrium. The activities have therefore been designed to provide as many opportunities as possible for answering questions by the application of these chemical concepts.

O1.1 What is the relationship between a solvent and the substances that dissolve in *it*?

Safety note Information about hazardous chemicals is given on the activity sheet.

Cyclohexane may be substituted for hexane.

This activity provides an opportunity to revise and extend some of the ideas about dissolving which arise out of **From Minerals to Elements** and **Aspects of Agriculture**. It can become repetitive if all students do all the tests, and the work could be shared out among the members of the class.

- a NaCl and CaCl₂ are ionic.
 Glucose, propanone and water are covalent, with polar molecules.
 Wax and hexane are covalent, with non-polar molecules.
- **b** Covalent solids with non-polar molecules dissolve well in non-polar solvents. Ionic solids or covalent solids with polar molecules dissolve well in polar solvents.
- **c** Students should be aware that solubility is related to the overall increase or decrease in strength of attractive forces between particles, which could accompany a change.

They should be clear about the difference between ionic and covalent molecular solids in this respect.

A2 LEVEL

Solid	Principal interactions in solid	Solvent	Principal interactions in solvent	Principal interactions in solution	Enthalpy change which would accompany the formation of a solution as a result of these changes in interactions	Is the solid likely to dissolve?
NaCl	ionic	hexane	instantaneous dipole–induced dipole forces	ion–induced dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		propanone	permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces	ion–dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		water	hydrogen bonding	strong ion– dipole forces	strong interactions before and after	solid dissolves
CaCl ₂	ionic	hexane	instantaneous dipole–induced dipole forces	ion–induced dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		propanone	permanent dipole– permanent dipole and instantaneous dipole–induced dipole forces	ion–dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		water	hydrogen bonding	strong ion– dipole forces	strong interactions before and after	solid dissolves
glucose	strong covalent bonds within molecules; hydrogen bonds between molecules	hexane	instantaneous dipole–induced dipole forces	permanent dipole–induced dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		propanone	permanent dipole– permanent dipole and instantaneous dipole–induced dipole forces	permanent dipole– permanent dipole forces	weaker interactions in solutions; endothermic	solid does not dissolve
		water	hydrogen bonding	hydrogen bonding	strong interactions before and after	solid dissolves
wax	strong covalent bonds within molecules; instantaneous dipole–induced dipole forces between molecules	hexane	instantaneous dipole–induced dipole forces	instantaneous dipole–induced dipole forces	weak interactions before and after	solid dissolves
		propanone	permanent dipole– permanent dipole and instantaneous dipole–induced dipole forces	permanent dipole–induced dipole forces	weaker interactions in solution; endothermic	solid does not dissolve
		water	hydrogen bonding	permanent dipole–induced dipole forces	weaker interactions in solution; endothermic	solid does not dissolve

O1.1 Table 1 Changes in interactions between particles when a solid dissolves

O1.2 What changes occur when an ionic solid dissolves?

Safety note Information about hazardous chemicals is given on the activity sheet.

Calcium chloride and iron(III) chloride each take in water from the air. It is important to use *fresh anhydrous* samples and to work quickly.

Part 1: Enthalpy changes

Some typical results are shown below.

lonic solid	Temperature change/K	Enthalpy change/kJ	∆ <i>H</i> _{solution} /kJ mol ^{−1}
NaCl	-2	+0.4	+4
CaCl ₂	+30	-6.3	-63
FeCl ₃	+40	-8.4	-84

A2 LEVEL

Part 2: Volume changes

Some typical results are shown below.

lonic solid	Volume change/cm ³	Percentage change in volume
NaCl	-0.5	-1%
CaCl ₂	-3.5	-7%
FeCl ₃	-3.0	-6%

When an ionic solid dissolves, ionic bonds between ions in а the lattice are broken and also some hydrogen bonds between water molecules. (Bond-breaking is an endothermic process.) The ions in solution are hydrated and new attractions form between the ions and polar water molecules. (Bond-formation is an exothermic process.)

For sodium chloride, the overall enthalpy change of solution is small. The highly exothermic changes for calcium chloride and iron(III) chloride can be explained in terms of strong hydration of Ca^{2+} and Fe^{3+} ions.

The contractions arise because fairly randomly arranged b H₂O molecules in liquid water become 'tightly locked' onto the ions when they are in their hydrated form. Ca^{2+} and Fe³⁺ are extensively hydrated resulting in a significant contraction in volume.

01.3 What factors affect the enthalpy change of formation of an ionic compound?

Part 1: Constructing an enthalpy cycle

- Stage (1) (a), (c) 1 Stage (2) (b), (d) Stage (3) (e)
- 2 Equation (a) (iii) Equation (b) (v)
 - Equation (c) (iv) Equation (d) (ii)
 - Equation (e)



4 Δ
$$H_{f}^{\Theta}$$
 (Na Cl(s)) = (iii) + (iv) + (v) + (ii) + (i)

Data for spreadsheet: 5

Part 2: Using the cycle

The first series (NaF to NaI) gives a clear answer: changes 6 in $\Delta H_{\rm LE}^{\bullet}$ dominate the changes in $\Delta H_{\rm f}^{\bullet}$. In the second series (LiCl to RbCl) there are no clear dominating factors. Indeed, for example, ΔH_{LE}^{\bullet} changes tend to counterbalance changes in ΔH_{at}^{\bullet} and $\Delta H_{i}^{\bullet}(1)$ for M.

To adapt the cycle for the halides of Group 2 elements: values quoted for X need to be doubled. First and second ionisation enthalpies for M needed.

03.1 The enthalpy change of vaporisation of water

Part 1: Measuring the enthalpy change of vaporisation of water (optional extension)

You may prefer to do this as a class demonstration. (The physics department may have a similar apparatus already made up.) Use hot water to speed up the heating process. The method can be extended (with appropriate safety precautions) to measure ΔH_{vap} for other liquids. The method gives more reliable results for liquids with low surface tension eg cyclohexane and hexane, than for water. Water has a tendency to 'hold-up' in the apparatus and not distil over

If you experience difficulties soldering the copper and nichrome wires together, the following may help:

- clean both wires with emery paper
- clean the copper wire by dipping into phosphoric acid
- coat with a thin layer of solder (ordinary soft electrical solder)
- clean the nichrome wire with phosphoric acid in the same way and coat with solder. You may need a little more solder here.
- clamp the two wires so that the coated ends overlap and heat with the soldering iron to allow the soldered surfaces to bind together.

Part 2: Looking at your results

All students should work through the questions in Part 2 even if they have not done the practical work in Part 1.

- а Values are likely to be in excess of $+40 \text{ kJ} \text{ mol}^{-1}$. (The results quoted give a value of +49.4 kJ mol⁻¹.)
- The boiling tube is lagged to reduce heat loss from the b hot liquid and vapour during evaporation. The condenser is cooled to encourage heat loss from the vapour during condensation.
- This is to allow the whole apparatus to reach equilibrium С with the water which is boiling. In particular, it allows the appropriate pieces of glassware to warm up to 100 °C

Compound MX	Enthalpy of atomisation of M / kJ mol ⁻¹	First ionisation enthalpy of M/kJ mol ⁻¹	Enthalpy of atomisation of X / kJ mol ⁻¹	Electron affinity of X/kJ mol ⁻¹	Lattice enthalpy /kJ mol ⁻¹	Enthalpy change of formation /kJ mol ⁻¹
NaF NaCl NaBr Nal	107 107 107 107	502 502 502 502 502	79 122 112 107	-334 -355 -331 -301	-928 -788 -751 -700	-574 -412 -361 -285
LiCl NaCl KCl RbCl	159 107 89 81	519 502 425 409	122 122 122 122	-355 -355 -355 -355	-862 -788 -717 -693	-417 -412 -436 -436

before any measurements are taken.

- **d i** Water is the only liquid in the table in which the molecules are held together by hydrogen bonds. The molecules in the other liquids are held together by weaker forces resulting from instantaneous dipole–induced dipole interactions (and permanent dipole–permanent dipole interactions in the case of trichloromethane).
 - **ii** Ethanol also contains hydrogen bonding between molecules, which has to be broken on vaporisation.
- e There is a large increase in the entropy of the system.

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i \Delta S_{\text{total}} = 0 at equilibrium.
ii Since \Delta S_{\text{total}} = \Delta S_{\text{total}} + \Delta S_{\text{total}}
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f

n	Since	ΔS_{total}	$=\Delta S_{vap}$	+	Δ3 _{surr,}	
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Liquid	$\Delta \mathbf{S}_{\mathrm{surr}} / \mathbf{J} \mathbf{K}^{-1} \mathbf{mol}^{-1}$	$\Delta {f S}_{ m vap}^{}/{f J}{f K}^{-1}{ m mol}^{-1}$
trichloromethane	-87.5	+87.5
hexane	-84.2	+84.2
cyclohexane	-85.0	+85.0
methylbenzene	-87.0	+87.0
water	-108.8	+108.8

 $\Delta S_{\text{vap}} = -\Delta S_{\text{surr}}$ at the boiling point. **iii** Values are

- **g i** ΔS_{vap} values are shown in the table above.
 - **ii** The four values are very similar; average $+86 \text{ J K}^{-1} \text{ mol}^{-1}$.
 - **iii** The four organic compounds have similar intermolecular forces and a similar degree of order in the liquid. The increase in entropy which results from spreading out the molecules from the liquid to occupy a much greater volume in the vapour is very similar in each case.
 - **iv** Water has a significantly more positive ΔS_{vap} value. Hydrogen bonding between molecules in the liquid causes water to have a more ordered structure than most liquids. Hence there is a greater gain in entropy

Formula	<i>M</i> _r	$\Delta H_{ m vap}/ m kJ^{-1} m kg^{-1}$
CHCl3	119.5	+245
C_6H_{14}	86	+335
$C_{6}H_{12}^{12}$	84	+358
C ₇ H ₈	92	+363
H ₂ O	18	+2256

on forming the random structure of the vapour.

h i

ii Answers should reflect the points made in The Oceans storyline, O3.

O3.2 What crystals form when a solution is cooled?

Safety note Information about hazardous chemicals is given on the activity sheet.

The practical part of this activity could be omitted if desired, but the interpretation and questions provide an important reinforcement of the ideas about entropy in **Chemical Ideas 4.3** and **4.4**. Students may need help when working through the 'What it means' section.

a The concentration: saturated copper sulphate solution produces copper sulphate crystals, dilute solutions form ice.

- **i** The density of the solution decreases**ii** The density increases.
- **c** The Antarctic deep water current forms when ice crystallises from cold seawater. The current could not form if the oceans were saturated with salt because salt crystals would form and the sea's density would decrease.

d
$$\Delta S_{\text{surr}} = \frac{-(-6010 \,\text{J}\,\text{mol}^{-1})}{273 \,\text{K}} = +22.0 \,\text{J}\,\text{K}^{-1} \,\text{mol}^{-1}$$

- **e** The water molecules are in a highly ordered structure in ice.
- **f** $\Delta S_{\text{total}} = 0$ because ice and water are in equilibrium at 0 °C.
- g i Copper(II) sulphate solution → ice, because the random distribution of ions in the solution contributes to its entropy so that the entropy of the solution is greater than the entropy of water.
 - **ii** ΔS_{surr} must be greater when copper sulphate solution freezes.

iii
$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T}$$
 or $\Delta H = -T\Delta S_{\text{surr}}$

Since ΔH is the same in both cases, *T* must be smaller when copper sulphate solution freezes than when water freezes, because ΔS_{surr} is greater.

04.1 Finding out more about weak acids

This activity applies and reinforces the ideas in **Chemical Ideas 8.2**.

- **a i** The pH scale gives a measure of the concentration of $H^+(aq)$ ions in a solution: $pH = -lg [H^+(aq)]$
 - **ii** As pH decreases, [H⁺(aq)] increases. A *decrease* in pH by 1 unit corresponds to a 10-fold *increase* in [H⁺(aq)].
- **b i** pH changes by 1 unit
 - ii pH changes by 1 unit
- c i A strong acid is one in which the reaction with water to produce H⁺(aq) ions goes to completion, e.g. HCl, H₂SO₄ and HNO₃. The strength of an acid is a measure of the extent to which it can donate H⁺ ions. It is a property of the acid. The *concentration* of an acid is a measure of the

amount of substance in a given volume of solution, typically measured in mol dm⁻³. It is possible to have concentrated solutions of both strong and weak acids.

- **ii** Since the reaction with water goes to completion, the amount in moles of $H^+(aq)$ ions in solution is equal to the amount in moles of the acid put into the solution. Hence, a 10-fold change in the concentration of a strong acid leads to a 10-fold change in $[H^+(aq)]$.
- **iii** Corresponds to the behaviour of a strong acid.
- d i In a *weak acid* only a small proportion of acid molecules react with water to produce H⁺(aq) ions. An equilibrium is established:

 $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

The position of equilibrium lies towards the left.

$$K_{a} = \frac{[H^{+}(aq)] [A^{-}(aq)]}{[HA(aq)]}$$

ii

- **iii** Equal amounts of $H^+(aq)$ and $A^-(aq)$ ions are produced from HA(aq). There are also $H^+(aq)$ ions in the solution from the ionisation of water, but their concentration is very much less than the concentration of $H^+(aq)$ ions from ethanoic acid.
- **iv** This is a reasonable assumption because ethanoic acid is a weak acid and the fraction which reacts with water to produce ions is very small.
- **v** For $0.1 \text{ mol dm}^{-3} \text{ CH}_3 \text{COOH}$:

$$1.7 \times 10^{-5} \text{ mol dm}^{-3} = \frac{[\text{H}^+(\text{aq})]^2}{0.1 \text{ mol dm}^{-3}}$$

For 0.001 mol dm⁻³ CH₂COOH:

$$1.7 \times 10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{0.001 \,\mathrm{mol}\,\mathrm{dm}^{-3}}$$

- **vi** For 0.1 mol dm⁻³ CH₃COOH: $[H^+(aq)] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$ For 0.001 mol dm⁻³ CH₃COOH: $[H^+(aq)] = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$ ie $[H^+(aq)]$ becomes 10× smaller when solution diluted by a factor of 100.
- vii There should be good agreement.

04.2 Investigating some buffer solutions

Safety note Information about hazardous chemicals is given on the activity sheet.

- **a Buffer A** and **Buffer D** should have the same pH.
- **b** On the ratio of the amounts since this is the same in **Buffer A** and **Buffer D**.

 $c \quad \text{pH should rise in the order } F < A < E.$

As more anions are added in the form of salt, the $[A^{-}(aq)]$ increases (and [HA(aq)] decreases). The equilibrium $HA(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq)$ is displaced further to the left, causing $[H^{+}(aq)]$ to fall and the pH to rise.

- d i The chemical systemii The proportions of acid and salt used.
- e 1.5 × 10⁻³ mol of H⁺(aq) ions are added.
 Buffer A contains 12.5 × 10⁻³ mol of ethanoate ions, which can counteract the addition of acid.
 Buffer D contains the same *ratio* of acid to salt as Buffer A, but the *amount* of ethanoate ions is only 1.25 × 10⁻³ mol not enough to counteract all the acid added.

The nitrate(V) ions in solution **G** do not react with the extra H⁺(aq) ions added. Solution **G** contains 5×10^{-6} mol of H⁺(aq) ions, so addition of the extra acid represents a huge increase in the amount of H⁺(aq) ions in solution and a consequent big drop in pH.

 ${\bf f} \quad {\rm The} \ 1.5 \times 10^{-3} \ {\rm mol} \ {\rm of} \ {\rm H}^+({\rm aq}) \ {\rm or} \ {\rm OH}^-({\rm aq}) \ {\rm ions} \ {\rm added} \ {\rm can} \ {\rm easily} \ {\rm be} \ {\rm counteracted} \ {\rm by} \ {\rm the} \ {\rm weak} \ {\rm acid} \ {\rm or} \ {\rm salt} \ {\rm in} \ {\rm the} \ {\rm buffers}.$