All at sea? The chemistry of the oceans

Figure 1 The Pacific Ocean viewed from space by the solid state imager on the Galileo space probe

Those few people lucky enough to have seen the planet Earth from space often call it the blue planet because of the large area of surface covered by oceans (Figure 1). In fact the Earth's oceans hold about 1.5 x 10^{18} tonnes of water, which in turn contains 0.05 x 10^{18} tonnes of dissolved salts. So a lot of chemistry can take place in the oceans. The oceans also interact chemically with the Earth's rocks, with the atmosphere and with living things.

For many purposes, the Earth can be divided into four sections or 'spheres'. These are:

- the **lithosphere** – this consists of the solid rock and soil component of the crust and upper mantle;
- the **hydrosphere** – the water on, in and around the Earth;
- the **atmosphere** – the gases surrounding the Earth; and
- the **biosphere** – the living things on the Earth.

See Figure 2

Although the detail of the chemistries of each of these areas is complex, we can make some very broad generalisations.

The chemistry of the lithosphere is essentially that of **giant ionic structures**.

The hydrosphere consists of s**mall molecules with dissolved ions**.

The atmosphere is made up of **small molecules**.

The chemistry of the biosphere is based on that of **long chain polymers**.

This article will concentrate of the chemistry of the hydrosphere but it will also look at how this interacts with the other spheres.

Q1.

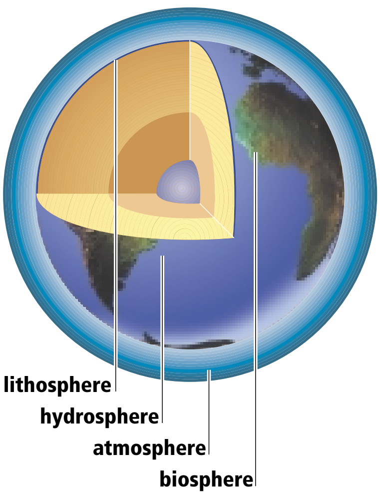
a) Explain what is meant by the terms giant ionic structure, small molecule and long chain polymer. You will probably need to draw diagrams to help your explanation. For each category, give an example of a substance with that structure.

b) In a substance made up of small molecules, what type of bonding occurs

(i) between the atoms within the molecule?

(ii) between the molecules themselves?

c) Explain why substances with giant structures and substances with long chain polymeric structures are solids while those made up of small molecules are liquids or gases.



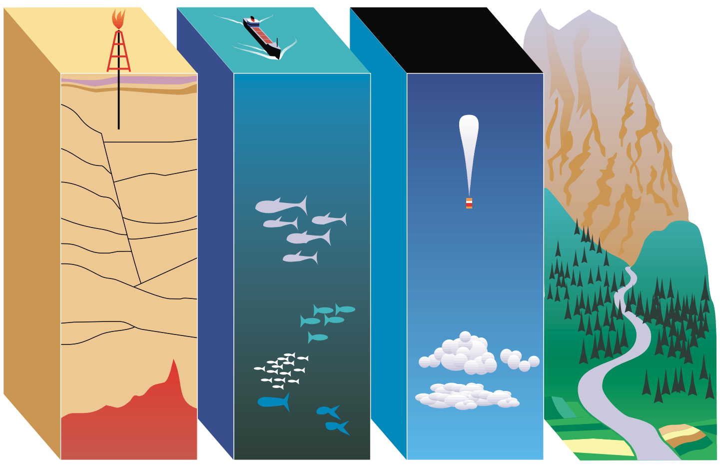


Figure 2 The Earth's four spheres

The hydrosphere – facts, figures and estimates

The total mass of water on the Earth is about 1.5 x 10^{18} tonnes. (10^{18} is a shorthand way of writing 1000 000 000 000 000 000 – one followed by 18 zeros, so 1.5 x 10^{18} could be written as 1500 000 000 000 000 000). Many of the quantities we will talk about when dealing with the hydrosphere can conveniently be expressed in units of 10^{18} tonnes. The prefix 'exa' is used to signify 10^{18} in the same way that 'kilo' means 10^3 and 'mega' 10^6, so the mass of water on the Earth could be referred to as 1.5 exatonnes.

For comparison, the mass of the Earth is about 6 x 10^{24} tonnes, or 6000 000 exatonnes.

95.7% of this water is found in the oceans, 4.1% in rocks and soil, 0.2% as ice, lakes and rivers and 0.001% in the atmosphere.

The likely source of all this water is from the gases that were released by volcanoes in the first 500 million years after the formation of the Earth. To put this in context, the Earth is about 4.5 billion (4.5 thousand million, *ie* 4.5 x 10^9) years old. This source of water seems likely because 70% of gases ejected from present day volcanoes consist of water vapour.

Perhaps surprisingly, no one knows for certain where this water came from originally. Possibly the answer will be found as we explore other planets, by unmanned probes as we are doing now, and later by manned expeditions.

Q2. Use the percentages above to work out the actual masses of water in:

a) the oceans,

b) rocks and soil,

c) ice, lakes and rivers,

d) the atmosphere.

Use units of exatonnes.

The water cycle

Although the proportions of water in the oceans, soil, ice, rivers and atmosphere remain more or less constant, the water is not static. It is estimated that every year, 0.000 42 x 10^{18} tonnes of water circulate around the water cycle, Figure 3. That is, it evaporates from the oceans to form water vapour in the atmosphere and then condenses to fall as rain, snow or hail, collectively called precipitation. It has been calculated that the average time that a molecule of water remains as vapour in the atmosphere between evaporation and precipitation is a mere 12 days.

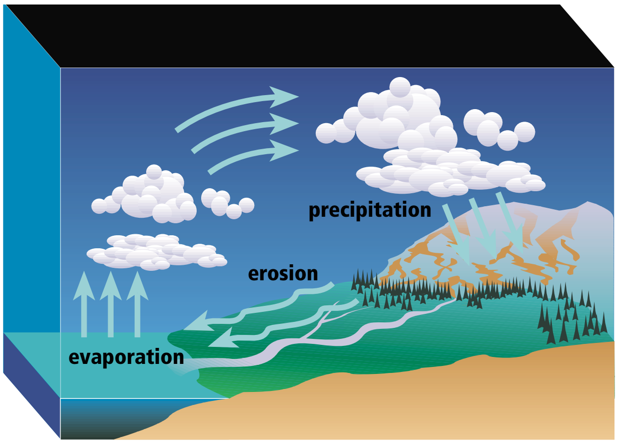


Figure 3 The water cycle

After falling as rain or snow, water returns to the oceans via streams and rivers. In doing this it carries weathered and eroded material from the Earth's crust into the oceans. Each year, 8 x 10^{12} tonnes of material is transported from the Earth's crust into the oceans. About two-thirds of this is insoluble (rocks, pebbles, sand, silt *etc*) and the rest is in solution.

The ions in seawater

Everyone knows that the sea is salty. Common salt is sodium chloride. It exists in solution as separate hydrated sodium ions (Na^+(aq)) and hydrated chloride ions (Cl^-(aq)). Dissolved ions are independent, and we cannot say that a particular ion is part of a particular compound. In fact the sodium and chloride ions that make the sea salty almost all came from different sources – virtually none came from solid sodium chloride that dissolved. So it is better to think about the ions dissolved in the sea, rather than different compounds.

Tables 1 and 2 show the ions dissolved in the sea.

Q3. To break up a giant ionic structure into separate ions, ions of opposite charge have to be pulled apart – a process which requires an input of energy. Explain how it is that many ionic compounds, such as sodium chloride, dissolve in water with little energy change. You may need to include in your answer an energy level diagram and a diagram to show the part played by water molecules.

In fact, since sodium (Na^+) is by far the most common positive ion and chloride (Cl^-) by far the most common negative ion, it is not unrealistic to say that the sea contains sodium chloride.

Table 1 The twelve most common ions in the sea

Ion	Concentration / mg dm^{-3}	% by mass of the total dissolved solids	Concentration / mol dm^{-3}
Chloride, Cl^-	19 000	55.04	0.535
Sodium, Na^+	10 500	30.42	0.457
Sulfate(VI), SO_4^{2-}	2 655	7.69	0.028
Magnesium, Mg^{2+}	1 350	3.91	0.056
Calcium, Ca^{2+}	400	1.16	0.010
Potassium, K^+	380	1.10	0.009 7
Carbonate, CO_3^{2-}	140	0.41	0.002 3
Bromide, Br^-	65	0.19	0.000 81
Borate, BO_3^{3-}	20	0.06	0.000 34
Silicate, SiO_3^{2-}	8	0.02	0.000 11
Strontium, Sr^{2+}	8	0.02	0.000 09
Fluoride, F^-	1	0.003	0.000 05

Table 2 The most common ions in the sea arranged as positive and negative ions

Positive ions	Concentration / mol dm^{-3}	Negative ions	Concentration / mol dm^{-3}
Sodium	0.457	Chloride	0.535
Magnesium	0.056	Sulfate(VI)	0.028
Calcium	0.010	Carbonate	0.002 3
Potassium	0.009 7	Bromide	0.000 81
Strontium	0.000 09	Borate	0.000 34
		Silicate	0.000 11
		Fluoride	0.000 05

Q4. Look at Tables 1 and 2

a) From which two groups in the Periodic Table do all the metal ions come? Suggest why this is so.

b) Use the charges of the ions in the table to work out the formulae of the following compounds:

(i) potassium bromide
(ii) strontium fluoride
(iii) sodium silicate
(iv) strontium carbonate

c) The relative atomic mass of chlorine is 35.5. Do a calculation to confirm that a concentration by mass of 19 000 mg dm^{-3} of chloride ions is the same as a concentration of 0.535 mol dm^{-3}.
1 mg is 1/1000 g.

d) Which ion, Na^+, or Cl^-, is in excess in seawater? Hence what is the effective concentration of sodium chloride in seawater?

e) What is the maximum mass of sodium chloride that could be extracted from 1 dm^3 of seawater?

Where do these ions come from?

The positive ions in seawater are all metal ions, and all come from the weathering of minerals in the Earth's crust. The common negative ions (except for silicate) are derived from simple molecules, and most of them probably came originally from the atmosphere. For example, sulfate(VI) ions are derived from sulfur dioxide by reaction with oxygen and water in the atmosphere:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

The H_2SO_4 exists in solution as the ions H^+ and SO_4^{2-}.

Weathering mainly affects the continental crust of the Earth (*ie* dry land). This is made up mostly of silicates and aluminosilicates of metals in Groups 1 and 2 of the Periodic Table and of silicates and aluminosilicates of iron. The crust also contains carbonates of these metals. These are present in smaller amounts but weather more rapidly.

Q5. a) What elements are present in:

(i) the silicate ion?
(ii) the aluminosilicate ion?

b) Explain how the names tell you what elements are present.

Chemical weathering is the action of water that contains acids on metal silicates and carbonates. Natural water is usually acidic because of its reaction with carbon dioxide, in the atmosphere and in soil, to form carbonic acid, H_2CO_3, which dissociates to produce H^+ ions in aqueous solution.

Q6. Write equations for the reaction of water with carbon dioxide to form carbonic acid and for the dissociation of carbonic acid.

The atmosphere also contains smaller amounts of sulfuric(VI) acid and nitric(V) acid produced when oxides of sulfur and nitrogen respectively react with water in the atmosphere. The concentrations of these acids in rainwater are increasing at present because of the activities of humans.

Q7. Explain how human activities are responsible for producing sulfur oxides and nitrogen oxides in the atmosphere.

Some compounds dissolve as acidic rainwater percolates through the soil and underlying rocks, and the dissolved ions are eventually washed into the sea. This is where most of the dissolved metal ions in the sea have come from.

However, the Earth's crust does not contain many compounds that contain fluoride, chloride, bromide, sulfate(VI) and borate ions. Since these are found in seawater, they must have come from another source. It is probable that they have come from gases produced by volcanoes. These gases then dissolved in rainwater.

So the salt (sodium chloride) dissolved in seawater has come from two sources – the sodium ions directly from the Earth's crust and the chloride ions from volcanic gases.

Is the sea getting saltier?

The simple answer to this is 'no', we believe that the oceans reached their present degree of saltiness (on average 3.5% of dissolved ions) quite rapidly (compared with the age of the oceans) and that they have maintained the same degree of saltiness for a very long time.

VARIATIONS IN THE SALTINESS OF THE SEA

Although on average the sea contains 3.5% of dissolved solids, there are considerable variations from place to place, see Table 3 and Figure 4.

Table 3
The saltiness of different seas

Location	Dissolved solids / %
Open ocean	3.5
Mediterranean Sea	3.9
Red Sea (northern end)	4.1
Dead Sea	27.0

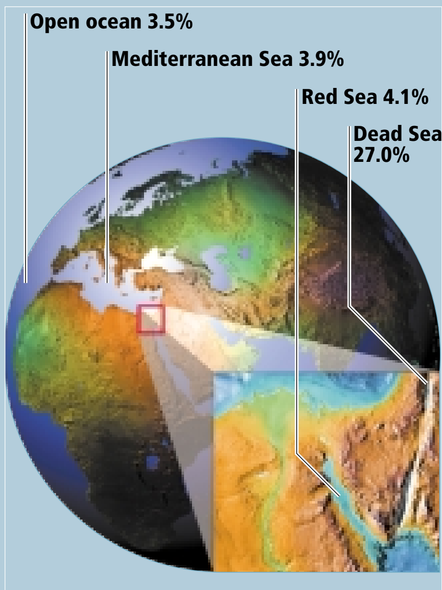


Figure 4
World map showing location of the sea areas shown in the table.

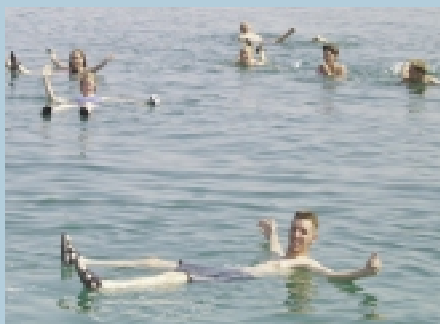


Figure 5
The Dead Sea is so salty that floating is easy.

Q 8. What sort of climates do the Mediterranean Sea, the Red Sea and the Dead Sea have? What sort of geographical surroundings do they have? You could use an atlas, CD-ROM or an internet search to help you find this information. Suggest why these seas (especially the Dead Sea) are saltier than the open ocean.

Maintaining the composition of seawater

Since rivers are transporting around 2.5×10^{12} tonnes of dissolved material into the sea each year, this means that dissolved ions must be being removed at the same rate to keep the composition of seawater the same. The ways in which ions are removed from seawater include:

Evaporation

This takes place especially in hot, dry climates where the sea is shallow and enclosed. Solid deposits of salts such as rock salt (sodium chloride, NaCl) and gypsum (calcium sulfate(VI), $CaSO_4$) are formed.

Q9. What ions are removed from seawater when a deposit of

a) rock salt
b) gypsum
is formed?

Precipitation

If the concentrations of the ions that make up a particular compound become too great, that compound will come out of solution and form a solid precipitate. For example calcium ions and carbonate ions combine together to form insoluble calcium carbonate (limestone):

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

Q10. Describe a simple test to show that a fossil sea shell contains a carbonate.

Biochemical

Living things in the sea may remove ions from seawater for a variety of purposes. The shells of sea creatures are made from calcium carbonate, as is coral. A number of organisms concentrate ions from seawater, sometimes by a factor of 10^5 or more. Some examples include:

- **sea squirts** which concentrate vanadium;
- other **tunicates** (creatures that feed by filtering seawater) which concentrate niobium;
- **oysters** which concentrate zinc (some people believe that zinc is the reason that oysters have their supposed aphrodisiac effect);
- **lobsters** which concentrate copper; and
- **shellfish** which concentrate mercury.

The last example was the cause of a tragedy at Minamata in Japan. Here, industrial waste containing mercury was discharged into the sea. Once diluted by the seawater, the mercury concentration was quite low, but it got into the following food chain:

algae → shellfish → fish → humans

eventually causing a number of deaths of humans as well as birth defects.

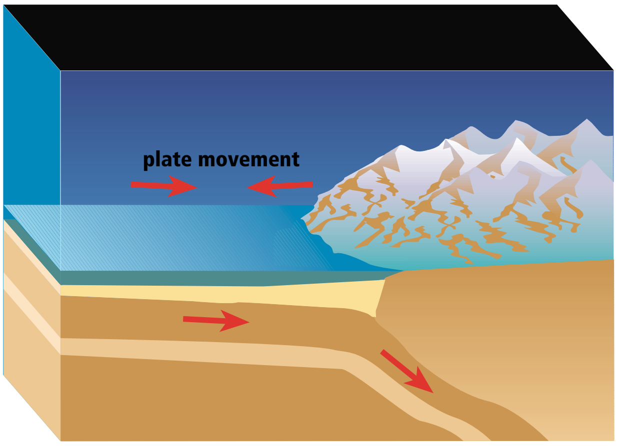


Figure 6 Subduction

Tectonic

In some places below the sea bed, the margins of tectonic plates are moving towards each other and one plate slides below the other – a process called subduction, see Figure 6. During this process, seawater is dragged into the Earth's crust.

Trace elements in seawater

Small amounts, called trace amounts, of all the other elements are present in seawater many of them in tiny concentrations – less than one millionth of that of sodium. These concentrations have been measured by looking at the light given out when they are heated in a high temperature flame. This is a variation on the flame test method that you might have used to identify metals from the colours they produce in flames – orange-yellow for sodium, green for copper *etc* – and is called Flame Emission Spectrophotometry – see Box.

Gold in seawater

Even gold compounds are present dissolved in seawater. The concentration of gold is 0.000 004 mg dm^{-3}. This may not sound much, but this means that there are four millionths of a gram of gold in a tonne of seawater and 5.6 million tonnes of gold in the whole of the Earth's oceans!

Not surprisingly, chemists have tried to extract gold from seawater. Perhaps the most famous attempt was that by the German chemist Fritz Haber, (who also developed the process for making ammonia that is named after him). Haber intended to use the money he hoped to make to help pay off Germany's debts resulting from the First World War. However, the scheme failed.

FLAME EMISSION SPECTROPHOTOMETRY

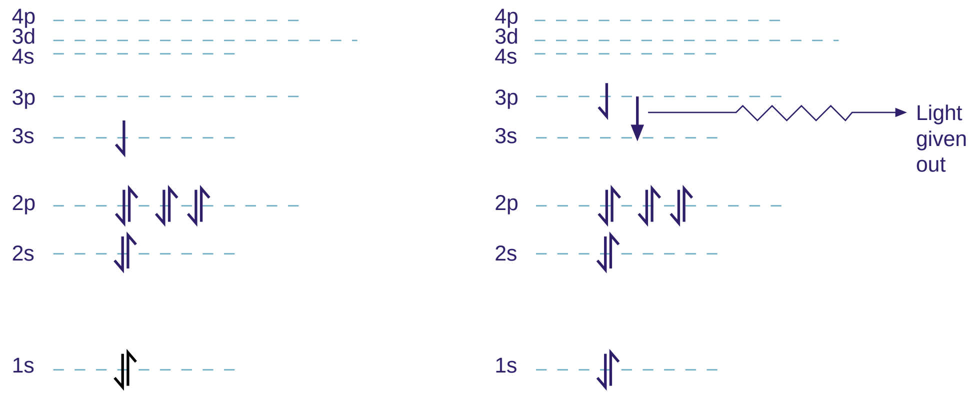
One way of measuring small concentrations is by a technique called Flame Emission Spectrophotometry. The electrons in atoms exist in particular energy levels called orbitals. The spacing of these levels is different in every element. Normally the electrons in an atom are found in the lowest possible levels – this is called the ground state of the atom. Heating the atom to a high temperature will supply the energy to move one or more of the electrons into orbitals of higher energy than normal - this is called an excited state of the atom. The electrons in an excited atom then drop back to the lower levels of the ground state. As each one does so, it gives out an amount of energy, E, equal to the difference in energy between the two levels, see Figure 8 below. This energy is given out in the form of electromagnetic radiation whose frequency, ν, is given by the equation

Figure 7
Flame emission spectrophotometer
(photograph by courtesy of Pekin Elmer Ltd)

$E = h\nu$

where h is Planck's constant (6.6×10^{-34} Js).

This radiation is normally in the visible or ultraviolet regions of the electromagnetic spectrum.



(a) The ground state of sodium

(b) An excited state of sodium. The light given out when the electron falls back from 3p to 3s is in the yellow region of the spectrum and is the reason that sodium gives a yellow flame.

Figure 8 The energy levels in the sodium atom

Because each element has a unique set of electronic energy levels, every element has its own pattern of frequencies that it gives out after being excited. This can be used to identify the element. By comparing the intensity of the radiation with that from a sample of known concentration, the concentration of a particular element in, say, seawater can be measured. With this technique, concentrations of the order of 10^{-8} mol dm^{-3} (depending on the element) can be measured.

Q11. Look at Figure 8 above. The yellow light given out when the electron in level 3p of the excited state falls back into level 3s has a frequency of 5.08×10^{14} s^{-1}.

a) Use the equation $E = h\nu$ to calculate the energy gap between levels 3p and 3s in sodium.

b) Your answer to (a) will be in J / atom. What does this correspond to in kJ mol^{-1}? (Take the Avogadro constant to be 6×10^{23} mol^{-1}.)

c) Compare your answer with the value of a typical bond energy. Does your answer seem reasonable?

Figure 9
Salt lagoons in France

GETTING A FEEL FOR THE FIGURES

1 cm^3 of water has a mass of 1 g, so 1 m^3 of water has a mass of 100 x 100 x 100 = 1000 000 g, which is 1000 kg or 1 tonne. The water in an average bath has a mass of about one-fifth of a tonne.

Q12. The price of gold is about £5000 kg^{-1}. (The price of gold varies, you could look up the current price in a newspaper, Ceefax or on the internet.)

a) What is all the gold in the oceans worth?

b) Use the figures above to work out what the gold in a bath of seawater would be worth.

Q13. Suggest what problems would be found when trying to extract gold from seawater.

Q14. Entropy, ΔS, is a measure of the disorder of chemical systems.

a) What can be said about the entropy change, ΔS, of processes which occur naturally?

b) Which is larger, the entropy of a block of metallic gold or that of the same amount of gold present as a dilute solution of gold ions dissolved in water? What does this suggest about the feasibility of extracting gold from seawater?

Q15. Gold is present in seawater in the form of $AuCl_4^-$ ions.

a) What is the oxidation number of gold in this ion?

b) What is the oxidation number of metallic gold?

c) What type of reaction is required to convert $AuCl_4^-$ ions into metallic gold?

Useful materials from the sea

The dissolved ions in the sea form an essentially free source of materials to anyone with access to the sea.

Evaporation of seawater produces sodium and potassium chlorides. This is carried out mostly in hot countries where the heat of the Sun is used to evaporate the water (and there is little rain to re-dissolve the solid salt that has been produced). In some countries, such as Saudi Arabia, seawater is separated to provide pure water (for drinking etc) while the salts form a by-product.

Q16.

a) Explain why using the Sun's heat to evaporate seawater is commercially attractive.

b) Find out the main source of sodium chloride in the UK. What is the connection with seawater?

Treating seawater (which contains magnesium chloride) with an alkali such as calcium hydroxide forms a precipitate of magnesium hydroxide. This is used in the manufacture of magnesium metal.

Q17. Write the word and balanced symbol equations for the reaction of magnesium chloride with calcium hydroxide.

Bromine is made by reacting seawater, which contains bromide ions, with chlorine.

Q18.

a) Write an equation for the reaction of chlorine with bromide ions.

RS•C

b) Work out the oxidation numbers of all the species involved before and after the reaction. Which species is the oxidising agent?

c) Given the following values of $E^{\ominus}$:

$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^{\ominus} = +1.07$ V

$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^{\ominus} = +1.36$ V

Work out $E^{\ominus}$ for the reaction of chlorine with bromide ions.

d) Using the sign and value of $E^{\ominus}$, state which of the following phrases best describes the equilibrium position for the reaction between chlorine and bromide ions:

(i) goes to completion;

(ii) does not occur;

(iii) an equilibrium well over to the right; or

(iv) an equilibrium well over to the left?

Acknowledgements

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Figure 1 courtesy of NASA.

Figure 5 courtesy of Eric Zeller **www.ewz.com**..

Figure 7 courtesy of Perkin Elmer Ltd.

Figure 9 Spectrum Photo Library.

Answers

1. a) Giant ionic structure. A three-dimensional array of positive and negative ions in which each positive ion is surrounded by negative ions and vice versa. The structure can extend without limit. See Figure 10.

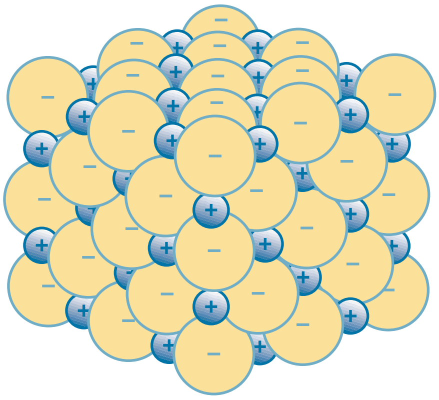

Figure 10 Part of a giant ionic structure

Small molecule. A group of a few atoms held together with covalent bonds.

Long chain polymer. A large molecule held together with covalent bonds and consisting of many smaller molecules (monomers) linked together.

b) (i) Covalent

(ii) Intermolecular forces such as van der Waals, dipole-dipole or hydrogen bonding, depending on the actual molecule.

c) Giant ionic and covalent structures are held together by ionic and covalent bonding respectively. These forces are stronger than the intermolecular forces that act between small molecules. In a long chain polymer, the sum total of the intermolecular forces between the molecules is greater than those between small molecules.

2.

a) 1.44 exatonnes

b) 0.062 exatonnes

c) 3×10^{-3} exatonnes

d) 1.5×10^{-5} exatonnes

3. The process of dissolving an ionic compound involves putting energy in to separate the ions (the lattice energy) but also involves hydration of the ions, a process in which energy is given out. In many cases, the two energy changes approximately cancel one another out as is the case with sodium chloride, see Figure 11.

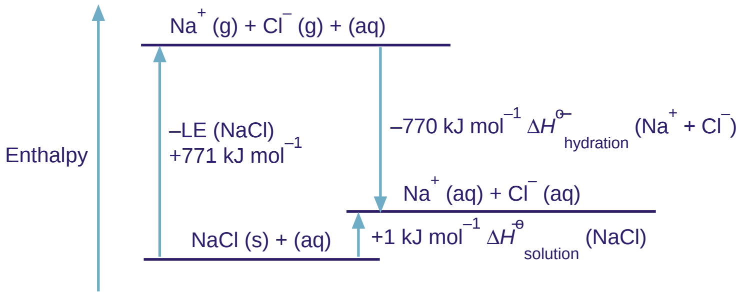

Figure 11
An enthalpy diagram for the dissolution of sodium chloride

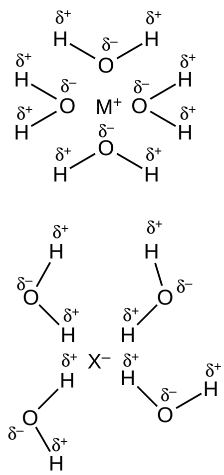

Figure 12
Hydration of cations, M^+, and anions, X^-, by water molecules

4.

a) Groups 1 and 2, because most simple compounds containing these ions are soluble in water.

b) (i) KBr (ii) SrF_2 (iii) Na_2SiO_3 (iv) $SrCO_3$.

c) 19 000 mg is 19 g This is 19/35.5 = 0.535 mol

d) The chloride ion is in excess, so the effective concentration of sodium chloride in seawater is determined by the sodium ion concentration, 0.457 mol dm^{-3}

e) 0.457 x 58.5 = 26.7 g

5.

a) (i) Silicon and oxygen

(ii) Aluminium, silicon and oxygen.

c) The ending 'ate' indicates the presence of oxygen.

6. $H_2O(l) + CO_2(g) \rightarrow H_2CO_3(aq)$

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

7. When wood and fossil fuels are burned, small amounts of sulfur that they contain are converted to sulfur dioxide. In high temperature burning processes, some of the oxygen and nitrogen in the air combine to form a mixture of nitrogen oxides.

8. They have hot, dry climates. They are largely surrounded by land. Water evaporates readily from these seas leaving behind greater than normal salt concentrations. As the seas are landlocked, or nearly so, little or no mixing with the oceans occurs.

9.

a) Sodium and chloride

b) Calcium and sulfate(VI).

10. Add some of the shell to a little dilute hydrochloric acid. Test any gas that comes off with limewater (calcium hydroxide solution). If a gas is produced that turns the limewater cloudy, then the shell contains carbonate.

11.

a) $\Delta E = h\nu$

$= 6.6 \times 10^{-34} \times 5.08 \times 10^{14}$

$= 3.35 \times 10^{-19}$ J per atom

b) $\Delta E = 201\ kJmol^{-1}$

c) This is comparable with a typical bond energy and is therefore reasonable.

12.

a) £ 2.8×10^{13}

b) A typical bath contains 0.2 tonne of water, which is 200 $dm^{3.}$

This contains 200 x 0.000 004 = 8×10^{-4} mg gold.

This is 8×10^{-10} kg of gold.

This is worth £4×10^{-6}. This is about 1/2000 p.

13. Vast quantities of water must be removed. The small quantities of gold compounds must be separated from much larger quantities of other compounds. The gold compounds must be reduced to metallic gold.

14.

a) The entropy increases.

b) The entropy of the block of gold is much smaller.
Energy will be needed to drive the process.

15.

a) +III

b) 0

c) Reduction

16.

a) The energy is essentially free.

b) Underground deposits in Cheshire and the North East of England. These were formed by the evaporation of ancient seas.

17. magnesium chloride + calcium hydroxide
→ magnesium hydroxide + calcium chloride

$MgCl_2(aq) + Ca(OH)_2(aq) \rightarrow Mg(OH)_2(s) + CaCl_2(aq)$

18.

a) $Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

b) Cl_2 0; Br^- -I; Br_2 0; Cl^- -I;

c) + 0.29 V

d) (iii) an equilibrium well over to the right.