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.

2. a 1.72 moles of positive charge
   b 1.72 moles of negative charge
   Overall 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 Mg²⁺ and Ca²⁺ 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 × 10⁶ km²; average depth = 3.7 km
   b Volume of the oceans = 1.33 × 10²³ km³
   c 1 km = 10 dm; therefore 1 km³ = 10¹² dm³
   d 1.33 × 10¹⁰ g or 13.3 × 10³ t
   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.

6. a

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

   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 × 10¹⁵ kg) × (2260 kJ kg⁻¹) = 8.1 × 10¹⁹ kJ of energy released annually.
   b (8.1 × 10¹⁹ kJ) ÷ (6 × 10¹⁵ kJ) = 1.4 × 10⁴ power stations. In other words, well over 1 million power stations.
   c CaCO₃(s) → CaO(s) + CO₂(g)
   d 4.4 times more soluble.
   e The CO₂ bubbling out of the water made it seem that the lake was simmering.
   f 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.

9. a CaCO₃(s) → CaO(s) + CO₂(g)
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   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 ΔH° values are:
    CaCO₃(s) → Ca²⁺(aq) + CO₃²⁻(aq)
    ΔH° = –1207 kJ mol⁻¹
    Ca²⁺(aq) + CO₃²⁻(aq) → CaCO₃(s)
    ΔH° = –543 kJ mol⁻¹
    CO₂(g) + H₂O(l) → H⁺(aq) + HCO₃⁻(aq)
    ΔH° = –675 kJ mol⁻¹
    b If the equilibrium moves to the left to produce more calcium carbonate, the concentration of CO₃²⁻(aq) will decrease. This in turn will cause equilibrium reactions to take place, such as:
    HCO₃⁻(aq) → H⁺(aq) + CO₂(g)
    and equilibrium reactions:
    CO₂(g) + H₂O(l) → H⁺(aq) + HCO₃⁻(aq)
    to move to the right, (or, using the overall equation, the equilibrium:
    CO₂(g) + H₂O(l) → 2H⁺(aq) + CO₃²⁻(aq)
    will move to the right).
    The resulting decrease in the concentration of CO₂(aq) will cause equilibrium:
    CO₂(g) → CO₂(aq)
    to move to the right and more carbon dioxide will dissolve.
Aqueous calcium ions are strongly hydrated. Arranging water molecules around the $\text{Ca}^{2+}$ ions, rather than leaving them moving randomly in the liquid, corresponds to an entropy decrease.

The equilibrium in reaction 6 is displaced further to the right-hand side by an increased $\text{CO}_2$ concentration.

Precipitation is mainly caused by the fall in the concentration of gaseous $\text{CO}_2$, which is 10 to 40 times lower in the cave than in the soil. The high $\text{CO}_2$ concentration in the soil displaces the equilibrium in reaction 6 to the right as explained in (a). The lower $\text{CO}_2$ concentration in the cave displaces the equilibrium back to the left-hand side, forming solid $\text{CaCO}_3$.

On a planet without life, there would be no photosynthesis, respiration, decaying organisms, etc, on which the levels of $\text{CO}_2$ depend. Calcium carbonate rock would probably not exist on such a planet. Also, there would not be the different concentrations of gaseous $\text{CO}_2$ which are needed to make the process occur.

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.) Other $\Delta H_f$ values are:

- $\text{SO}_4^{2-} (\text{aq}) = -909 \text{ kJ mol}^{-1}$
- $\text{S}^2- (\text{aq}) = +33 \text{ kJ mol}^{-1}$
- $\text{CO}_2 (\text{g}) = -394 \text{ kJ mol}^{-1}$
- $\text{H}_2\text{O}(\text{l}) = -286 \text{ kJ mol}^{-1}$

\[ \Delta H_{\text{reaction}} = 2(-490 \text{ kJ mol}^{-1}) + (+33 \text{ kJ mol}^{-1}) + 2(-394 \text{ kJ mol}^{-1}) - 2(-694 \text{ kJ mol}^{-1}) - (-909 \text{ kJ mol}^{-1}) = -10 \text{ kJ mol}^{-1} \]

- $\text{CH}_3\text{CH(OH)COOH(aq) + 3O}_2 (\text{g}) \rightarrow 3\text{CO}_2 (\text{g}) + 3\text{H}_2\text{O(l)}$
- $\Delta H_{\text{reaction}} = 3(-394 \text{ kJ mol}^{-1}) + 3(-286 \text{ kJ mol}^{-1}) - (-694 \text{ kJ mol}^{-1}) = -1346 \text{ kJ mol}^{-1}$

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

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.

NaCl and $\text{CaCl}_2$ are ionic.

Glucose, propanone and water are covalent, with polar molecules.

Wax and hexane are covalent, with non-polar molecules.

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.

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.

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

<table>
<thead>
<tr>
<th>Solid</th>
<th>Principal interactions in solid</th>
<th>Solvent</th>
<th>Principal interactions in solvent</th>
<th>Principal interactions in solution</th>
<th>Enthalpy change which would accompany the formation of a solution as a result of these changes in interactions</th>
<th>Is the solid likely to dissolve?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>ionic</td>
<td>hexane</td>
<td>instantaneous dipole–induced dipole forces</td>
<td>ion–induced dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
<tr>
<td></td>
<td>propanone</td>
<td></td>
<td>permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces</td>
<td>ion–dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td></td>
<td>hydrogen bonding</td>
<td>strong ion–dipole forces</td>
<td>strong interactions before and after</td>
<td>solid dissolves</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>ionic</td>
<td>hexane</td>
<td>instantaneous dipole–induced dipole forces</td>
<td>ion–induced dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
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<td></td>
<td>propanone</td>
<td></td>
<td>permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces</td>
<td>ion–dipole forces</td>
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<td>solid does not dissolve</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td></td>
<td>hydrogen bonding</td>
<td>strong ion–dipole forces</td>
<td>strong interactions before and after</td>
<td>solid dissolves</td>
</tr>
<tr>
<td>glucose</td>
<td>strong covalent bonds within molecules; hydrogen bonds between molecules</td>
<td>hexane</td>
<td>instantaneous dipole–induced dipole forces</td>
<td>permanent dipole–induced dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
<tr>
<td></td>
<td>propanone</td>
<td></td>
<td>permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces</td>
<td>permanent dipole–permanent dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td></td>
<td>hydrogen bonding</td>
<td>hydrogen bonding</td>
<td>strong interactions before and after</td>
<td>solid dissolves</td>
</tr>
<tr>
<td>wax</td>
<td>strong covalent bonds within molecules; instantaneous dipole–induced dipole forces between molecules</td>
<td>hexane</td>
<td>instantaneous dipole–induced dipole forces</td>
<td>instantaneous dipole–induced dipole forces</td>
<td>weak interactions before and after</td>
<td>solid dissolves</td>
</tr>
<tr>
<td></td>
<td>propanone</td>
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<td>permanent dipole–permanent dipole and instantaneous dipole–induced dipole forces</td>
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<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
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<td>water</td>
<td></td>
<td>hydrogen bonding</td>
<td>permanent dipole–induced dipole forces</td>
<td>weaker interactions in solution; endothermic</td>
<td>solid does not dissolve</td>
</tr>
</tbody>
</table>

### 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.

<table>
<thead>
<tr>
<th>Ionic solid</th>
<th>Temperature change/K</th>
<th>Enthalpy change/kJ</th>
<th>$\Delta H_{solvation}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>−2</td>
<td>+0.4</td>
<td>+4</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>+30</td>
<td>−6.3</td>
<td>−63</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>+40</td>
<td>−8.4</td>
<td>−84</td>
</tr>
</tbody>
</table>
Part 2: Volume changes
Some typical results are shown below.

<table>
<thead>
<tr>
<th>Ionic solid</th>
<th>Volume change/cm³</th>
<th>Percentage change in volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-0.5</td>
<td>-1%</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>-3.5</td>
<td>-7%</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>-3.0</td>
<td>-6%</td>
</tr>
</tbody>
</table>

a When an ionic solid dissolves, ionic bonds between ions in 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 Ca²⁺ and Fe³⁺ ions.

b The contractions arise because fairly randomly arranged H₂O molecules in liquid water become ‘tightly locked’ onto the ions when they are in their hydrated form. Ca²⁺ and Fe³⁺ are extensively hydrated resulting in a significant contraction in volume.

O1.3 What factors affect the enthalpy change of formation of an ionic compound?

Part 1: Constructing an enthalpy cycle

1. Stage (1) (a), (c)
   Stage (2) (b), (d)
   Stage (3) (e)

2. Equation (a) (iii)
   Equation (b) (v)
   Equation (c) (iv)
   Equation (d) (ii)
   Equation (e) (i)

3. Na(s) + ½Cl₂(g) → NaCl(s) [ΔH° (i)]

4. ΔH° (NaCl(s)) = (iii) + (iv) + (v) + (ii) + (i)

5. Data for spreadsheet:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy of atomisation of M / kJ mol⁻¹</th>
<th>First ionisation enthalpy of M/kJ mol⁻¹</th>
<th>Enthalpy of atomisation of X / kJ mol⁻¹</th>
<th>Electron affinity of X/kJ mol⁻¹</th>
<th>Lattice enthalpy /kJ mol⁻¹</th>
<th>Enthalpy change of formation /kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>107</td>
<td>502</td>
<td>79</td>
<td>-334</td>
<td>-928</td>
<td>-574</td>
</tr>
<tr>
<td>NaCl</td>
<td>107</td>
<td>502</td>
<td>122</td>
<td>-355</td>
<td>-788</td>
<td>-412</td>
</tr>
<tr>
<td>NaBr</td>
<td>107</td>
<td>502</td>
<td>112</td>
<td>-331</td>
<td>-751</td>
<td>-361</td>
</tr>
<tr>
<td>NaI</td>
<td>107</td>
<td>502</td>
<td>107</td>
<td>-301</td>
<td>-700</td>
<td>-285</td>
</tr>
<tr>
<td>LiCl</td>
<td>159</td>
<td>519</td>
<td>122</td>
<td>-355</td>
<td>-862</td>
<td>-417</td>
</tr>
<tr>
<td>NaCl</td>
<td>107</td>
<td>502</td>
<td>122</td>
<td>-355</td>
<td>-788</td>
<td>-412</td>
</tr>
<tr>
<td>KCl</td>
<td>89</td>
<td>425</td>
<td>122</td>
<td>-355</td>
<td>-717</td>
<td>-438</td>
</tr>
<tr>
<td>RbCl</td>
<td>81</td>
<td>409</td>
<td>122</td>
<td>-355</td>
<td>-693</td>
<td>-436</td>
</tr>
</tbody>
</table>

Part 2: Using the cycle

6. The first series (NaF to NaI) gives a clear answer: changes in ΔH° LE dominate the changes in ΔH° f. In the second series (LiCl to RbCl) there are no clear dominating factors. Indeed, for example, ΔH° LE changes tend to counterbalance changes in ΔH° f and ΔH° (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.

O3.1 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 e.g 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.

a Values are likely to be in excess of +40 kJ mol⁻¹. (The results quoted give a value of +49.4 kJ mol⁻¹.)

b The boiling tube is lagged to reduce heat loss from the hot liquid and vapour during evaporation. The condenser is cooled to encourage heat loss from the vapour during condensation.

c This is to allow the whole apparatus to reach equilibrium with the water which is boiling. In particular, it allows the appropriate pieces of glassware to warm up to 100 °C.
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, \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \). 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:

\[ \text{HA(aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq) \]

The position of equilibrium lies towards the left.

ii \( K_a = \frac{[\text{H}^+(aq)] \times [\text{A}^-(aq)]}{[\text{HA(aq)}]} \)
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.

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.

For $0.1 \text{ mol dm}^{-3} CH_3COOH$:

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

For $0.001 \text{ mol dm}^{-3} CH_3COOH$:

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

For $0.1 \text{ mol dm}^{-3} CH_3COOH$:

$$[H^+(aq)] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$$

For $0.001 \text{ mol dm}^{-3} CH_3COOH$:

$$[H^+(aq)] = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$$

ie $[H^+(aq)]$ becomes 10x smaller when solution diluted by a factor of 100.

There should be good agreement.

### O4.2 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** 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

$$HA(aq) = H^+(aq) + A^-(aq)$$

is displaced further to the left, causing $[H^+(aq)]$ to fall and the pH to rise.

- **d i** The chemical system
- **d ii** The proportions of acid and salt used.
- **e** $1.5 \times 10^{-3}$ mol of $H^+$ (aq) ions are added.

Buffer A contains $12.5 \times 10^{-3}$ 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 $1.25 \times 10^{-3}$ 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 $5 \times 10^{-6}$ 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.

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