

MODULE 3

water

Life as we know it depends upon water. Water makes up about 65% of the human body, or from 60 to 95% of the mass of all life forms. Without water no living organism could survive.

Fortunately water is the most abundant liquid on the Earth: 70% of the Earth's surface is covered by water. The huge quantities of water combined with its special properties mean that water has a great moderating influence on the climate of Earth.

Although there are huge quantities of water on Earth, 97% of it is salt water (mainly in oceans) and only 0.1% of the remainder (0.003% of the total) is available to humans and most other life forms; the rest is locked away in ice caps or glaciers or buried so deep as to be inaccessible. Fortunately water is effectively recycled through the environment by evaporation, transpiration, run-off and precipitation (rain and snow)—the so-called water cycle. Consequently this small proportion has been adequate to meet all our needs, though perhaps not indefinitely, if population, per capita usage and pollution continue to increase at current rates.

Water has some very special properties that make it so well suited to supporting Earth's life forms:

- Water is the only substance that can exist in the three states (solid, liquid and gas), under the normal range of environmental conditions.

(a)



(b)



(c)



- Water is one of few substances that expands on freezing (which has enormous consequences for aquatic organisms).
- Water is able to absorb comparatively large quantities of heat for relatively small temperature increases.
- Water is an excellent solvent for a wide range of substances, and so it is the medium in which many chemical reactions occur—both natural ones and human-induced ones.

In this module, then, Chapter 7 looks at these and other special properties of water, examines its structure and uses that structure to develop explanations for the properties. This will require an extension of the discussion of chemical bonding begun in Chapter 2 to include intermolecular forces. The nature of solutions of different classes of substances will also be discussed.

Chapter 8 discusses what are called precipitation reactions. It also introduces the idea of reversible reactions and chemical equilibrium. Calculations involving volumes and concentrations of solutions, and using quantities of heat, are included.



WATER IS SO ESSENTIAL

for our very existence as living organisms that we store it in dams for domestic and municipal use (d), obtain it in arid regions from underground artesian basins (a), and use it to irrigate crops (e). Water also shapes the landscape (c) and is a source of great aesthetic pleasure (b)



Water—‘uses’, properties and structure

IN THIS CHAPTER

The ‘role’ of water in the Earth
 Properties of water
 Structure of water and other simple compounds
 Polar covalent bonds
 Dipole–dipole forces
 Hydrogen bonds
 Explaining properties of water

Water as a solvent
 Aqueous solutions of ionic compounds
 Water of crystallisation and hydrates
 Aqueous solutions of molecular substances
 Molecular substances that react with water
 Solubility summarised

We saw in Chapter 3 that water was the major constituent of the hydrosphere and that it was present in significant amounts in the atmosphere (as vapour) and in the lithosphere. It is the only substance (element or compound) that exists naturally on Earth in the three physical states, solid, liquid and gas. Table 7.1 shows the states and proportions of water in various parts of the Earth.

TABLE 7.1 Water in the Earth

Zone of the Earth	Water present as	% of the zone that is water
atmosphere	vapour or tiny liquid droplets (in clouds)	0.5 to 5%
hydrosphere	liquid (with other substances dissolved in it) and solids (in polar icecaps)	>95% in oceans, >99% in polar icecaps, lakes and rivers
lithosphere	as ground water and chemically bound as ‘water of crystallisation’ in many minerals	<10% (though the lithosphere probably contains more water than the hydrosphere!)
living matter	liquid (with other substances dissolved in it)	between 60 and 90% overall, but 50 to 75% in humans (decreases with age), up to 95% in jellyfish

7.1 THE 'ROLE' OF WATER IN THE EARTH

On Earth water is:

- *a necessity for all types of living matter* in the form of:
 - a raw material (used in the chemical reactions that constitute life)
 - a solvent in which life processes (reactions) occur
 - a transport medium for bringing nutrients to cells and removing waste products
 - a thermal regulator by smoothing out sudden and large temperature variations
- *a habitat* for some life forms such as fish, algae and bacteria—the place where they live. Water bodies have the advantage that they show less fluctuation in temperature than do land and air masses.
- the major *weathering and eroding agent* of the Earth. When geological action produces mountains, water erodes them away over many millennia. There are three processes:
 - rain and rivers wash loose material to lower altitudes and eventually to the sea
 - glaciers cut a swathe from mountain tops through weaker rocks to the oceans, and
 - a freeze–thaw mechanism sees liquid water seep into small cracks in rocks, freeze and expand and so widen the crack until large fragments of rock break away.

The end result is a more gently sloping landscape with no steep mountains. Even in an old geological formation such as Australia, rain and rivers continue to erode the landscape, washing more and more earthy material into the ocean.

- *a natural resource for humans* to use:
 - for drinking, food preparation, washing and recreation
 - for irrigating crops and watering livestock
 - as a working fluid in electricity generating stations and as a coolant in them and in many industries
 - for generating electricity directly (hydro-electricity)
 - in industry as a reactant, solvent and cleaning agent, and for waste disposal and settling dust
 - as a mode of transport (ships, which are less important today with railways and aircraft)
 - for recreational purposes (swimming, boating, skiing) and for aesthetic enjoyment.

7.2 PROPERTIES OF WATER

The wide distribution and importance of water on Earth arise from its properties. Some of these, along with the comparable properties of several other liquids, are presented in Table 7.2. Some of the properties in this table need explanation.

Surface tension is a measure of the resistance of a liquid to increasing its surface area. The higher the value, the greater the tendency of the liquid to form a spherical drop rather than spread out as a thin film.

Viscosity is a measure of the resistance of a liquid to being poured or to flowing through a tube. The higher the viscosity, the less easily the liquid flows. Honey and motor oil have much higher viscosities than water.

Thermal conductivity was defined on page 103.

Specific heat capacity of a substance is the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (or by 1 Kelvin). It will be discussed in more detail in Section 8.11.

TABLE 7.2 Properties of water and other common liquids (density, surface tension, viscosity and thermal conductivity are for 20°C)

Liquid	Density (g/mL)	Melting point (°C)	Boiling point (°C)	Surface tension (mN m ⁻¹)	Viscosity (mPa s)	Thermal conductivity (J s ⁻¹ m ⁻¹ K ⁻¹)	Specific heat capacity (J K ⁻¹ g ⁻¹)
water	0.998	0	100	72.8	1.00	0.60	4.18
ethanol	0.785	-114.1	78.3	22.8	1.2	0.17	2.44
ethylene glycol	1.11	-15.6	198	47.7	19.9		2.39
glycerol	1.26	20.0	290.0	63.4	1490	0.29	2.38
acetone	0.785	-94.7	56.1	23.7	0.33	0.19	2.17
chloroform	1.48	-63.5	61.7	27.1	0.58	0.12	0.96
hexane	0.655	-95.3	68.7	18.4	0.33	0.13	2.26
mercury	13.5	-39	357	440	1.55	8.4	0.14

Melting and boiling points and density generally increase as molecular weight increases. Water has by far the lowest molecular weight of the compounds in Table 7.2, yet its melting and boiling points and densities are higher than those of most of the other liquids. Its surface tension and thermal conductivity are higher than for any other liquid (except mercury) and its viscosity is also quite high. The high *specific heat capacity* of water is one reason that oceans heat up and cool down more slowly than do land masses. In addition, water is one of very few substances that expand when they freeze (ice floats in water: for most substances the liquid sits on top of the solid).

It is clear then that water has some quite unusual properties. Let us see if we can find reasons for these in its structure.

Exercises

- To measure the densities of water and ice a group of students performed the following experiments. For water they pipetted volumes of water into a weighed beaker, then re-weighed the beaker and contents. Results, including the temperature of the experiment, are recorded below.



Mass of beaker before water added (g)	112.2	137.1	162.1	188.4
Volume of water added (mL)	25	25	25	25
Mass of beaker after addition of water (g)	137.1	162.1	188.4	213.2
Temperature of water in beaker (°C)	18.4	18.2	18.6	18.4

For ice they put water in a measuring cylinder to about the 50 mL mark, noted the volume and weighed the cylinder plus water. They then took an ice cube from a freezer and promptly added it to the contents of the measuring cylinder (taking care not to lose any water by splashing). They kept the ice cube submerged with a stiff wire and quickly noted the volume of the ice plus water. Finally, they weighed the cylinder plus contents again. They assumed that the temperature of the ice was that of the freezer, namely -4°C. The experiment was repeated several times. Results are given on the next page.

Volume of water in measuring cylinder (mL)	50	52	48	50
Mass of measuring cylinder plus water (g)	163.4	165.2	161.3	163.6
Volume of water plus ice (mL)	68	69	71	71
Mass of cylinder plus water plus ice (g)	179.5	181.4	182.5	183.8

- a** Calculate the density of ice or water from each experiment performed. Calculate the average densities of ice and water. Also state the range of densities for each substance. Is the difference between the densities of water and ice significant? Explain why or why not.
- b** What feature in these experiments was included to improve the reliability of the results? How could reliability be further improved?
- c** What would be the major sources of error in these experiments? Would these errors lead to the densities being consistently high or consistently low, or would they lead to just random fluctuations? Explain. How would you minimise the errors you have identified? Which of the densities would you consider to be the more accurate, that of water or that of ice? Explain.
- 2** A long graduated Pyrex glass tube (old burette sealed off at the 50 mL mark) was used for the following experiment. Exactly 40.0 mL of water was placed in the tube. The increase in mass was 39.92 g. With the open end covered to prevent evaporation, the tube and contents were placed in a coldroom at -2°C overnight. The water froze to ice. When inspected the next morning the ice had a volume of 43.5 mL. Calculate the density of water at room temperature and of ice at -2°C .
- 3** Use the data below to plot density of water against temperature. Draw a smooth curve through the points.

Temperature ($^{\circ}\text{C}$)	0	5	10	15	20	25
Density (g/mL)	0.9998	1.0000	0.9997	0.9991	0.9982	0.9970

- *a** Describe the way that the density of water varies with temperature.
- b** What is the significance of this variation in density for natural water bodies and aquatic life forms?
- 4** To determine the effect of ethylene glycol (commercial anti-freeze) upon the melting (freezing) point and boiling point of water, the following experiment was performed. Measured masses of ethylene glycol were dissolved in 1000 g quantities of water. Separate portions of each solution were used to measure the freezing and boiling points. Results are tabulated below.

Mass of glycol used (g)	100	200	300	450
Freezing point ($^{\circ}\text{C}$)	-2.9	-6.5	-10.5	-16.5
Boiling point ($^{\circ}\text{C}$)	100.7	102.0	102.9	104.2

- *a** Draw separate graphs of melting point and boiling point against mass of ethylene glycol. Draw smooth curves through the points and summarise how melting point and boiling point vary with mass of ethylene glycol present.
- b** If you wanted a solution to stay as liquid down to -6°C , what mass of ethylene glycol would you dissolve per 100 g water? At what temperature would this solution boil?
- c** Why is ethylene glycol added to cooling systems of motor cars?
- d** If a sample of pure water is boiled in an open beaker, the temperature remains constant throughout the process. However if a sample of water containing anti-freeze is similarly boiled in an open beaker, the temperature gradually increases during the boiling process. Explain these different observations.

7.3 STRUCTURE OF WATER AND OTHER SIMPLE COMPOUNDS

In Section 2.17 we saw that the water molecule had an oxygen atom covalently bonded to two hydrogen atoms; the electron-dot structure is reproduced in Figure 7.1. Some other simple covalent molecular compounds are ammonia, NH_3 , methane, CH_4 , and hydrogen sulfide, H_2S . Their electron-dot structures are also shown in Figure 7.1. Remember that the number of valence electrons on an atom is the group number from the Periodic Table, meaning 5 for N, 4 for C and 6 for S. Hence there are covalent bonds to 3 H atoms in ammonia, to 4 H atoms in methane and to 2 H atoms in hydrogen sulfide (to make up eight valence electrons around the central atom).

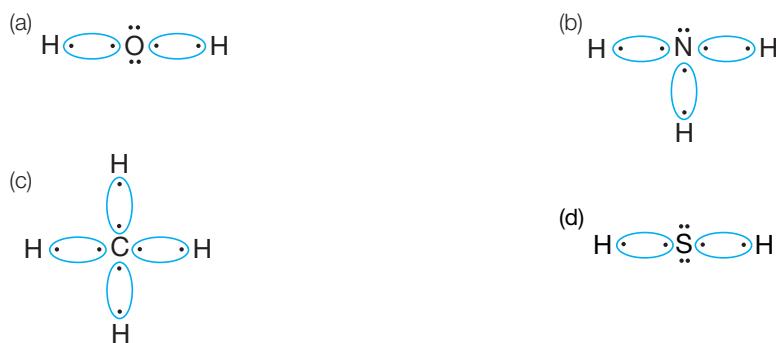


FIGURE 7.1
Electron-dot structures for
(a) water
(b) ammonia
(c) methane and
(d) hydrogen sulfide

Electron-dot structures do not tell us anything about the shape of molecules; they just tell us how valence electrons are arranged and how many covalent bonds are formed. The four molecules in Figure 7.1 have the shapes shown in Figure 7.2. By ‘shape’ we mean the geometrical arrangement of atoms in the molecule. Water and hydrogen sulfide have a bent shape with the $\text{H}—\text{O}—\text{H}$ and $\text{H}—\text{S}—\text{H}$ angles being about 100° . Ammonia has a pyramidal shape and methane is tetrahedral.

The melting and boiling points of these four substances are shown in Table 7.3. Methane, ammonia and hydrogen sulfide are gases at room temperature, while water is a liquid.

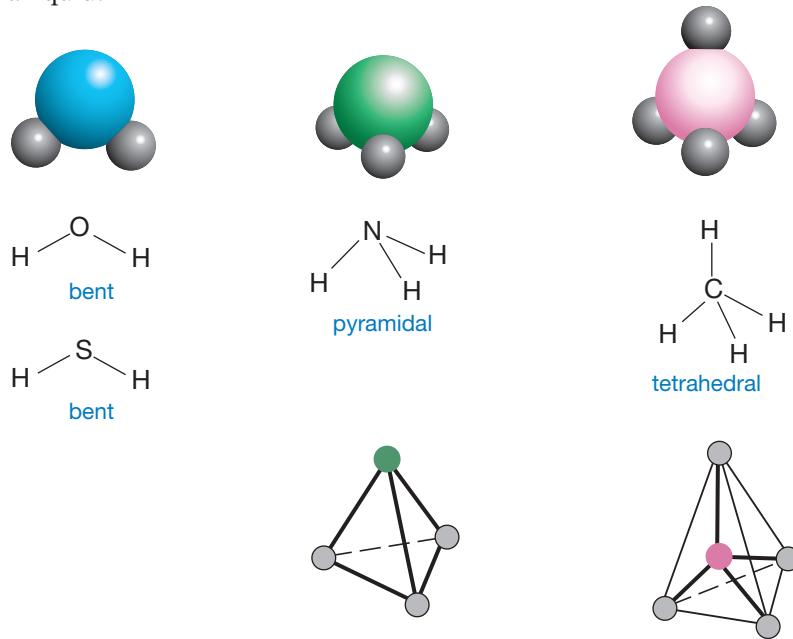


FIGURE 7.2
Shapes of the water,
ammonia, methane
and hydrogen sulfide
molecules

TABLE 7.3 Melting and boiling points for water, ammonia, methane and hydrogen sulfide

	H ₂ O	NH ₃	CH ₄	H ₂ S
Molecular weight	18	17	16	34
Melting point (°C)	0	-78	-183	-86
Boiling point (°C)	100	-33	-162	-60

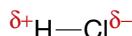
Although water, ammonia and methane have similar molecular weights, they have very different melting and boiling points—methane very low, ammonia quite low, and water much higher. Hydrogen sulfide has a higher molecular weight than water, so we should expect it to have higher melting and boiling points but in fact they are much lower.

Electron-dot structures do not explain the differing melting and boiling points of these compounds, because as we saw in Section 2.22 melting and boiling points depend upon the strength of intermolecular forces, not upon the strength of the covalent bonds within the molecules.

Before considering intermolecular forces we need an understanding of what are called polar covalent bonds.

7.4 POLAR COVALENT BONDS

When pairs of electrons are shared between identical atoms as in H₂, Cl₂ and N₂, they are shared very evenly. However in many **heteroatomic** molecules such as HCl, H₂O and NH₃, *the electron pairs are unevenly shared*: the electrons spend more time near one nucleus than the other. In hydrogen chloride, HCl, the shared pair of electrons spends more of its time near the chlorine atom than near the hydrogen atom. This means that the chlorine end of the molecule is slightly negative (more electrons on average around it than protons in the nucleus), while the hydrogen end is slightly positive. We write this as:



where δ (delta) means ‘small amount of’. These ‘delta charges’ are much smaller than whole electron or proton charges.

Covalent bonds in which the electrons are unequally shared are called **polar covalent bonds**.

The H—Cl bond above is a polar covalent bond. Similarly, the H—F, H—Br, H—I bonds are polar as are the O—H, N—H and S—H bonds.

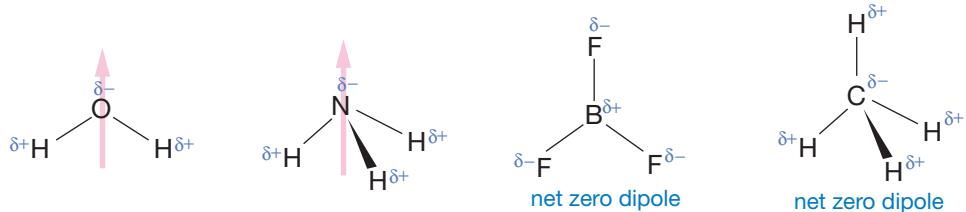
A pair of equal and opposite charges separated in space as in the H—Cl molecule is called a **dipole**. **Polar molecules** are molecules that have a net dipole.

Diatomeric molecules that have a polar covalent bond are polar molecules.

However for polyatomic molecules (more than two atoms), the presence of polar covalent bonds does not guarantee that the molecule will be polar. This is because two or more dipoles in the one molecule may cancel each other out. The shape of the molecule determines whether dipoles cancel out or add up to give a net dipole.

The two δ^- O—H δ^+ polar bonds in water combine to give a net dipole as shown in Figure 7.3. Similarly the three polar δ^- N—H δ^+ bonds in ammonia combine to give a net dipole (also in Figure 7.3). This makes water and ammonia polar molecules. In hydrogen sulfide also, the two polar bonds combine to produce a polar molecule.

Sometimes the shape of the molecule is such that the individual dipoles cancel out. Boron trifluoride, BF_3 , is a flat molecule—it has what is called a trigonal planar shape: the three bonds are at angles of 120° to one another in the one plane (Figure 7.3). Each bond is polar but the three cancel one another out, so that this molecule is non-polar. Contrast the effect of this planar shape with ammonia's pyramidal (non-planar) shape.



In the tetrahedrally shaped methane molecule, each of the four C—H bonds is slightly polar, but when they combine together, they cancel one another out. This means that methane is a non-polar molecule.

A particular covalent bond between two atoms will be polar if one atom has a greater electron-attracting power than the other. We saw in Section 6.5 that *electronegativity* measures electron-attracting power: electronegativity increases from left to right across the Periodic Table and decreases from top to bottom. For the common elements the order in decreasing electronegativity is:

$$\mathbf{F} > \mathbf{O} > \mathbf{N} \approx \mathbf{Cl} > \mathbf{Br} > \mathbf{C} \approx \mathbf{S} \approx \mathbf{I} > \mathbf{P} \approx \mathbf{H} > \mathbf{Si} \quad \dots (7.1)$$

Common polar bonds are therefore H—O, H—N, C—O and C—Cl, with the first-named atom in each bond being the positive end. Some non-polar bonds are N—Cl, C—S and P—H. The C—H bond is very slightly polar, but for all practical purposes we regard it as non-polar.

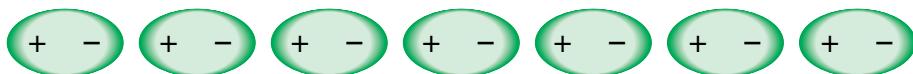
In summary, to decide whether a particular molecule is polar or not:

- use *electronegativities* to decide whether it contains any polar bond(s), then
- use the *shape* of the molecule to decide whether the polar bonds cancel out (to produce a non-polar molecule) or combine to produce a net dipole (polar molecule).

Whether a molecule is polar or not affects the strength of intermolecular forces.

7.5 DIPOLE–DIPOLE FORCES

Because polar molecules have positive and negative ends, they are able to line up so that the positive end of one molecule attracts the negative end of another molecule as in Figure 7.4. Therefore electrostatic attraction holds the molecules to one another more strongly than would be the case for non-polar molecules. These electrostatic attractions are called **dipole–dipole forces**.



Dipole–dipole forces are present in hydrogen sulfide, ammonia and water but not in (non-polar) methane. Hence intermolecular forces are stronger in the first three substances than in methane, and so those first three compounds have higher melting and boiling points than does methane.

There are intermolecular forces in methane—just as there were in bromine (also non-polar) in Section 2.22 (Figure 2.15). They are called **dispersion forces**.

FIGURE 7.3
Dipoles add up in water and ammonia but cancel out in boron trifluoride and in methane. The arrows point from the positive end to the negative end of the dipoles.

FIGURE 7.4
Dipole–dipole forces in polar covalent substances.

They are quite weak in substances with small molecules. There are always dispersion forces present. The combination of dipole–dipole forces plus dispersion forces is stronger than dispersion forces alone would be in that substance.

Dispersion forces will be discussed further towards the end of Section 9.9.

However, these dipole–dipole forces plus dispersion forces do not explain why the higher molecular weight hydrogen sulfide has lower melting and boiling points than do water and ammonia.

This is because there is another type of intermolecular force involved in water and ammonia, called hydrogen bonding.



Exercises

7.6 HYDROGEN BONDS

The third and strongest type of intermolecular force is what is called a hydrogen bond.

A **hydrogen bond** is a type of intermolecular force that involves a hydrogen atom bonded to an O, N or F atom in one molecule becoming attached to an O, N or F atom in a different molecule.

Water and ammonia display hydrogen bonding as shown in Figure 7.5.

O, N and F atoms have very strong electron-attracting powers—they are the three most electronegative elements (Section 6.5 and Table 6.7). This means that the bonding electrons in O—H, N—H and F—H bonds are strongly attracted

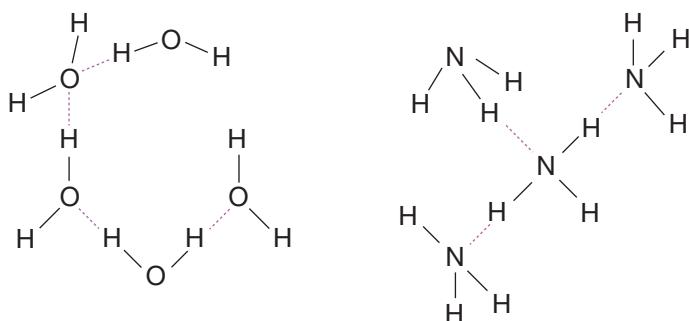


FIGURE 7.5
Hydrogen bonding in water and ammonia. Dotted lines are hydrogen bonds, solid lines are covalent bonds. The O atom of a water molecule can hydrogen bond to two other molecules, though for clarity this has been shown for only one of the molecules here.

to the O, N and F atoms respectively, giving those atoms significant negative charges with the H atom becoming positively charged. In addition, the small size of the H atom means that two adjacent molecules can get close together: the positive H atom, bonded to the O, N or F atom in one molecule, forms a strong attraction to an O, N or F atom on the adjacent molecule and so there is a strong attractive intermolecular force. This is shown schematically in Figure 7.6.

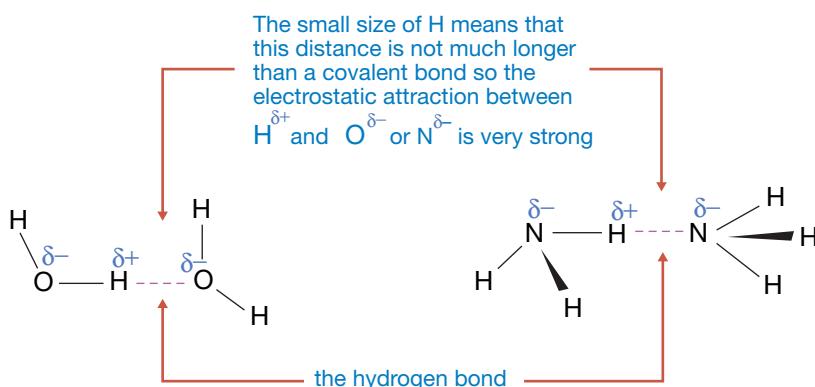


FIGURE 7.6
The hydrogen bond in more detail

Hydrogen bonds are much stronger than ordinary dipole–dipole forces. Their relative strength arises from the facts that the hydrogen nucleus (a bare proton only) is extremely small and that the F, O and N atoms are strongly electron-attracting.

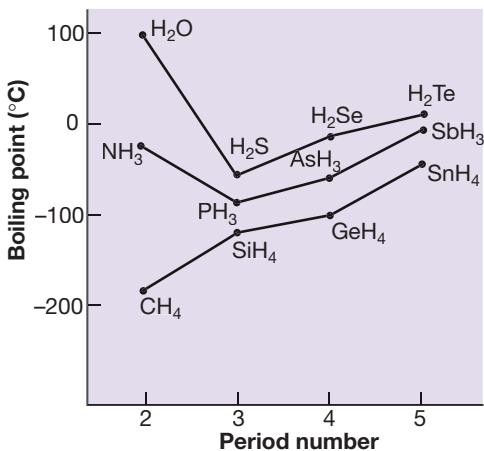
The strength of a hydrogen bond is typically about one-tenth that of a normal covalent bond.

Hydrogen bonding explains why water and ammonia in Table 7.3 have much higher melting and boiling points than the much higher molecular weight compound hydrogen sulfide.

The effect of hydrogen bonding is illustrated in Figure 7.7. Normally when we compare sets of similar compounds, we find that boiling point increases as we go down a group of the Periodic Table; that is, for similar compounds boiling point increases as molecular weight increases. This is what we observe for the hydrides of carbon, silicon, germanium and tin. However, for the hydrides of the nitrogen and oxygen groups, we find that the boiling point of the lightest member is anomalously high. This is due to hydrogen bonding.

While H_2O and NH_3 are the classic examples of substances that display hydrogen bonding, it also occurs in many other compounds in which hydrogen is attached to O or N; some examples are hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), methanol (CH_3OH) and other alcohols, carbohydrates (sugars), amino acids and proteins.

FIGURE 7.7
Boiling points for hydrides of Groups 4, 5 and 6



The relative strengths of the various intermolecular forces are summarised in Table 7.4.

TABLE 7.4 Strengths of intermolecular forces in small molecules^a

(relative to a covalent bond arbitrarily set at 100)

hydrogen bond	10
dipole–dipole forces plus dispersion forces	1 to 3
dispersion forces alone	0.1 to 1

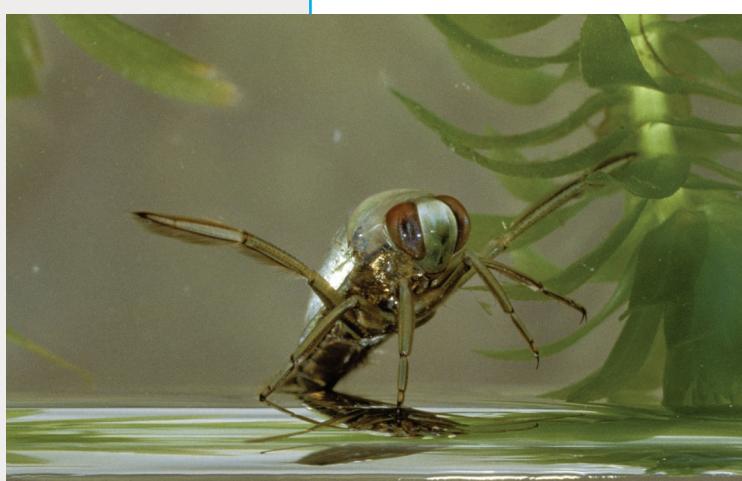
(numbers are very approximate—chosen to illustrate order of magnitude only)

^a When the total number of electrons becomes large—say over 100—dispersion forces can be much stronger than indicated here (e.g. in I₂ and C₁₆H₃₄).

Hydrogen bonding has explained the high melting and boiling points of water: it is also the key to understanding many other properties of water.

7.7 EXPLAINING OTHER PROPERTIES OF WATER

Other properties of water are also consequences of hydrogen bonding.



Surface tension allows insects to walk on water

Surface tension

A molecule well inside a liquid experiences intermolecular attractions from other molecules all around it. A molecule in the surface layer of a liquid experiences intermolecular forces only from molecules below and beside it; there are no molecules (or attractions) above it. This is shown in Figure 7.8. These unbalanced forces on surface molecules result in a downward or inward force acting on surface molecules. This is why liquids display surface tension.

The stronger the intermolecular

forces, the greater will be the surface tension of the liquid. Water with its strong hydrogen bonding has strong intermolecular forces and so a high surface tension.

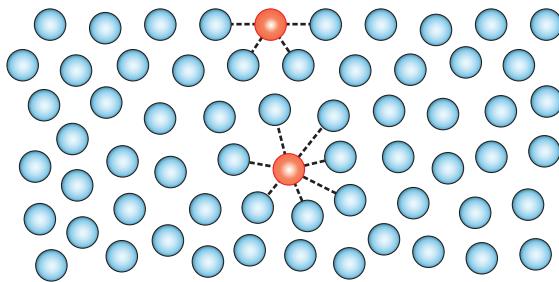


FIGURE 7.8
Unbalanced forces on surface molecules give rise to surface tension

Viscosity

As stated in Section 7.2, viscosity measures the resistance of a liquid to flow through a tube. Motor oils, syrup, honey (particularly when cold) and glycerol have very high viscosities (flow very sluggishly); water, ethanol and octane (petrol) have relatively low viscosities (flow very easily).

Flowing involves molecules moving over other molecules. There are two factors that affect the ease with which molecules can move over one another. One is the size and complexity of the molecules themselves. Motor oil has a high viscosity because it contains very long floppy molecules that get tangled up and so do not flow easily. The other factor is intermolecular forces. The stronger the forces of attraction between pairs of molecules the more resistance there is to flow. Syrup and honey are solutions of sucrose, glucose and fructose in water. All these four compounds (and glycerol as well) contain O—H groups and so there is extensive hydrogen bonding between the sucrose, glucose and fructose molecules and water in the solutions and between pairs of glycerol molecules. This gives rise to the high viscosity of syrup, honey and glycerol.

Compared to the above liquids water seems to have a low viscosity (it pours easily); however when we compare it with many other pure liquids (such as the ethanol, acetone, chloroform and hexane of Table 7.2), its viscosity is comparatively high (by a factor of about two to five). Water has this relatively high viscosity because there is extensive hydrogen bonding involving all the atoms of the molecule.

Water with its strong hydrogen bonding has a much higher resistance to flow than its small molecular size might suggest.

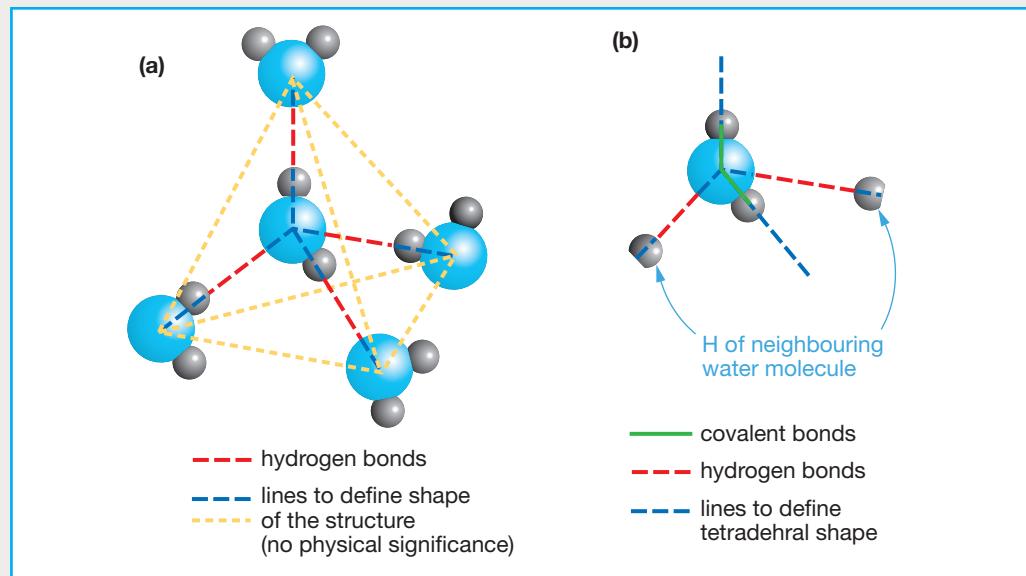
Expansion on freezing

As noted in Section 7.2, water is one of very few substances which expand when they freeze. This is also due to hydrogen bonding.

Hydrogen bonding is much more directional than simple dipole–dipole forces. In ice nearly all the molecules are hydrogen bonded to one another. Each oxygen atom has four H atoms around it—two that are covalently bonded to it (to make its molecule) and two (from other molecules) that are held to it by hydrogen bonding. These four H atoms are tetrahedrally arranged around the central O atom, similarly to the four H atoms around the C atom in methane. This tetrahedral arrangement, illustrated in Figure 7.9, gives a fairly open structure to ice. When ice melts, the individual water molecules are able to move about more vigorously and so they break up some of the hydrogen bonding. A consequence of less hydrogen bonding is that the molecules are often considerably closer to one another. This means that water has a higher density than ice (a given number of molecules, that is, a given mass, occupies a smaller volume).

FIGURE 7.9

(a) The tetrahedral arrangement of four water molecules around a central water molecule in ice. This arrangement exists around every water molecule; it gives ice a more open structure than water. (b) The tetrahedral arrangement of bonds (two covalent, two hydrogen) around the O atom in each water molecule. This tetrahedral arrangement is better seen by constructing a three-dimensional model.



Exercises

- 9** Use the data below to plot boiling point against period number of the Periodic Table for each of the two series of compounds. Draw a curve or series of straight lines, whichever is appropriate, through the points of each set. Identify any anomalous compound, explaining why you think it is anomalous. Offer some explanation for its ‘behaviour’.

Compound	CH_4	SiH_4	GeH_4	SnH_4
Boiling point (°C)	-162	-112	-88	-52
Compound	HF	HCl	HBr	HI
Boiling point (°C)	19	-85	-67	-35

- 10** The table below presents melting points of hydrides from three groups of the Periodic Table. On the one graph plot melting point against period number for each set of compounds. Draw curves or series of straight lines through the points for each set. Does this graph present any evidence for hydrogen bonding and, if so, for which compounds? Explain fully.

Compound	CH_4	SiH_4	GeH_4	SnH_4
Melting point (°C)	-183	-185	-165	-150
Compound	NH_3	PH_3	AsH_3	SbH_3
Melting point (°C)	-78	-133	-116	-88
Compound	H_2O	H_2S	H_2Se	H_2Te
Melting point (°C)	0	-86	-64	-49

- 11** In which of the following pure liquids would you expect there to be hydrogen bonding?
- a** phosphorus trichloride **d** dichloromethane, CH_2Cl_2
b hydroxylamine, HONH_2 **e** bromomethane, CH_3Br
c tetrafluoromethane, CF_4 **f** nitrous acid, HONO

For those with hydrogen bonding, draw diagrams which show it. (Include at least three molecules.)

- 12** In Exercise 3 you saw that the density of water passed through a maximum value at 5°C (actually with more extensive data it is at 4°C). Suggest an explanation for this.

7.8 WATER AS A SOLVENT

Recall from Section 1.12 that *a solution is a homogeneous mixture*. Common solutions are salt, sugar or ethanol in water or iodine in hexane. When one component is present in a much larger amount than the other(s), we call the major component the *solvent* and the other(s) the *solute(s)*.[†] We say that the *solvent* dissolves the *solute* to form a *solution*.

Water is the most widely used solvent both by humans and by nature. In all living matter most of the chemical reactions responsible for ‘life’ occur in water solutions, or *aqueous solutions* as they are called. Water dissolves nutrients from soil and carries them in solution to living cells. Water also carries waste products away from cells (again in solution).

Many drinks that humans use are aqueous solutions, as are many household products such as bleaches, disinfectants, cleaning agents and some medicines. Industry uses aqueous solutions of acids and alkalis and often makes or extracts products from aqueous solutions. For example, aqueous solutions are involved in the production of chlorine, sodium hydroxide and common fertilisers, and in the extraction of uranium, and purification of copper.

The nature of the solution formed depends upon the type of substance dissolved in the solvent.

7.9 AQUEOUS SOLUTIONS OF IONIC COMPOUNDS

Most ionic compounds are soluble in water.

When ionic substances such as common salt (sodium chloride, NaCl), baking soda (sodium hydrogen carbonate, NaHCO₃), or Epsom salts (magnesium sulfate, MgSO₄) dissolve in water, they break up into their basic structural units which are *ions*. These ions then move freely and independently of one another through the solution, as shown in Figure 7.10.

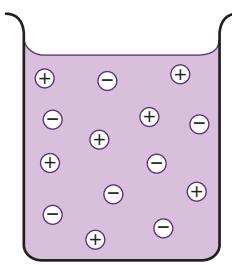


FIGURE 7.10
A solution of an ionic substance (such as sodium chloride). The separated ions are dispersed throughout the whole solution. Their size is greatly exaggerated in this diagram

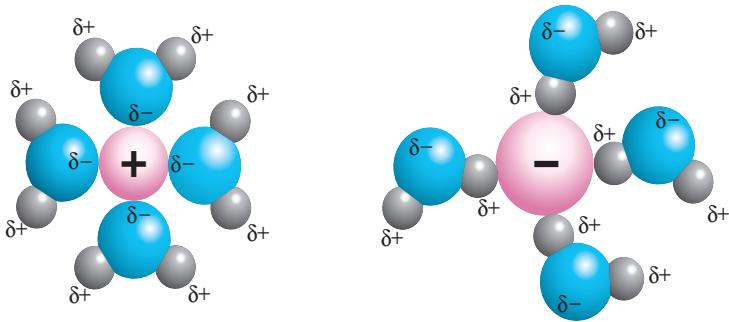
The reason why most ionic compounds dissolve in water is that polar water molecules have a strong attraction for charged ions: the negative end of the water molecule (the O atom) attaches to positive ions—several water molecules per ion—while the positive ends (the H atoms) attach to negative ions—again several molecules per ion. We say that the ions become *hydrated*. Figure 7.11 shows this. If the attractive forces between water and the ions are stronger than the attractive forces between the positive and negative ions, then the ionic solid dissolves in water.

Water is called a **polar solvent**. This is because it consists of polar molecules.

[†] In some solutions two components are present in comparable amounts. Examples are gin and whiskey (nearly 50% of each water and ethanol) and brass (a solid solution of 45% to 65% copper with 55% to 35% zinc.) For such solutions it is inappropriate to use the terms solvent and solute.

FIGURE 7.11

Polar water molecules readily attach to ions. This is why most ionic solids are soluble in water



7.10 WATER OF CRYSTALLISATION AND HYDRATES

Sometimes ionic substances crystallise from aqueous solution with the molecules of water still attached to the ions.

Water that becomes bound to a pure substance during crystallisation is called **water of crystallisation**.

Copper sulfate crystallises with five water molecules per ion pair (formula unit). We write this as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The $5\text{H}_2\text{O}$ tells us that there are five water molecules attached to each copper sulfate ion pair. A dot is used to separate the compound from its water of crystallisation. Some other substances that crystallise with water of crystallisation are:

sodium carbonate (washing soda)	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
magnesium sulfate (Epsom salts)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
calcium sulfate (gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
barium hydroxide	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

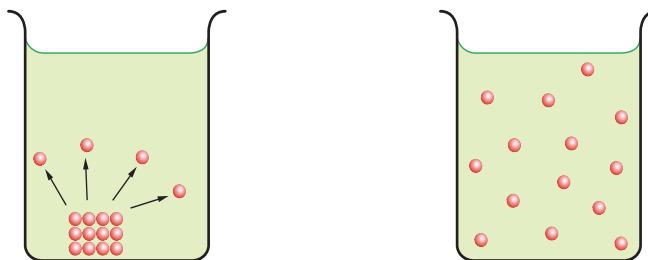
Salts that contain water of crystallisation are called **hydrates**. The term **anhydrous** is used to describe forms of salts that do not contain water of crystallisation. Anhydrous copper sulfate is CuSO_4 , while hydrated copper sulfate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Anhydrous barium hydroxide is $\text{Ba}(\text{OH})_2$; hydrated barium hydroxide is $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

The name for hydrated copper sulfate is copper sulfate pentahydrate, penta meaning five. Similarly $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is called barium hydroxide octahydrate. The other common prefixes are di- for two, tri- for three, tetra- for four, hexa- for six, hepta- for seven and deca- for ten. So the other compounds in the above list are sodium carbonate decahydrate, magnesium sulfate heptahydrate and calcium sulfate dihydrate.

7.11 AQUEOUS SOLUTIONS OF MOLECULAR SUBSTANCES

Most molecular substances such as hexane, kerosene, paraffin wax and chloroform are insoluble in water. However, some very important molecular substances, such as sugars, are soluble.

When a substance such as sugar (sucrose) or urea (a common fertiliser) dissolves in water, the crystals of the solid break up and disperse throughout the solvent, and they break up right down to the molecular level. So a solution of sucrose or urea in water consists of individual sucrose or urea molecules dispersed throughout the solvent water. This is shown schematically in Figure 7.12.



Crystal of sugar is dropped into water.
Molecules break away and disperse through the solvent.

After dissolution individual molecules of sucrose are dispersed uniformly throughout the solvent.

A molecular substance only dissolves in water if water can form stronger attachments to the molecules than the intermolecular forces in the molecular substance. Generally the only molecular substances which dissolve in water are ones that have very polar molecules or ones that can form hydrogen bonds with water. Common sugars such as sucrose, glucose and fructose contain many O—H groups. Water can hydrogen bond to these and so sugars (carbohydrates) are soluble in water. Urea and the amino acids have N—H groups and exposed O atoms; these can form hydrogen bonds to water, so these compounds are soluble in water.

Most molecular substances are neither strongly polar nor do they form hydrogen bonds with water. This is why most molecular substances are not soluble in water.

However, some non-polar molecular substances such as oxygen and nitrogen gases and iodine are slightly soluble in water. The solvent–solute interactions are weak dispersion forces (Section 7.5). Because these interactions are weak, the solubilities of such substances are quite low.



FIGURE 7.12
Dissolution of a crystal of a molecular substance such as sucrose in water (the size of molecules is greatly exaggerated)

Non-aqueous solutions of non-polar substances

A **non-polar solvent** is a liquid which consists of non-polar molecules.

Hexane (C_6H_{14}) and carbon tetrachloride (CCl_4) are non-polar solvents.

Many molecular substances dissolve in non-polar solvents such as hexane or carbon tetrachloride. A common example is a solution of iodine in hexane. This solution consists of individual iodine molecules dispersed uniformly through the solvent. As with sugar in water, for a solution to form, the solvent–solute molecular interactions must be stronger than the solute–solute ones. In this case the interactions are just dispersion forces.

Covalent lattices and ‘big’ molecules

Covalent lattices such as diamond and silicon dioxide are insoluble in water. This is because water is not able to break up the strong covalent bonds between the particles (atoms) in these lattice solids.

Many substances used in the home are aqueous solutions

In living matter there are many large covalent molecules, typically with molecular weights into the hundreds of thousands. Common examples are cellulose (stems of plants, wood, cotton) and structural proteins (skin, hair, wool, silk). There are discrete molecules of these substances, but they are so large, and held to one another in such orderly fashions by hydrogen bonds, that water is not able to separate them from one another and so they are insoluble.

Synthetic plastics (more correctly called *polymers*) such as polyethylene (polyethene or polythene) and polyester similarly consist of very large molecules, and for the same reason these are insoluble in water.

On the other hand, there are many proteins (including enzymes) and some carbohydrates (amylose, a type of starch, and glycogen, used for energy storage in animals) which are soluble in water, even though they have large molecular weights. These molecules have very complex structures that do not pack together neatly into crystals, so water is able to separate molecules and form solutions (again with much hydrogen bonding).

As this discussion shows, the most important factors for causing solubility in water are the highly polar nature of the water molecule and the ability of water to form hydrogen bonds with other molecules.

7.12 MOLECULAR SUBSTANCES THAT REACT WITH WATER

So far we have had molecular substances that:

- dissolve in water by forming hydrogen bonds (such as glucose)
- and those that
- dissolve slightly via dispersion forces (O_2 and I_2)
- and others that
- are insoluble in water (carbon tetrachloride, olive oil, paraffin wax).

In addition, there are some polar molecular substances that dissolve in water by chemically reacting with it. An example is hydrogen chloride; this is a covalent gas. It dissolves readily in water to form hydrogen and chloride ions:



This hydrogen ion, H_3O^+ , is often called the **hydronium ion**. We call the solution hydrochloric acid.

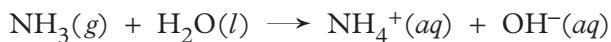
While it is often convenient to write the hydrogen ion as H^+ , it is more accurately described as H_3O^+ , an H^+ attached to a water molecule. Free H^+ does not exist in aqueous solution. When we say (as we did in Section 4.9) that an acid is a substance that in solution produces hydrogen ions, we really mean that it produces H_3O^+ ions.

Our other common acids, sulfuric acid and nitric acid, are covalent molecular liquids. They dissolve in water by reacting with it, again to form hydrogen ions. For nitric acid:



where NO_3^- is called the *nitrate* ion.

Other polar covalent molecules dissolve in water by reacting with it to form the hydroxide ion, OH^- . An example is ammonia, which as we saw in Section 7.3 is a covalent gas:



The NH_4^+ ion is called the *ammonium* ion.

Substances that dissolve in or react with water to form hydroxide ions are called **alkalis**; the solutions formed are called **alkaline solutions**.

Ammonia is an alkali and its solution in water is alkaline.

The reactions described here, in which covalent molecular substances react with water to form ions, are called **ionisation reactions**. We say that nitric acid ionises to form hydrogen ions and nitrate ions, that ammonia ionises to form ammonium ions and hydroxide ions.

7.13 SOLUBILITY SUMMARISED

Solubilities of different classes of substances in water are summarised in Table 7.5.

TABLE 7.5 Solubility in water and bonding type

Bonding type	Solubility in water	Examples
ionic	<ul style="list-style-type: none">■ most are soluble	<ul style="list-style-type: none">■ NaCl, MgSO_4, $\text{Cu}(\text{NO}_3)_2$
polar molecular	<ul style="list-style-type: none">■ soluble if H bonds possible■ soluble by reacting with it■ otherwise insoluble	<ul style="list-style-type: none">■ ethanol, glucose■ HCl, HNO_3, H_2SO_4, NH_3■ ether, dichloromethane
non-polar molecular	<ul style="list-style-type: none">■ some are slightly soluble■ most are insoluble	<ul style="list-style-type: none">■ I_2, O_2■ CCl_4, benzene, paraffin wax
very large molecules	<ul style="list-style-type: none">■ insoluble if highly structured■ a few soluble	<ul style="list-style-type: none">■ cellulose, structural proteins, synthetic polymers■ starch, glycogen, enzymes
covalent lattices	<ul style="list-style-type: none">■ insoluble	<ul style="list-style-type: none">■ diamond, SiO_2
metals	<ul style="list-style-type: none">■ insoluble■ unless they react with water	<ul style="list-style-type: none">■ Al, Zn, Fe■ Li, Na, K, Ca, Ba

About solubility more generally

Another generalisation about solubility (not restricted to just water as the solvent) is:

Like dissolves like.

Or stated more fully, *polar (including ionic) substances dissolve in polar solvents such as water and do not dissolve in non-polar solvents such as hexane. Non-polar substances dissolve in non-polar solvents but do not dissolve in polar ones.*

Covalent lattices (network solids) do not dissolve in any solvents.



Exercises

- 13 Which of the following compounds would you expect to be soluble in water? Explain why.
- HBr, SiO₂, MgCl₂, CS₂, BF₃, ZnBr₂, H₂SO₄, hexachloroethane (C₂Cl₆), silicon tetrachloride (SiCl₄), hydrogen peroxide (H₂O₂), fructose (a sugar, C₆H₁₂O₆), octane (C₈H₁₈), urea (NH₂CONH₂), boron
- 14 a Iron(II) sulfate, FeSO₄, crystallises with seven molecules of water per ion pair of iron(II) sulfate. Write the formula for the hydrate.
b Magnesium nitrate, Mg(NO₃)₂, crystallises as a hexahydrate. Write its formula.
*c Calcium nitrate, Ca(NO₃)₂, crystallises with four molecules of water per ion pair of calcium nitrate. Write a formula for the hydrate and name it.
*d Lithium bromide, LiBr, crystallises as a dihydrate. Write its formula.
- 15 Vitamin C and the B group vitamins are soluble in water whereas Vitamins A, D, E and K are not. What, if anything, can you deduce about the structures of these vitamins?
- *16 Hydrogen bromide and methane are small covalent molecules. Hydrogen bromide readily dissolves in water whereas methane does not. Explain why.
- 17 Pure sulfuric acid is a covalent liquid. It dissolves in water by reacting with it. Write an equation for the reaction.

Important new terms

You should know the meaning of the following terms:

alkaline solution (p. 199)
alkalis (p. 199)
anhydrous (p. 196)
dipole (p. 188)
dipole–dipole forces (p. 189)
dispersion forces (p. 189)
heteroatomic (p. 188)
hydrates (p. 196)

hydrogen bonds (p. 190)
hydronium ion (p. 198)
ionisation reactions (p. 199)
non-polar solvent (p. 197)
polar covalent bond (p. 188)
polar molecule (p. 188)
polar solvent (p. 195)
specific heat capacity (p. 185)
surface tension (p. 184)
viscosity (p. 184)
water of crystallisation (p. 196)

CHAPTER 7

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 In what physical state(s) do you find water in each of the major ‘spheres’ of the Earth—atmosphere, hydrosphere, lithosphere—and in living matter?
- 3 Roughly what percentage of living matter is water?
- 4 How is water used: a by living matter b in the everyday activities of human societies?
- 5 How does water contribute to the weathering and eroding of the Earth?
- 6 What is unusual about the physical states in which water exists on Earth?
- 7 Compare five physical properties of water with the corresponding property of other common liquids.

- 8** Draw electron-dot structures for water, ammonia, methane and hydrogen sulfide.
- 9** What are the shapes of the molecules listed in Question 8?
- 10** In which of the substances listed in Question 8 are there **a** dipole–dipole interactions **b** hydrogen bonds? What are the consequences for melting and boiling points? Explain why.
- 11** What is the experimental evidence for believing that there is hydrogen bonding in water, ammonia and hydrogen fluoride?
- 12** Draw a diagram to show hydrogen bonding in aqueous solutions of **a** ammonia and **b** methanol, $\text{CH}_3\text{—OH}$.
- 13** Explain why water expands on freezing whereas most liquids contract.
- 14** What do chemists mean when they say that ions in solution are hydrated? A diagram may help.
- 15** Write the formula for copper sulfate pentahydrate. Name $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.
- 16** Name two substances that react with water as they dissolve and write equations for the reactions.
- 17** Why are some proteins (such as enzymes) and polysaccharides (such as amylose and glycogen) soluble in water, while others such as hair, skin and cellulose are not?
- 18** Summarise the solubility in water for most of the compounds in each of the following classes: ionic substances, polar covalent molecules, non-polar covalent molecules, covalent lattices, polymers (both synthetic and natural).

CHAPTER 8

Ions in aqueous solution

IN THIS CHAPTER

Precipitation reactions
Solubility data and its use
Types of equations
Saturated solution, concentration and solubility
Dissolution and precipitation
Other reversible reactions
Different measures of concentration

Molarity
Thermal properties of water
Temperature, quantity of heat and heat capacity
Heat changes when substances dissolve
Consequences of the thermal properties of water for living organisms
Thermal pollution

Having considered the nature of ionic solutions, we can now look at some reactions involving ions in solution. In particular let us look at what are called precipitation reactions.

8.1 PRECIPITATION REACTIONS

Sometimes when clear solutions of two substances are mixed, they react to produce a finely divided solid.

A solid produced by reaction between two clear solutions is called a **precipitate**. Such reactions are called **precipitation reactions**.

The verb, to precipitate, means to fall out—solids fall out of solution. Common examples of precipitation reactions are as follows:

- 1 When colourless solutions of potassium chloride and silver nitrate are mixed, a white precipitate of silver chloride is formed.
- 2 When a colourless solution of sodium hydroxide is added to a clear blue solution of copper sulfate, a blue precipitate of copper hydroxide forms.
- 3 Colourless solutions of sodium iodide and lead nitrate react to form a bright yellow precipitate of lead iodide.
- 4 Yellow iron(III) chloride solution and colourless sodium hydroxide solution when mixed react to form a dark brown precipitate of iron(III) hydroxide.

Figure 8.1 shows these precipitates.

Recall from Section 3.1 that in a chemical reaction the starting substances are called *reactants* and the substances formed, *products*. In (1) potassium chloride and silver nitrate are the reactants while silver chloride is a product.

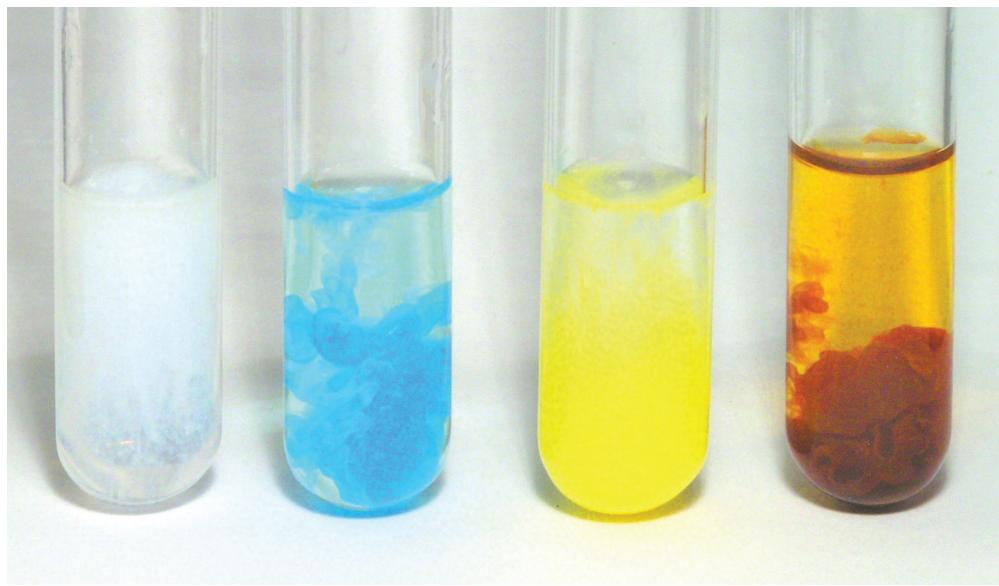


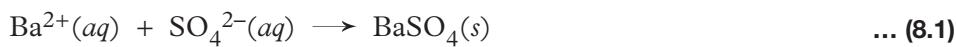
FIGURE 8.1
Precipitates of silver chloride, copper hydroxide, lead iodide and iron(III) hydroxide

The nature of ionic solutions provides an explanation of how and why precipitates form when certain solutions are mixed. As we saw in Section 7.9, a solution of an ionic compound consists of positive and negative ions moving randomly and independently throughout the whole volume of water they are present in.

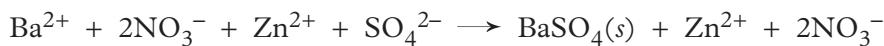
When solutions of zinc sulfate and magnesium nitrate are mixed, the resulting solution consists of Zn^{2+} , SO_4^{2-} , Mg^{2+} and NO_3^- ions all moving randomly throughout the whole volume of the liquid. This mixed solution is identical with one formed by mixing solutions (of appropriate concentrations) of zinc nitrate and magnesium sulfate. Both mixed solutions contain the same four types of ion moving freely around.

Similarly, a mixture of solutions of sodium chloride and copper sulfate is identical with a mixture of solutions of sodium sulfate and copper chloride—both mixtures consist of Na^+ , Cu^{2+} , Cl^- and SO_4^{2-} ions moving randomly throughout the whole volume.

However if we mix barium nitrate and zinc sulfate solutions, a heavy white precipitate forms. In solution, barium nitrate consists of separated Ba^{2+} ions and NO_3^- ions, while in zinc sulfate solution there are separated Zn^{2+} and SO_4^{2-} ions. Now barium sulfate is insoluble, so when Ba^{2+} and SO_4^{2-} ions collide, they stick together to form solid barium sulfate which falls out of (precipitates from) solution:



This precipitation reaction can be written in two other ways:



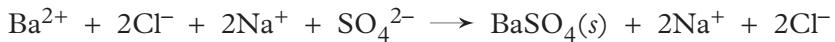
As the nitrate and zinc ions are not actually involved in the reaction, we call them *spectator ions* in the same way as we used this term in Section 4.9.

The ‘driving force’ behind a precipitation reaction is the formation of an insoluble substance. When solutions of two ionic substances are mixed, precipitation occurs if one type of positive ion present can combine with one type of negative ion present to form an insoluble substance.

Barium ions combine with sulfate ions to form a precipitate of barium sulfate, regardless of what spectator ions are involved. Mixing solutions of:

- 1 barium chloride and sodium sulfate
- 2 barium hydroxide and potassium sulfate
- 3 barium bromide and sulfuric acid

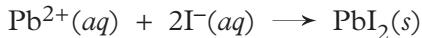
all result in precipitation of barium sulfate. Reaction 8.1 occurs in every case, though we can write each reaction in other ways if we wish. For example, for 1 we can write:



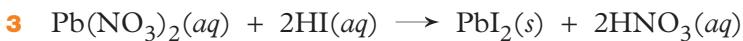
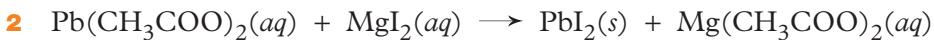
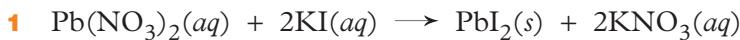
Lead iodide is an insoluble substance; it precipitates out when we mix solutions of:

- 1 lead nitrate and potassium iodide
- 2 lead acetate (ethanoate) and magnesium iodide
- 3 lead nitrate and hydroiodic acid

In all cases the essential reaction is:



though we can write the individual reactions as:



or in complete ionic form (for 1 and 2):



This latter form emphasises that K^+ and NO_3^- in 1 and Mg^{2+} and CH_3COO^- in 2 are spectator ions; they are not actually involved in the reaction.

Since precipitation occurs through the formation of insoluble substances, we need to know which substances are soluble and which are insoluble. We need a table of solubility data.

8.2 SOLUBILITY DATA

By taking solutions of a soluble compound of each of the cations (positive ions) we are interested in, and systematically mixing samples of these with solutions of the anions (negative ions) we are interested in, we can establish experimentally which substances are soluble and which are insoluble. We can then summarise the results of these experiments into a table of solubility data. This table can then be used to predict what, if any, precipitation reactions will occur when solutions of other substances are mixed.

Table 8.1 summarises the solubility of common ionic compounds. The cations covered by this table are Group 1, Group 2, NH_4^+ , Al^{3+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} , Sn^{2+} .

'Soluble' means that the compound dissolves to more than 10 g/L; 'insoluble' that it dissolves to less than 1 g/L. Some substances have solubilities in the range

1 to 10 g/L and are often classed as ‘sparingly soluble’. Common sparingly soluble compounds (included in Table 8.1) are silver acetate, lead chloride, calcium sulfate, silver sulfate and calcium hydroxide.

TABLE 8.1 Solubility of ionic compounds

Compounds that are soluble	Compounds that are insoluble
<ul style="list-style-type: none"> ■ Group 1 and NH_4^+ compounds ■ nitrates ■ acetates (ethanoates) ■ chlorides, bromides and iodides (except Ag^+ and Pb^{2+}) ■ sulfates (except Ag^+, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}) 	<ul style="list-style-type: none"> ■ carbonates ■ sulfites ■ phosphates ■ hydroxides ■ oxides ■ sulfides <p style="margin-left: 20px;">} (except Group 1 and NH_4^+ compounds)</p> <p style="margin-left: 20px;">} (except Group 1, NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+})</p> <p style="margin-left: 20px;">} (except Groups 1, 2 and NH_4^+)</p>

Sometimes when only a small amount of a precipitate is formed, it does not settle to the bottom of the test tube as an obvious solid, but stays in suspension and makes the mixture look cloudy or turbid. We need to distinguish between a colourless solution (completely transparent or clear), a coloured solution (still transparent) and a turbid suspension (can be coloured but is not fully transparent). Examples are shown in Figure 8.2. If mixing two clear (coloured or colourless) solutions produces turbidity (cloudiness), then a precipitate has been formed. We need to recognise that cloudiness signals the formation of a precipitate.

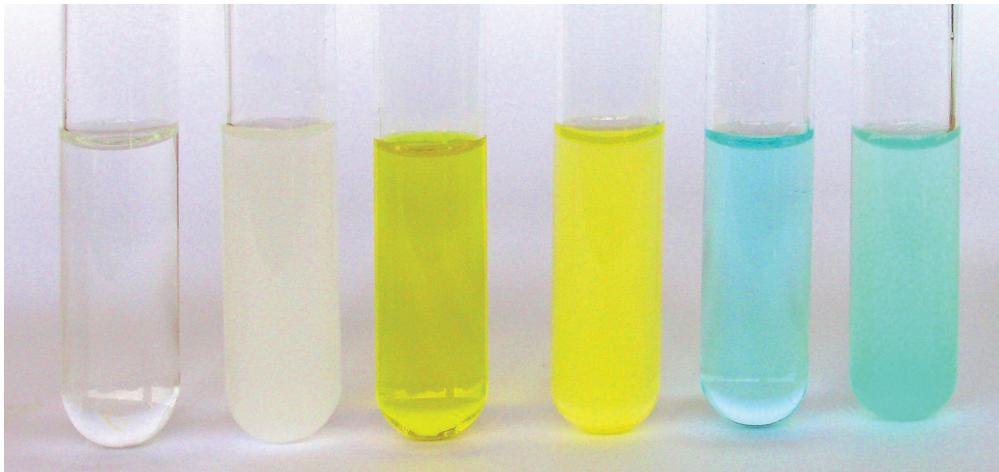


FIGURE 8.2
Solutions and suspensions. From left to right: a colourless solution of sodium chloride (clear), a white precipitate (suspension) of silver chloride (turbid), a yellow solution of potassium chromate (clear), a yellow precipitate (suspension) of lead iodide (turbid), a coloured solution of copper sulfate (clear), and a blue precipitate (suspension) of copper hydroxide (turbid)

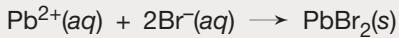
8.3 USING THE SOLUBILITY TABLE

Table 8.1 can be used to predict what will happen when solutions of particular substances are mixed, as the following examples illustrate.

Example 1

What precipitate (if any) will form when aqueous solutions of sodium bromide and lead nitrate are mixed?

In solution, there will be Na^+ , Br^- , Pb^{2+} and NO_3^- ions moving freely around. We could possibly form sodium nitrate, NaNO_3 , and lead bromide, PbBr_2 . From Table 8.1 sodium nitrate is soluble, but lead bromide is insoluble. Hence lead bromide precipitates out:

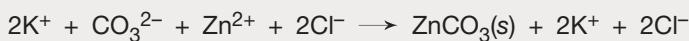




Example 2

What reaction (if any) will occur when a solution of potassium carbonate is added to a solution of zinc chloride?

By ‘changing partners’ the cations could form potassium chloride and zinc carbonate. From Table 8.1 KCl is soluble, but zinc carbonate is insoluble, so it will precipitate out:



Example 3

When solutions of ammonium chloride and magnesium nitrate are mixed, what, if anything, will precipitate?

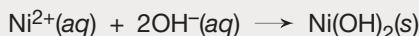
By a change of partners we could form ammonium nitrate and magnesium chloride, but both NH_4NO_3 and MgCl_2 are soluble, so nothing happens. This mixed solution merely has NH_4^+ , Cl^- , Mg^{2+} and NO_3^- ions moving randomly around throughout its whole volume; it is in no way different from the mixture formed from solutions (of appropriate concentration) of magnesium chloride and ammonium nitrate.



Example 4

Does sodium hydroxide solution react with nickel chloride solution? If so what is formed?

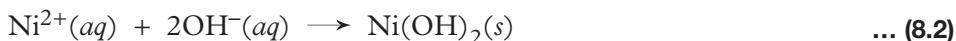
We note that a change of partners could form sodium chloride and nickel hydroxide. From Table 8.1 Ni(OH)_2 is insoluble so that:



8.4 WHICH EQUATION?

Three different types of equation have been written for precipitation reactions:

- 1** *net ionic* equations such as:



- 2** *complete ionic* equations such as:



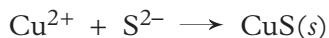
- 3** *neutral species* equations such as:



The question then arises, which is the best type of equation to write? Actually there is no ‘best’ type; *we write the equation that is most appropriate to the context*. If all we wish to state is that nickel ions react with hydroxide ions to form nickel hydroxide, regardless of which spectator ions are present, we should prefer Equation 8.2. If we wished to make it clear which particular compounds had been used to prepare our sample of nickel hydroxide, then we should use either Equation 8.3 or 8.4. Equation 8.3 emphasises the ionic nature of the reaction and clearly shows that Na^+ and Cl^- are spectator ions, so if these points need emphasising Equation 8.3 is preferred.

There is a further aspect of writing equations that needs comment; it concerns the question of when should we show the physical state (solid, *s*; liquid, *l*; gas, *g*; aqueous solution, *aq*) on our equations? Again there is no firm answer to suit all situations. If a reaction ‘goes’ because a gas is formed (as when some

metals react with acids) or because a precipitate is formed, we *must always* denote the physical state of the gas or precipitate to emphasise the driving force of the reaction:



If we write a precipitation equation in the neutral species form (Equation 8.4), we should specify that the reactants are in aqueous solution (because they can exist as solids), and also that the ‘left-over’ substance, NaCl in Equation 8.4, is an aqueous solution. If the complete ionic form, Equation 8.3, is used it is not necessary to include (*aq*) on each species if it is clear from the context that the ions are in aqueous solution; however the (*s*) on the precipitate is essential.

These symbols, (*s*), (*l*), (*g*), (*aq*), are called **state symbols** or **phase descriptors**. If in doubt about whether to include them or not, it is safest to put them in.

Exercises

- 1 Which of the following substances are soluble in water?

a copper sulfide	f copper nitrate	k ammonium sulfide
b magnesium sulfate	g calcium bromide	l sodium phosphate
c aluminium chloride	h potassium iodide	m magnesium hydroxide
d iron(II) sulfide	i iron(II) hydroxide	n silver bromide
e zinc hydroxide	j lead sulfate	o barium hydroxide

- 2 Write the formulae for the substances in Exercise 1.
- 3 Mixed solutions (of suitable concentrations) of what pairs of substances would be identical to solutions containing mixtures of:
- a sodium sulfate and magnesium nitrate
 - b barium hydroxide and potassium chloride?
- 4 Name and give the formula of the precipitate (if any) that forms when solutions of the following pairs of substances are mixed.
- a lead nitrate and ammonium sulfate
 - b zinc sulfate and potassium carbonate
 - c sodium chloride and magnesium sulfate
 - d iron(II) chloride and sodium hydroxide
 - *e copper sulfate and hydrogen sulfide
 - *f nickel sulfate and cadmium chloride
 - *g potassium bromide and lead nitrate
 - *h sodium sulfide and iron(III) sulfate
- 5 i Write complete ionic equations for the reactions (if any) in a, d and *g of Exercise 4.
ii Write net ionic equations for the reactions in part i of this exercise.
- 6 i Write neutral species equations for the reactions (if any) which occur in b, *e and *h of Exercise 4.
ii Write net ionic equations for the reactions in part i of this exercise.
- 7 Which solutions would you mix to produce a precipitate of:
a barium carbonate b silver bromide *c aluminium hydroxide?
- 8 i Write net ionic equations for all the reactions in Exercise 7.
ii Write complete ionic equations for these reactions.



Let us look more closely at what happens when an ionic solid dissolves in water and when a precipitate forms, but first some new technical terms.

8.5 SATURATED SOLUTION, CONCENTRATION, SOLUBILITY

We find that we can only dissolve a certain amount of a particular substance in a given volume of a solvent (at a particular temperature). If we try to dissolve more, the extra solute just remains undissolved at the bottom of the container. We say such a solution is *saturated*. Thirty-six grams of sodium chloride can be dissolved in 100 millilitres of water at room temperature, but if we add more than this, the extra does not dissolve no matter how hard or long we shake the mixture.

A **saturated solution** is one in which no more of the particular solute can be dissolved in a given quantity of the solvent at the specified temperature. A solution which contains less than this maximum amount of solute is called an **unsaturated solution**.

A solution containing 36 g NaCl/100 mL water at 25°C is a saturated solution; a solution containing 20 g NaCl/100 mL is an unsaturated one.

The **concentration** of a solution is the amount of solute present in a specified amount of solvent or solution.

Concentration can be given in a variety of units, for example as 36 grams NaCl per 100 mL of water; 360 grams per litre of water; 36 g/100 g water; 360 grams per kilogram of water; or 0.36 grams per gram of water. We shall look at other measures of concentration in Sections 8.9 and 8.10 below.

The **solubility** of a substance in a particular solvent is the concentration of its saturated solution at the specified temperature. It is the maximum amount of the substance that will dissolve in a given amount of the solvent at that temperature.

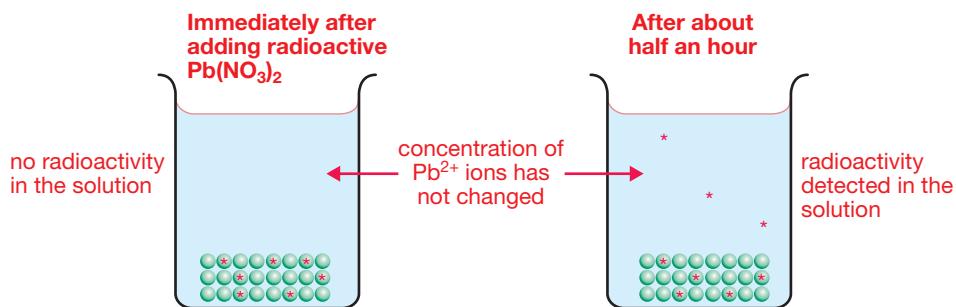
Since the amount of solute which can be dissolved in a given quantity of solvent varies as temperature is changed, it is essential to state the temperature to which a particular solubility value applies. Hence we say that the solubility of sodium chloride in water at 25°C is 36 g/100 g; or the solubility of potassium nitrate is 37 g/100 g water at 25°C and 245 g/100 g at 100°C.

8.6 DISSOLUTION AND PRECIPITATION

We saw in Section 7.9 that when an ionic substance dissolves in water, it breaks up into ions which move independently through the solution. When a solution becomes saturated, ions still continue to break away from the crystals of solid and go into solution, but in addition an equal number of ion pairs from the solution precipitate out on to the solid. The following experiment demonstrates this.

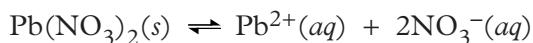
Suppose we have a saturated solution of lead nitrate in contact with lead nitrate crystals. Let us now add some lead nitrate crystals that contain radioactive lead. Radioactive lead is identical with ordinary lead except that it emits a special form of radiation called beta rays, which can easily be detected with a radiation counter. We find that just after adding this radioactive lead nitrate solid, all the radioactivity is in the solid: there is none in the solution. However, as time passes we find that some of the radioactivity moves into the solution even though the total concentration of lead ions in the solution does not change. Eventually the

same fraction of the lead ions in the solution is radioactive as in the solid. This is illustrated in Figure 8.3.

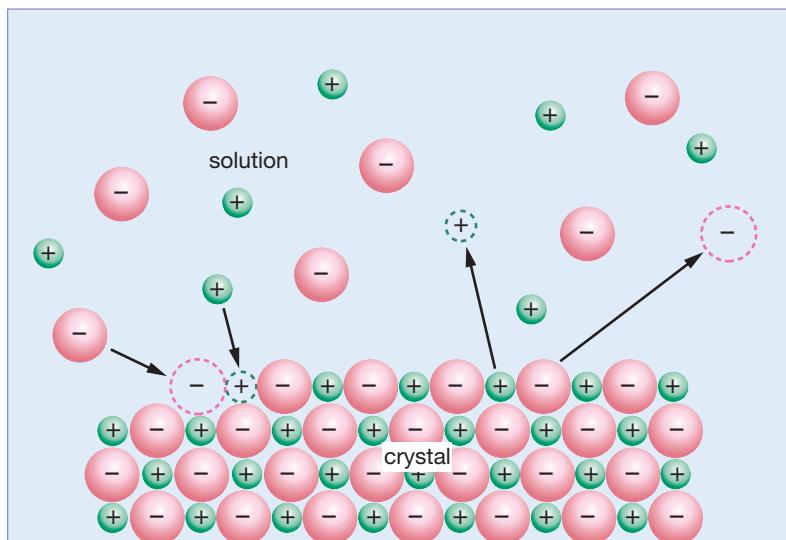


This experiment shows that some lead ions move from the solid into the solution, though this does not change the concentration of lead ions in the solution! This must mean that some lead ions (and nitrate ions) move back from the solution to the solid to balance things out.

This experiment, and many others like it, show that when a solid is in contact with its saturated solution there is a *dynamic balance* between dissolution and precipitation: both are occurring, but at equal rates so that there is no overall change in concentration in the solution. We call this a **dynamic equilibrium**. We say that the solid is *in equilibrium* with the solution and write it as:



The two-way arrow indicates that both processes are occurring—solid going into solution and ions in solution going to solid. This dynamic equilibrium is shown schematically in Figure 8.4.

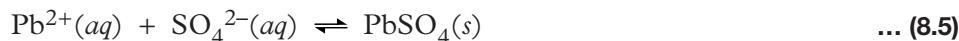


Precipitation occurs if the concentrations of relevant ions in a solution are greatly above what they should be in a saturated solution. For example, imagine we mix solutions of, say, lead nitrate and sodium sulfate. Immediately after mixing the concentrations of lead and sulfate ions will be far greater than can exist in a saturated lead sulfate solution, so whenever these ions collide they fall out of solution as solid lead sulfate. This precipitation continues until the concentrations of the ions fall back to the saturated solution levels. At that stage

FIGURE 8.3
Adding radioactive solid lead nitrate to a saturated solution of non-radioactive lead nitrate does not change the concentration of lead ions in the solution, but some of the radioactivity (represented by red asterisks) transfers to the solution. This demonstrates the dynamic nature of the precipitation-dissolution equilibrium

FIGURE 8.4
The dynamic equilibrium between an ionic solid and a solution of its ions

we observe no further precipitation. However, some ion pairs are still falling out of solution to add to the solid, but an equal number of ion pairs is breaking away from the solid to go back into solution. With the rates of these two processes equal we again have a dynamic equilibrium. We represent it by:



We call this a **reversible reaction**, meaning that it is able to go in either direction. If we shake some solid lead sulfate with pure water, some of the solid goes into solution as ions: Reaction 8.5 goes from right to left until equilibrium is established. If we mix sulfate ions and lead ions, they combine to form solid lead sulfate: Reaction 8.5 goes from left to right, again until equilibrium is reached.

Dissolution of a solid and precipitation of a solid from solution are basically the same reaction—just going in opposite directions.

In reversible reactions (equilibrium reactions) we talk about the **forward reaction**, meaning the reaction going from left to right as written, and the **reverse or backward reaction**, meaning the reaction going from right to left. In Equation 8.5 the forward reaction is precipitation of $\text{PbSO}_4(s)$, while the reverse reaction is the dissolution of PbSO_4 to form Pb^{2+} and SO_4^{2-} ions in solution.

8.7 OTHER REVERSIBLE REACTIONS[†]

All precipitation reactions are reversible reactions. However there are many reversible reactions that are not precipitation reactions. Some examples are:



Limestone caves are formed by the reversible chemical reaction $\text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq)$. Under certain conditions the limestone dissolves to form the cave. Under changed conditions calcium carbonate crystallises out to form stalactites, stalagmites and columns

[†] This section is not required by the Preliminary Course syllabus. It has been included to reinforce the basic ideas about reversible reactions and to give some indication of the wide range of reactions (apart from precipitation reactions) that are reversible.

- 1** Potassium chromate, K_2CrO_4 , dissolves in water to form a yellow solution. If dilute acid is added to it, the solution goes orange: potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is formed. The equation for the reaction is:



Potassium dichromate dissolves in water to form an orange solution. If we add a small amount of alkali solution (to use up the acid that forms), the solution goes yellow. The reaction is:

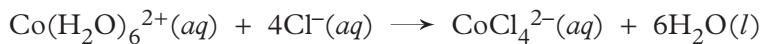


This is therefore a reversible reaction, which we write as:

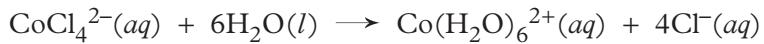


Regardless of which side we start from, the reaction proceeds until the rates of the forward and reverse reactions are equal. At that point there will be no observable change: we say that *the reaction has reached equilibrium*. As with precipitation it is a dynamic equilibrium—both the forward and reverse reactions are still occurring but at equal rates.

- 2** A saturated solution of cobalt nitrate is pink. If concentrated hydrochloric acid is added to a sample of this solution, it goes blue. The reaction is:



If water is added to this blue solution, it changes back to pink. The reaction is:



This is another reversible reaction which we write as:



Yellow potassium chromate (left) and orange potassium dichromate solutions

The equilibrium 8.7 is used in self-indicating silica gel desiccant: blue pellets turn pink when they become saturated with water

With a high concentration of chloride ion the reaction goes from left to right (pink to blue): if the solution is greatly diluted (water added), the reaction goes from right to left. When no further change is observable, we say that the reaction has come to equilibrium. But as with all reversible chemical reactions it is a dynamic equilibrium: both the forward and reverse reactions are occurring at equal rates.

This reversible reaction is used in some novelty devices for measuring the relative humidity (water content) of air.



Exercises

- 9 A solution containing 0.100 mol silver nitrate was mixed with another solution containing 0.100 mol sodium acetate $\text{CH}_3\text{CO}_2\text{Na}$ ($= \text{Na}^+ + \text{CH}_3\text{CO}_2^-$). The total volume was 1.00 L. A white precipitate of silver acetate formed. Write an equation for the reaction occurring. If this reaction went to completion, how many moles of silver acetate would form? In fact only 0.055 mol was produced. What does this tell you about the reaction?

In another experiment 0.200 mol silver acetate solid was mixed with 1.00 L of water. The mixture was thoroughly shaken and allowed to stand for several hours. Would you expect to find any ions in the solution? Would there be any solid remaining? Explain fully.

- 10 a When a brown iodine solution and a colourless arsenious acid solution (each containing the same number of moles) are mixed, the brown colour of the iodine fades noticeably as the following reaction occurs:

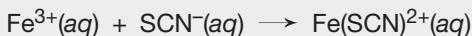


(H_3AsO_3 is arsenious acid; H_3AsO_4 is arsenic acid)

However, the brown colour does not completely disappear. What do you conclude about the reaction? Explain.

- b If colourless solutions of arsenic acid and hydroiodic acid ($\text{HI} = \text{H}^+ + \text{I}^-$) were mixed, what would you observe? Explain.
c If a very small amount of arsenious acid containing radioactive arsenic was added to the pale brown solution at the end of the experiment in (a) and a few hours allowed to pass, would you expect to find the radioactive arsenic: i still solely in the arsenious acid, ii distributed over both the arsenious and arsenic acids, or iii solely in the arsenic acid? Explain fully.

- *11 Iron(III) ions react with thiocyanate ions, SCN^- , to form a blood-red solution:



The intensity of the colour is proportional to the amount of $\text{Fe}(\text{SCN})^{2+}$ ion in the solution. Volumes of two solutions containing 0.0010 mol Fe^{3+} and SCN^- respectively were mixed and then divided equally between two test tubes. To one tube some extra Fe^{3+} was added. If the original reaction had gone to completion, would you expect any change in intensity of the colour when this extra Fe^{3+} was added? In fact the intensity of the colour increased (by reference to the second test tube). What does this tell you about the reversibility or otherwise of this reaction? Explain fully.

8.8 DIFFERENT MEASURES OF CONCENTRATION

In Section 8.5 concentration was defined as the amount of solute in a specified amount of solvent or solution. This can be expressed in many ways. Some of the more common are:

- mass of solute per 100 mL or 1 L of solvent
 - mass of solute per 100 mL or 1 L of solution
 - volume of solute per 100 mL or 1 L of solvent
 - volume of solute per 100 mL or 1 L of solution
 - %(w/v) standing for per cent, weight, volume (should be m/v, mass, volume), which means mass of solute per 100 mL of solution
 - %(v/v) standing for per cent, volume, volume, meaning volume of solute per 100 mL of solution.
- } convenient for solid solutes,
such as sodium chloride
} convenient for liquid
solutes, such as ethanol

All the above measures are in terms of volume of solvent or solution. This is generally the most convenient way of making solutions. However we can express concentration in terms of mass of solvent or solution. Common ones are:

- % (w/w), **per cent by weight**, meaning mass of solute per 100 g solution, and
- ppm, standing for **parts per million**, meaning grams of solute per million grams of solution.[†]

If % is used on its own, it generally means % (w/w), mass of solute in 100 g of solution.

Why different measures of concentration?

Several ways of expressing concentration are used because each method has advantages for particular situations. In commerce, industry and shopping, where the main concern is with how much solute is present, then mass per unit volume is very convenient. If we want a desired mass of the solute, we can then just measure out the necessary volume of the solution. It is usually easier to measure out volumes than masses.

If the solute is a liquid, then volume per unit volume is often preferred because we generally think in terms of volumes of liquids rather than masses.

In environmental contexts concentrations are usually quite low. Masses per unit volume or per cent compositions generally lead to very small numbers, so ppm gives more manageable numbers. For example, 1.5 ppm is more convenient to say and write than 0.000 15% or 0.0015 g per litre (a litre is approximately a kilogram).

When we want to measure quantities in chemical reactions, we will find (in the next section) that another measure of concentration in terms of moles is more convenient.

Using concentrations

Some examples will illustrate how we use concentrations.

[†] ppm has a different meaning in gaseous mixtures as will be explained in Chapter 4 of *Conquering Chemistry HSC Course*.

Example 5

- a 1.32 g potassium permanganate, KMnO_4 , was dissolved in water and the volume made accurately to 250 mL. Calculate the concentration of this solution in i g/100 mL and ii g/L of solution.

We have 1.32 g KMnO_4 in 250 mL of solution.

$$\begin{aligned}\text{i} \text{ Mass of } \text{KMnO}_4 \text{ in 100 mL solution} &= \frac{100}{250} \times 1.32 \\ &= 0.528 \text{ g/100 mL}\end{aligned}$$

$$\begin{aligned}\text{ii} \text{ Mass of } \text{KMnO}_4 \text{ in 1 L} (= 1000 \text{ mL}) &= \frac{1000}{250} \times 1.32 \\ &= 5.28 \text{ g/L}\end{aligned}$$



- b** 13.6 g copper sulfate was dissolved in 500 mL water. Calculate the %(w/w) copper sulfate in this solution. Assume that the mass of 500 mL of water is 500 g.

$$\begin{aligned}\text{Total mass of the solution} &= 13.6 + 500 \\ &= 513.6 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Percentage CuSO}_4 \text{ in this solution} &= \frac{13.6}{513.6} \times 100 \\ &= 2.65\%(\text{w/w})\end{aligned}$$



Example 6

- a** What mass of sodium chloride has to be dissolved in 250 mL water to make a 0.90%(w/v) solution (the common saline solution in hospitals)? Assume that the solution has a volume of 250 mL.

A 0.90%(w/v) solution contains 0.90 g NaCl in 100 mL of solution.

$$\text{In 250 mL of solution we require } \frac{250}{100} \times 0.90 = 2.3 \text{ g}$$

- b** What volume of alcohol (ethanol) is present in 750 mL of a 14%(v/v) solution of alcohol in water (a red wine)?

In 100 mL there are 14 mL of alcohol, so:

$$\text{volume of alcohol in 750 mL} = \frac{750}{100} \times 14 = 105 \text{ mL}$$

- c** A solution contained 500 ppm mercury(II) ion. Express this as a %(w/w).

500 ppm means 500 g mercury(II) ion per 10^6 g solution.

%(w/w) means grams per 100 g solution, so:

$$\begin{aligned}\text{mass of mercury(II) ion in 100 g} &= \frac{100}{10^6} \times 500 \\ &= 0.050 \text{ g}\end{aligned}$$

Therefore the solution is **0.050%(w/w)**.

Apparatus for measuring solutions

Apparatus commonly used to measure out volumes of solutions is shown in Figure 8.5.

- *Measuring cylinders* are used when we only require *approximate* amounts. Volumes from measuring cylinders are accurate only to about $\pm 5\%$. Common sizes are 10, 100, 250 and 500 mL.
- *Pipettes and burettes* deliver accurate volumes (to about ± 0.2 to $\pm 0.5\%$). Burettes deliver variable volumes, generally from zero to 50 mL. Pipettes deliver fixed volumes: common pipette sizes are 5, 10 and 25 mL, though 1, 2 and 50 mL are sometimes available.
- *Volumetric flasks* contain fixed volumes (accurate to about ± 0.2 to 0.5%) when filled to the mark engraved on their necks: common sizes are 100, 250, 500 mL and 1 L, although 50 mL and 2 L are sometimes available.

To make an aqueous solution of accurately known concentration, we measure out the required amount of solute (sensitive balance for mass or pipette for volume), transfer it to a volumetric flask, then, after dissolving it in some water, fill the flask to its graduation mark. This gives us a concentration in mass or volume

per unit volume of *solution*. If we want concentration in mass or volume per unit volume of *solvent*, we would have to measure out a suitable volume of solvent in a volumetric flask (or pipette if only a small volume is required), then mix solute and solvent in a beaker. If only an approximate concentration is required, say $\pm 10\%$, then we can use a measuring cylinder for dispensing the solvent.

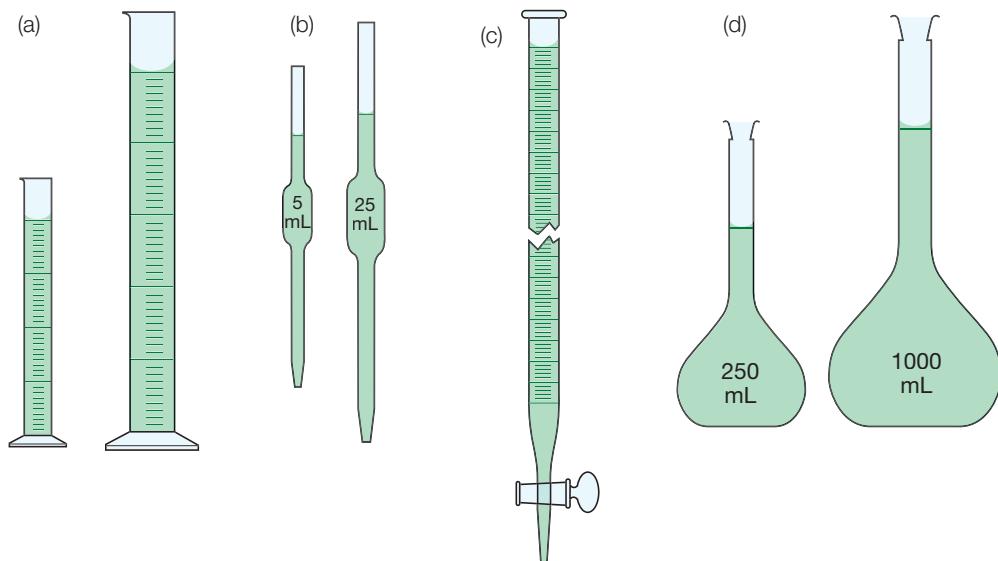


FIGURE 8.5
Apparatus for measuring volumes of solutions
(a) measuring cylinders,
(b) pipettes,
(c) burette,
(d) volumetric flasks. We fill volumetric glassware until the bottom of the meniscus (curved surface of the liquid) sits accurately on the graduation mark

Dilution

Frequently we need to dilute a solution from one concentration to a lower one. We do this by measuring out a volume of the original solution and adding water to make the new volume. The volume to dilute the solution to is calculated from the fact that the *amount of solute (or the number of solute particles) in the diluted solution is the same as was in the volume of the original solution that was taken* (because the only thing that was done was to add water). Figure 8.6 illustrates this. Now:

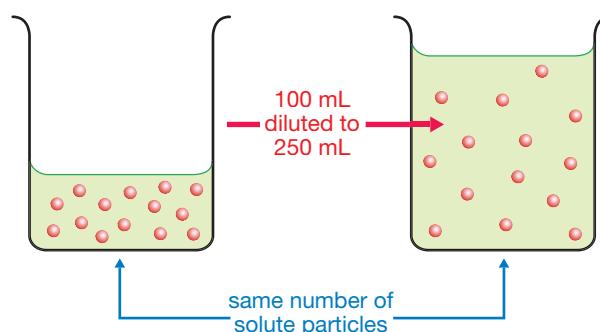


FIGURE 8.6
Dilution: the same number of solute particles in a larger volume of solvent

$$\text{amount of solute in original solution} = \text{original concentration} \times \text{original volume}$$

$$\text{amount of solute in diluted solution} = \frac{\text{concentration of}}{\text{diluted solution}} \times \text{final volume}$$

Because the amount of solute is the same:

$$\left(\frac{\text{concentration of}}{\text{diluted solution}} \right) \times \text{final volume} = \left(\frac{\text{original}}{\text{concentration}} \right) \times \text{original volume}$$

... (8.8)

This equation can be written in symbols as:

$$c_2 V_2 = c_1 V_1$$

or as $cV = \text{constant}$

Equation 8.8 can be used to calculate the volume to which a given solution must be diluted to produce a required concentration. An example will illustrate but first a comment on accuracy and significant figures.

Accuracy and significant figures

If you have not already done so, this would be a good time to read the *Appendix: Significant figures* on page 310.

Note particularly the point about volumetric glassware. Stating that a pipette, burette or volumetric flask was used effectively tells you the accuracy of the volume and hence the number of significant figures, even though the numbers may be written less precisely. 25 mL by pipette or 500 mL in a volumetric flask implies a volume of 25.0 or 500.0 mL respectively.



Example 7

- a 25 mL of an aqueous sucrose solution of concentration 84.1 g/100 mL solution was diluted to 500 mL (using a pipette and volumetric flask). What is the concentration of the diluted solution?

Using Equation 8.8:

$$\begin{aligned}\text{concentration of diluted solution} &= \frac{\text{original concentration} \times \text{original volume}}{\text{final volume}} \\ &= \frac{84.1 \times 25}{500} \\ &= \mathbf{4.21 \text{ g/100 mL}}\end{aligned}$$

Alternatively, using basic principles instead of Equation 8.8:

$$\begin{aligned}\text{mass of solute taken} &= \frac{25}{100} \times 84.1 \\ &= 21.03 \text{ g}\end{aligned}$$

This mass ends up in 500 mL of solution, so:

$$\begin{aligned}\text{concentration of diluted solution} &= \frac{21.03}{500} \times 100 \\ &= \mathbf{4.21 \text{ g/100 mL}}\end{aligned}$$

- b To what volume should 50 mL of a 30 g/100 mL solution of potassium nitrate be diluted to make a solution which is 6.0 g/100 mL?

Using Equation 8.8:

$$\begin{aligned}\text{final volume} &= \frac{\text{original concentration} \times \text{original volume}}{\text{concentration of diluted solution}} \\ &= \frac{30 \times 50}{6.0} \\ &= \mathbf{250 \text{ mL}}\end{aligned}$$

If we only wanted an approximate dilution, we would measure out 50 mL of the starting solution in a small measuring cylinder, transfer it to a larger one and make the volume to 250 mL. If we wanted an accurate dilution, we would use a pipette to transfer 50 mL of the original solution into a 250 mL volumetric flask, then add water to bring the volume to exactly 250 mL (meniscus sitting on the mark on the neck of the flask).

An intuitive approach to dilution problems is this: if you want to dilute a solution by a factor of x , then you need to increase the volume by a factor of x . To dilute a solution by a factor of 5, dilute 50 mL to 250 mL (or 10 mL to 50 mL).

Exercises

- 12 a** 7.3 g sodium sulfate was dissolved in 75 mL water. Calculate the concentration of this solution in **i** g/100 mL of solution **ii** g/L of solution **iii** %(w/v). Assume that the volume after dissolution is still 75 mL.
- b** 15 mL ethanol (which has a mass of 11.9 g) was dissolved in 80 mL water. Assuming that the final volume is 95 mL, calculate the concentration of the solution in **i** mL/100 mL of solution **ii** g/100 mL of solution **iii** mL/L of solution **iv** %(v/v).
- 13 a** What mass of potassium nitrate do you need to dissolve in 50 mL water to make a 2.5%(w/v) solution?
- b** What mass of glucose do you need to dissolve in 200 g water to make a 7.0%(w/w) solution?
- c** What mass of mercury(II) nitrate should be dissolved in 500 mL water to make a 750 ppm solution? 500 mL water is approximately 500 g.
- 14 a** How would you make 250 mL of an aqueous solution of ammonium chloride having a concentration of 3.5 g/100 mL of solution?
- b** How would you make 500 mL of an aqueous solution of ethanol having a concentration of 15.0 mL ethanol per 100 mL solution? What apparatus would you use?
- 15 a** How would you make 250 mL of a 8.0%(w/v) solution of sodium carbonate?
- b** Using the solution in (a), how would you prepare a 0.40% solution of sodium carbonate?
- c** Given a 15 mL/100 mL acetic acid solution, how would you prepare a 6%(v/v) solution using standard glassware?
- 16 a** Some environmentalists wanted a 2.0 ppm solution of lead ions to use as a standard in some pollution monitoring. What mass of lead nitrate would they need to dissolve in exactly 1 litre (1 kg) of water to make such a solution?
- b** What is the problem in making the solution in this way? Suggest a better way of making the required solution.

Let us now turn to a more convenient measure of concentration to use when chemical reactions are involved.

8.9 MOLARITY

As explained in Section 5.9, when we want to calculate quantities involved in chemical reactions, the basic unit is the mole. We read chemical equations in moles not in grams. Therefore it is convenient to have a measure of concentration in terms of moles: it is called molarity.

The **molarity** of a solution is the number of moles of solute per litre of solution.

A molarity of 0.020 mol/L (alternatively written mol L⁻¹) means 0.020 moles of solute in one litre of solution.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in litres}}$$
$$= \frac{\text{number of moles of solute} \times 1000}{\text{volume of solution in millilitres}}$$

... (8.9)

To calculate the number of moles of solute in a particular volume of solution:

$$\left. \begin{aligned} \text{number of moles of solute} &= \text{molarity} \times \text{volume in litres} \\ &= \frac{\text{molarity} \times \text{volume in millilitres}}{1000} \end{aligned} \right\} \dots (8.10)$$

These important equations, along with Equation 5.1:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} \dots (5.1)$$

$$\text{or in symbols } n = \frac{m}{M}$$

are essential for calculations using molarities as the following examples will show.

Example 8

17.54 g of pure barium hydroxide was dissolved in water and made up to 500 mL (0.5000 L) in a volumetric flask. Calculate the molarity of the solution.

$$\begin{aligned} \text{Molar mass of Ba(OH)}_2 &= 137.3 + 2 \times (16.0 + 1.0) \\ &= 171.3 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{Number of moles of Ba(OH)}_2 \text{ used} &= \frac{17.54}{171.3} \\ &= 0.1024 \end{aligned}$$

From Equation 8.9:

$$\begin{aligned} \text{molarity} &= \frac{0.1024}{0.500} \\ &= \mathbf{0.2048 \text{ mol/L}} \end{aligned}$$

Example 9

What mass of pure sulfuric acid, H_2SO_4 , must be dissolved in water and made up to 250 mL in a volumetric flask to make a 0.550 mol/L solution?

$$\begin{aligned} \text{Molar mass of sulfuric acid} &= 2 \times 1.0 + 32.1 + 4 \times 16.0 \\ &= 98.1 \text{ g/mol} \end{aligned}$$

From Equation 8.10:

$$\begin{aligned} \text{number of moles of H}_2\text{SO}_4 \text{ required} &= 0.550 \times 0.250 \\ &= 0.138 \end{aligned}$$

$$\begin{aligned} \text{mass of H}_2\text{SO}_4 \text{ required} &= 0.138 \times 98.1 \\ &= \mathbf{13.5 \text{ g}^{\dagger}} \end{aligned}$$

Example 10

How many **a** moles **b** grams of NaCl are there in 45.3 mL of 0.148 mol/L sodium chloride solution?

[†] 13.49 g may be a marginally better answer in that it more closely reflects the accuracy of the least accurate input quantity, 0.550 mol/L implying $\pm 0.2\%$.

By Equation 8.10:

a number of moles = $0.148 \times \frac{45.3}{1000}$
= 6.70×10^{-3} mol

b molar mass of NaCl = 23.0×35.5
= 58.5 g

By Equation 5.1 (rearranged):

$$\begin{aligned} \text{mass of NaCl} &= 6.70 \times 10^{-3} \times 58.5 \\ &= 0.392 \text{ g} \end{aligned}$$

These three examples illustrate how to convert from mass or moles to molarity and vice versa. Now let us see how to calculate quantities from a reaction.

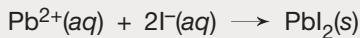


The molarities of these everyday solutions are:
NaCl in sea water, 0.60 mol/L; ammonia, 1.1 mol/L; hydrochloric acid, 8.2 mol/L; acetic acid in vinegar, 0.67 mol/L; chlorine in bleach, 0.56 mol/L; and ethanol in wine, 2.4 mol/L

Example 11

What mass of lead iodide is formed when 25 mL (from a pipette) of a 0.492 mol/L solution of potassium iodide is added to a solution containing excess lead ions?

First we write the equation for the reaction:



$$\begin{aligned} \text{Number of moles of potassium iodide used} &= 0.492 \times \frac{25}{1000} \\ &= 0.0123 \end{aligned}$$

From the chemical equation:

$$\frac{\text{number of moles of PbI}_2 \text{ formed}}{\text{number of moles of KI provided}} = \frac{1}{2}$$



$$\begin{aligned}
 \text{Therefore number of moles of PbI}_2 \text{ formed} &= \frac{1}{2} \times 0.0123 \\
 &= 6.15 \times 10^{-3} \\
 \text{molar mass of PbI}_2 &= 207.2 + 2 \times 126.9 \\
 &= 461.0 \text{ g/mol} \\
 \text{mass of PbI}_2, \text{ formed} &= 6.15 \times 10^{-3} \times 461.0 \\
 &= \mathbf{2.84 \text{ g}}
 \end{aligned}$$

The phrase ‘containing excess lead ions’ is a chemist’s shorthand way of saying that the solution contains more than enough lead ions to react with all the iodide added.



Exercises

- 17** Calculate the molarity of the solutions made by dissolving the following amounts of solute in water and making up to the stated volumes:
- a** 0.20 mole NaCl in 100 mL
 - d** 31.8 g sodium carbonate in 250 mL
 - b** 1.5 mole KNO₃ in 2.0 L
 - e** 5.04 g barium hydroxide in 500 mL
 - c** 0.51 mole Na₂SO₄ in 250 mL
 - f** 11.9 g silver nitrate in 100 mL
- 18** In each of the following, how many moles of the named solute do you need to make the volume of solution indicated?
- a** hydrochloric acid to make 2.00 L 0.400 mol/L solution
 - b** potassium bromide to make 250 mL 0.500 mol/L solution
 - c** copper sulfate to make 250 mL 2.50×10^{-3} mol/L
- 19** In each of the following, what mass of solute is needed to make the stated solution?
- a** hydrochloric acid to make 5.00 L 0.200 mol/L solution
 - b** sodium hydroxide to make 0.250 L 1.50 mol/L solution
 - c** sodium carbonate to make 2.0 L 7.25×10^{-2} mol/L solution
- 20** State how many moles of solute there are in:
- a** 25 mL 0.106 mol/L NaOH
 - c** 50 mL 0.055 mol/L MgCl₂
 - b** 7.2 mL 0.048 mol/L NaNO₃
 - d** 1.83 L 0.36 mol/L NaI
- 21** How many grams of solute are there in (a) and (c) of Exercise 20?
- 22** **a** How many moles of:
- i** calcium chloride **ii** calcium ions **iii** chloride ions
- are there in 17.7 mL 0.0330 mol/L calcium chloride solution?
- b** How many moles of:
- i** sodium sulfate **ii** sulfate ion **iii** sodium ion
- are there in 38.4 mL 0.110 mol/L sodium sulfate solution?
- 23** The volumes of solutions given in Column A in the following table were accurately diluted to the volumes in Column B. Calculate the molarity of the diluted solutions.

Column A	Column B
a 50 mL 0.106 mol/L NaCl	500 mL
b 25 mL 0.223 mol/L KOH	1 L
c 100 mL 0.304 mol/L Na ₂ SO ₄	250 mL
d 10 mL 1.52 mol/L HNO ₃	500 mL

- 24** The solutions listed under 'Solution A' in the table below are provided and it is required to prepare between 250 mL and 2 L of accurately diluted solutions having the concentrations given in Column B. Using only standard-sized volumetric glassware, what volumes of Solutions A should be diluted to what volumes to give the required concentrations?

Solution A	Column B
a 0.143 mol/L	0.0143 mol/L
b 1.260 mol/L	0.0315 mol/L
c 2.00 mol/L	0.400 mol/L

- 25** How many moles of Substance A below would be formed when an excess of a solution of the substance in Column B was added to the solution in Column C?

Substance A	Column B	Column C
a barium sulfate	sodium sulfate	50 mL 0.326 mol/L barium chloride
b lead bromide	lead nitrate	25 mL 0.509 mol/L sodium bromide
c iron(III) hydroxide	iron(III) nitrate	75 mL 0.087 mol/L NaOH

- 26** What mass of Substance A is formed in **a** and **c** in Exercise 25?

- 27** To measure the concentration of magnesium ion in a solution an analyst took 50 mL of the solution and added sodium hydroxide solution until no further precipitate (of magnesium hydroxide) formed. The precipitate was filtered off, dried and weighed: it had a mass of 1.72 g.

- a** What was the molarity of magnesium ion in the original solution?
- b** How many grams of magnesium ion were there per litre in the original solution?

- 28** What was the molarity of:

- a** silver ion in a solution, 50 mL of which produced 1.87 g silver chloride when excess sodium chloride solution was added to it?
- b** lead ion in a solution, 25 mL of which produced 3.19 g lead iodide when excess potassium iodide was added to it?

- 29** What was the concentration of lead ions in g/100 mL of solution in **b** of Exercise 28?

8.10 THERMAL PROPERTIES OF WATER

Having looked at several properties of water, its role as a solvent and its involvement in precipitation reactions, let us now turn to its thermal properties. In Section 7.1 it was pointed out that both industry and living organisms use water as a heat transfer fluid (to carry heat from one place to another) and as a temperature moderator (to maintain uniform temperatures despite fluctuations in environmental temperatures).

Water does these jobs effectively because:

- compared to other liquids, water has a relatively high thermal conductivity
- water has a high heat capacity—it can hold a large quantity of heat.

Let us clarify what is meant by heat capacity in particular, and quantity of heat in general.

8.11 TEMPERATURE, QUANTITY OF HEAT AND HEAT CAPACITY

Humans have the physiological sensation of hotness or coldness. The physical quantity used as a measure of this sensation is temperature.

Temperature is a measure of the degree of hotness or coldness of an object or substance. The hotter the object, the higher its temperature.

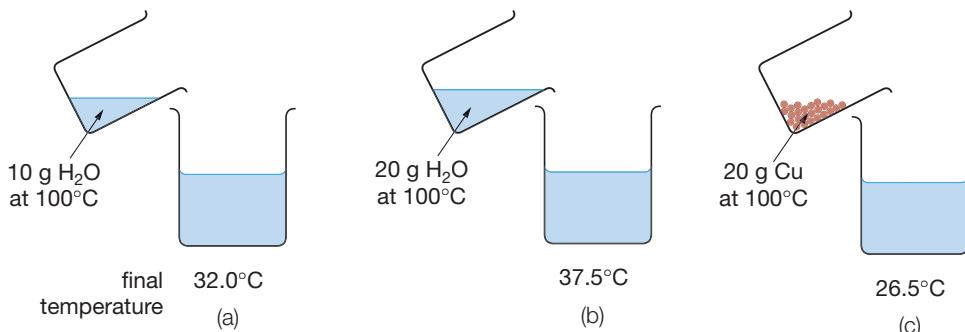
If two objects or samples of material are brought into contact, *heat will flow from the hot object to the cold one until the temperature of the two objects is equal*. When the temperature is uniform throughout both objects or samples of material, we say that **thermal equilibrium** has been reached.

Quantity of heat

Amount of heat (or **quantity of heat**) is different from temperature: two objects can be at the same temperature but contain very different amounts of heat. Consider a red-hot pin and a red-hot horseshoe—both have the same temperature but they contain very different quantities of heat. This is demonstrated by the experiments in Figure 8.7.

Three well-insulated beakers each contain 100 g of water at 25.0°C. To the first is added 10 g of water at 100°C, to the second is added 20 g of water at 100°C, and to the third is added 20 g of copper at 100°C. After mixing, the final temperatures are 32.0°C, 37.5°C and 26.5°C respectively.

FIGURE 8.7
Experiment demonstrating that quantity of heat depends upon mass, (a) and (b), and nature of substance, (b) and (c)



Since the final temperature in (b) is greater than in (a) of Figure 8.7, we conclude that the 20 g of water contains more heat than the 10 g of water. More refined experiments show that:

the amount of heat energy is proportional to the mass of the substance involved.

Comparison of (b) and (c) in Figure 8.7 shows that the 20 g of water contains more heat than the 20 g of copper. This and other experiments show that:

the amount of heat energy contained in equal masses of different substances depends upon the nature of the substances involved.

These observations lead to the following definition:

The **specific heat capacity**, C , of a substance is the amount of heat required to raise the temperature of unit mass of the substance by 1°C (or through 1 kelvin).

Specific heat capacity is therefore measured in joules per kelvin per gram, $\text{J K}^{-1} \text{ g}^{-1}$. Specific heat capacities of some common liquids are shown in Table 8.2. Others were listed in Table 7.2 on page 185.

High specific heat capacity of water

Tables 8.2 and 7.2 show that water has a much higher specific heat capacity than other common liquids. Consequences of this are that:

- water plays an important role in regulating the temperature of organisms and the environment of Earth generally as will be discussed in Section 8.13, and
- water is widely used to measure energy changes in chemical reactions, as will be explained in Section 10.3.

TABLE 8.2 Specific heat capacities of some common pure liquids
(see also Table 7.2 on page 185)

Substance	Specific heat capacity ($\text{J K}^{-1} \text{ g}^{-1}$)	Substance	Specific heat capacity ($\text{J K}^{-1} \text{ g}^{-1}$)
water	4.18	acetic acid	2.03
hydrogen peroxide	2.62	ethyl acetate	1.94
ethanol	2.44	toluene	1.68
ethylene glycol	2.39	carbon disulfide	0.99
octane (in petrol)	2.22	chloroform	0.96
acetone	2.17	gallium (<i>l</i> , $>30^\circ\text{C}$)	0.37
		mercury	0.14

Calculating quantities of heat

Specific heat capacities allow us to calculate the quantities of heat that flow from one object or substance to another.

From the above definition of specific heat capacity, when an object or a sample of a substance undergoes a change in temperature, the quantity of heat involved q is given by:

$$q = m C \Delta T \quad \dots (8.11)$$

where m is the mass, C the specific heat capacity and ΔT is the change in temperature:

$$\Delta T = \text{final temperature} - \text{initial temperature}$$

If temperature increases (ΔT positive), q is positive, which means that the object has gained heat. If temperature falls (ΔT negative), q is negative which means that the object has lost heat.

Let us illustrate this equation for quantity of heat with an example.



Example 12

Calculate the quantity of heat needed to raise the temperature of 155 g water from 17.0°C to 35.5°C.

We use Equation 8.11 along with the specific heat capacity in Table 8.2:

$$\begin{aligned}\text{amount of heat required} &= 155 \times 4.18 \times (35.5 - 17.0) \text{ g J K}^{-1} \text{ g}^{-1} \text{ K} \\ &\quad (\text{for temperature changes, } 1^\circ\text{C} = 1 \text{ K}) \\ &= 1.20 \times 10^4 \text{ J} (= 12.0 \text{ kJ})\end{aligned}$$



Exercises

- 30 What quantity of heat is needed to heat 1.00 kg water from 20°C to 100°C?
- 31 Using data from Table 8.2, calculate the amount of heat needed to increase the temperature of:
- a 25 g acetone from 18°C to 55°C
 - b 25 g mercury from 18°C to 55°C
 - c 250 g water through 36°C
 - d 150 g chloroform from 25°C to 50°C
 - e 3.5 g ethanol through 47 K
 - f 1.5 kg ethylene glycol through 54°C
- 32 A small electrical immersion heater was used to heat 125 g ethanol from 18.0°C to 23.6°C. The heater provided 1.73 kJ of energy. Calculate the specific heat capacity of ethanol. Assume that all the energy was used to heat the ethanol and that there were no losses to the surroundings.

8.12 HEAT CHANGES WHEN SUBSTANCES DISSOLVE

The nature of aqueous solutions of ionic and molecular substances was described in Sections 7.9 and 7.11.

When ionic substances dissolve in water, there is usually a noticeable change in temperature.

When sodium hydroxide dissolves in water, the solution heats up. The dissolution process releases heat, which then warms up the solution.

Processes that release heat are called **exothermic**.

The dissolution of sodium hydroxide is exothermic. Similarly, dissolving lithium bromide or sulfuric acid in water is exothermic.

When potassium nitrate dissolves in water, the solution cools. Dissolving potassium nitrate in water requires an input of energy; this energy is taken from the normal thermal energy of the water and solid substance, so the mixture (solution) becomes colder.

Processes that absorb heat are called **endothermic**.

The dissolution of potassium nitrate in water is endothermic. Similarly, dissolving ammonium chloride or silver nitrate is endothermic.

A special term is used for the heat change that accompanies the dissolution of a substance—the molar heat of solution.

Molar heat of solution

The **molar heat of solution**, ΔH_{soln} , of a substance is the heat absorbed when one mole of the substance dissolves in a large excess of water.

If ΔH_{soln} is positive, the process is endothermic (heat is absorbed: the temperature falls).

If ΔH_{soln} is negative, the process is exothermic (heat is released: the temperature rises).

We can calculate the molar heat of solution for a substance by measuring the temperature change when a known mass of the substance is dissolved in water.

Example 13

- a When 11.2 g sodium hydroxide at 19.2°C was dissolved in 200 mL water also at 19.2°C, the temperature rose to 31.4°C. Calculate the molar heat of solution of sodium hydroxide. Take the specific heat capacity of the final solution as $4.2 \text{ J K}^{-1} \text{ g}^{-1}$.

From the rise in temperature and the known mass of the solution we can calculate the quantity of heat released by the dissolution process.

$$\begin{aligned}\text{Mass of the final solution} &= 200 + 11.2 \quad (\text{200 mL water} = 200 \text{ g}) \\ &= 211.2 \text{ g}\end{aligned}$$

From Equation 8.11:

$$\begin{aligned}\text{heat released} &= 211.2 \times 4.2 \times (31.4 - 19.2) \\ &= 1.08 \times 10^4 \text{ J}\end{aligned}$$

This is the heat released by 11.2 g; we want the heat released by 1 mole.

$$\begin{aligned}\text{Molar mass of sodium hydroxide, NaOH} &= 23.0 + 16.0 + 1.0 \\ &= 40.0 \text{ g/mol}\end{aligned}$$

$$\begin{aligned}\text{Heat released by 1 mole NaOH} &= \frac{40.0}{11.2} \times 1.08 \times 10^4 \\ &= 3.86 \times 10^4 \text{ J/mol} \\ &= 39 \text{ kJ/mol}\end{aligned}$$

(only two significant figures are justified because of the 4.2)

Hence we can say that heat *absorbed* = -39 kJ/mol

$$\therefore \text{molar heat of solution, } \Delta H_{\text{soln}} = \mathbf{-39 \text{ kJ/mol}}$$

- b Use this heat of solution to calculate the expected temperature rise when 23.6 g sodium hydroxide is dissolved in 1.00 L (= 1000 g) water.

$$\begin{aligned}\text{Number of moles of NaOH used} &= \frac{23.6}{40.0} \\ &= 0.590 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Heat released when this NaOH dissolves} &= 0.590 \times 3.9 \times 10^4 \text{ J} \\ &= 2.30 \times 10^4 \text{ J}\end{aligned}$$

This heat warms up $1000 + 23.6 = 1023.6 \text{ g}$ of solution.

We calculate the temperature rise by using Equation 8.11 in the form:

$$\begin{aligned}\Delta T &= \frac{q}{m \times C} \\ &= \frac{2.30 \times 10^4}{1023.6 \times 4.2} \\ &= \mathbf{5.3^\circ\text{C}}\end{aligned}$$



Exercises

33 When 50 g of each of the following substances is dissolved in 250 mL water, the temperature rises or falls as indicated:

- a** sodium carbonate (temperature rises) **c** potassium iodide (temperature falls)
- b** barium nitrate (temperature falls) **d** magnesium sulfate (temperature rises)

For each substance, is the dissolution process exo- or endothermic and what is the sign of ΔH_{soln} , the heat of solution? For any that are endothermic, explain why the temperature rises or falls.

34 Calculate the molar heat of solution for the ionic substance involved in each of the following experiments which were carried out in well insulated plastic beakers using a thermometer which read to 0.1°C. Take the specific heat capacity of the final solutions as 4.2 J K⁻¹ g⁻¹.

- a** 5.3 g calcium chloride was dissolved in 250 mL (= 250 g) water at 18.6°C. The temperature rose to 22.0°C.
- b** 5.6 g sodium thiosulfate pentahydrate, Na₂S₂O₃.5H₂O (photographic hypo or fixer) was dissolved in 100 mL (= 100 g) water at 20.1°C. The temperature fell by 2.3°C.
- c** 8.3 g barium chloride was dissolved in 200 mL (= 200 g) water at 19.5°C. The temperature rose to 20.2°C.

* **35** The magnitudes of the values obtained for the molar heat of solution in the experiments of Exercise 34 were low compared with accepted literature values. Identify sources of error in these experiments and suggest ways of modifying the experiments to minimise or eliminate such errors.

- 36 a** Calculate the rise in temperature when 10 mL (= 18.4 g) concentrated sulfuric acid (98% pure) at room temperature is added to 100 mL (= 100 g) water at the same temperature. The molar heat of solution of concentrated sulfuric acid is -90 kJ/mol. Use 4.2 J K⁻¹ g⁻¹ for the specific heat capacity of the final solution.
- b** What will be the final temperature when 23.6 g ammonium nitrate is dissolved in 100 mL (= 100 g) water with both the water and solid being at 18.4°C? The molar heat of solution of ammonium nitrate is +26 kJ/mol. The specific heat capacity of the final solution is 4.2 J K⁻¹ g⁻¹.

8.13 CONSEQUENCES OF THE THERMAL PROPERTIES OF WATER FOR LIVING ORGANISMS

Living organisms can survive and reproduce only if their temperatures are maintained within fairly narrow ranges. Water within cells provides the necessary temperature regulation (that is, it smooths out rapid or large temperature fluctuations). It does this because of its:

- *high heat capacity* (large quantities of heat absorbed produce only small temperature rises)
- *high thermal conductivity* relative to other liquids (quickly removes heat from a hot location to a cooler one),

and because:

- water is such a *large proportion* of most living organisms.

For aquatic organisms the high heat capacity of water means that their environment (oceans, lakes, rivers) maintains a much more stable temperature

than the surrounding atmosphere or land. Stable temperatures allow aquatic organisms to thrive.

On a broader scale, the fact that water is such a large component of the biosphere means that it (mainly in the form of oceans) has a moderating influence on global temperatures, smoothing out the day-to-night and summer-to-winter fluctuations. This produces a more hospitable environment for all life forms including humans.

8.14 THERMAL POLLUTION

Thermal pollution is the discharge into a river or lake of quantities of hot water that are large enough to increase significantly the temperature of the water body. A 2 to 5°C increase can be ‘significant’.

Thermal pollution occurs when river or lake water is used for cooling in industry or electricity generation. Typically, cooling water is pumped from the natural water body through the factory or power station, then discharged back to the river or lake. The discharged water is typically 10 to 15°C hotter than the intake water. If the amount of water used is a significant proportion of the water in the river or lake, then the returning hot water can increase the temperature of the river or lake quite significantly.

One problem associated with thermal pollution concerns dissolved oxygen. Although for most solids and liquids solubility increases as temperature increases, for gases solubility in water *decreases* as temperature increases. This means that increasing the temperature of a natural waterway lowers the concentration of oxygen in the water. A 5°C increase in temperature can lower the oxygen concentration by about 10 to 15%. This harms aquatic life (particularly fish).

The detrimental effects of increased water temperature are:

- Less dissolved oxygen causes stress to organisms.
- Increased metabolism rates (because rates of chemical reactions generally increase as temperature increases) increase the demand for oxygen and so aggravate the low dissolved oxygen problem.
- Fish eggs do not develop or hatch if temperature is too high.
- False temperature cues are given to aquatic life, thus setting off migration and spawning at wrong times of the year.
- Lethal temperature limits may be exceeded (particularly in times of low flow in rivers).
- *Sudden* temperature changes (resulting from turning cooling on or off) can kill fish eggs even when the temperature change is within the survival range of the eggs.

Thermal pollution is a concern for the electricity generating stations on the shallow lakes along the NSW Central Coast (Lake Macquarie, Munmorah Lake and Tuggerah Lake). Thermal pollution is rarely a problem when the open ocean is used, because currents and tidal action effectively mix and disperse warm water discharges and so prevent any significant temperature rises.

Ways of combating thermal pollution include using cooling towers so that cooling water is completely recycled, and using cooling ponds (artificial lakes used exclusively for the power station).

CHAPTER 8

Important new terms

You should know the meaning of the following terms:

concentration (p. 208)
dilution (p. 215)
dynamic equilibrium (p. 209)
endothermic (p. 224)
exothermic (p. 224)
forward reaction (p. 210)
molar heat of solution (p. 224)
molarity (p. 217)
parts per million, ppm (p. 213)
per cent by weight, %(*w/w*) (p. 213)
phase descriptors (p. 207)

precipitate (p. 202)
precipitation reaction (p. 202)
quantity of heat (p. 222)
reverse reaction (p. 210)
reversible reaction (p. 210)
saturated solution (p. 208)
specific heat capacity (p. 222)
solubility (p. 208)
state symbols (p. 207)
temperature (p. 222)
thermal equilibrium (p. 222)
thermal pollution (p. 227)
unsaturated solution (p. 208)

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Why do precipitates form?
- 3 Write net ionic equations for three precipitation reactions.
- 4 Write three different equations for the reaction between aluminium chloride and sodium hydroxide solutions.
- 5 How can you tell whether a solution is saturated?
- 6 When a saturated solution of an ionic substance is in contact with some of the solid substance, what if anything is occurring at the particle level? What is the evidence for this?
- 7 Give an example of a reversible reaction and write an equation for it.
- 8 Why do some reversible reactions not go to completion?
- 9 List eight methods of giving the concentration of a solution.
- 10 15 g sodium chloride was dissolved in 50 g water. What is the concentration
a in g/100 g water **b** %(*w/w*)?
- 11 What apparatus would you use to make **a** an approximate 25-fold dilution **b** an accurate 25-fold dilution of a solution?
- 12 How do you calculate the molarity of a solution?
- 13 How do you calculate the number of moles in a given volume of a solution of known molarity?
- 14 How do you calculate quantity of heat from temperature change and specific heat capacity?
- 15 How do the specific heat capacity and thermal conductivity of water compare with those of other common liquids?
- 16 How do the thermal properties of water benefit living organisms?

- 17** What is the sign (+ve or -ve) of the heat of solution, ΔH_{soln} , for
a an endothermic **b** an exothermic dissolution?
- 18** What human activities produce thermal pollution? Under what conditions is thermal pollution most severe? What are the adverse effects of thermal pollution?

EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 3

For explanations about these New South Wales HSC exam-style questions, see p. 84.

MARKS

- 1 **Outline** the importance of water for living matter on Earth. 4
- 2 **Discuss** the importance of water as a solvent for living matter and for the industrial activities of humans. 6
- 3 **Explain** how you could measure the density of ice. What would be the main sources of error in this method, and how could you minimise them? 6
- 4 **Compare** the molecular weights and melting and boiling points of water and hydrogen sulfide. What can you **deduce** from these comparisons about the intermolecular and/or intramolecular forces in these two substances? 4
- 5 **Describe** an experiment you have performed to determine the effect of a solute such as ethylene glycol (anti-freeze) or common salt upon the boiling point of water. What was the effect? What (if any) quantitative or semi-quantitative observation did you make? 5
- 6 **Explain** with an example what is meant by hydrogen bonding and **outline** its effect upon physical properties of substances. 4
- 7 **Explain** how the boiling points of the hydrides of the elements of Groups 4 and 6 can be used as evidence for the existence of hydrogen bonding in water. 4
- 8 **Assess** the importance of molecular shape and bond polarity in determining the strength of intermolecular forces. 3
- 9 **Explain** why **a** water has a greater density than ice and **b** why the density of water passes through a minimum (at about 4°C). 4
- 10 **Describe** experiments that you have performed to **demonstrate** the surface tension and viscosity of water relative to the surface tension and viscosity of other liquids. How did your results for water **compare** with those of the other liquids? 5
- 11 **Describe** what happens on the particle (molecule or ion) level, and **explain** why it happens, when **a** sodium chloride **b** sucrose and **c** iodine dissolves in water. 6
- 12 **Describe** an experiment you have performed to test the solubilities in water of various compounds that are typical of the categories into which we commonly classify compounds, namely ionic, covalent molecular, covalent network and very large molecular. **Summarise** your conclusions about the water solubilities of substances in these various categories. 6
- 13 **Evaluate** the usefulness of a table of solubilities of different types of ionic compounds for deciding whether precipitates will form when solutions of ionic substances are mixed. 3

- 14** **Explain** with an example what is meant by a dynamic equilibrium. In addition, **explain** how the dynamic nature of one particular equilibrium could be demonstrated. **4**
- 15** **Justify** the use of many different measures of concentration of solutions. Mention at least four different measures. **4**
- 16** **Describe** an experiment you have performed to determine the solubility or insolubility of ionic compounds using precipitation reactions. Include a suitable table (headings, not specific results) for recording your results. What was the major potential source of error in your experiment and how did you avoid it? **6**
- 17** **Evaluate** the usefulness of including state symbols (phase descriptors) such as (s) (l) (g) (aq) in chemical equations. **3**
- 18** **Describe** an experiment you performed using a solid solute to prepare an aqueous solution of accurately known mass per unit volume of solution. In addition, **describe** how you carried out several stepwise dilutions of this solution in order to get a final solution with an accurately known concentration about 500 to 1000 times more dilute than the starting solution. Make sure that you name the pieces of apparatus you used at each stage of the experiment. **5**
- 19** **Outline** the problems associated with the discharge of hot water from factories and power stations into natural water bodies, and assess their significance for aquatic life in **a** small rivers and inland lakes and **b** oceans. **6**
- 20** **Discuss** the effectiveness of water as a heat transfer and temperature moderating agent in living organisms. **4**

REVISION TEST FOR MODULE 3

Total marks: 50 Suggested time: 90 minutes

- *Table 8.1 Solubility of ionic compounds (p. 205) may be consulted during this test.*
- *The order of decreasing electronegativities of common elements is:*



MULTIPLE CHOICE QUESTIONS (1 mark each)

Select the alternative **a**, **b**, **c**, or **d** which best answers the question.

- 1 Water has a higher boiling point than hydrogen sulfide (100°C as against -62°C) because:
 - a the OH covalent bonds in water are stronger than the SH ones in hydrogen sulfide
 - b water is a heavier molecule than hydrogen sulfide
 - c there are stronger intermolecular forces in water than in hydrogen sulfide
 - d water is a polar molecule whereas hydrogen sulfide is not
- 2 A solution of silver nitrate was made by dissolving 10.80 g silver nitrate in water and making the volume to 250 mL. The molarity of silver ions in this solution is:

a 0.400	c 0.254
b 0.0159	d 2.54×10^{-4}
- 3 The heat of solution of calcium chloride, ΔH_{soln} , is -75 kJ/mol . The specific heat capacity of water is $4.2 \text{ J K}^{-1} \text{ g}^{-1}$. When 0.020 mol calcium chloride is mixed with 100 g water, the temperature of the mixture will:

a increase by 0.0036°C	c decrease by 3.6°C
b increase by 3.6°C	d increase by 0.36°C
- 4 The pair of substances in aqueous solutions which will not form a precipitate when mixed is:
 - a magnesium chloride and sodium hydroxide
 - b sodium bromide and silver nitrate
 - c copper sulfate and sodium sulfide
 - d sodium nitrate and potassium carbonate
- 5 Samples of pure water and seawater were boiled in open beakers with the temperature of each boiling sample being measured as a function of time. Boiling continued until about 70% of the initial samples had boiled away. The temperature measurements during the experiment showed that:
 - a both temperatures remained constant
 - b both temperatures gradually increased
 - c the temperature of the pure water increased while that of the seawater decreased
 - d the temperature of the pure water remained constant while that of the seawater increased
- 6 The group of substances that are all soluble in water is:
 - a hydrogen peroxide (H_2O_2), boron trichloride, methane (CH_4)
 - b hydrogen bromide, hydroxylamine (H_2NOH), glucose

- c** sulfur hexafluoride, trichloromethane, sulfur dioxide
d ammonia, phosphine (PH_3), hydrogen chloride
- 7** 0.20 mol aluminium nitrate is dissolved in water and the volume made to 500 mL in a volumetric flask. The correct statement is:
- a** The concentration of nitrate ion is 0.30 mol L^{-1} .
b The concentration of aluminium ions is 0.10 mol L^{-1} .
c The concentration of nitrate ions is 1.2 mol L^{-1} .
d The concentration of aluminium ions is 0.13 mol L^{-1} .
- 8** When 1.00 g magnesium chloride dissolved in 200 mL water is added to excess silver nitrate solution, the number of moles of silver chloride formed is:
- a** 2.1×10^{-2} **c** 1.05×10^{-2}
b 1.05 **d** 5.25×10^{-3}
- 9** A person decided to take a bath using 250 L (= 250 kg) water at 46°C . The quantity of heat needed to heat this amount of water from 16°C to 46°C is:
- a** 31.4 kJ **c** $7.5 \times 10^3 \text{ kJ}$
b $3.14 \times 10^4 \text{ kJ}$ **d** 7.5 kJ
- 10** The most important properties of water that make it very effective in removing heat from living organisms and in smoothing out temperature fluctuations are:
- a** thermal conductivity and viscosity
b specific heat capacity and surface tension
c viscosity and surface tension
d specific heat capacity and thermal conductivity

SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- | | MARKS |
|--|-------|
| 11 a The molar mass of lead nitrate is 331.2 g/mol. What mass of lead nitrate is needed to make 250 mL 0.200 mol/L solution of lead nitrate? | 1 |
| b What volume of this 0.200 mol/L lead nitrate solution is just sufficient to react with all the iodide in 25 mL 0.247 mol/L potassium iodide solution? | 2 |
| 12 Draw electron-dot structures for water, ammonia and hydrogen sulfide and evaluate their usefulness in predicting physical properties of these substances. | 4 |
| 13 Assess the validity of the suggestion that the polarity of the water molecule is the major factor in determining the solubility of substances in water. | 4 |
| 14 Aqueous solutions of the following substances are provided:
sulfuric acid, magnesium chloride, copper nitrate, sodium hydroxide, barium bromide
a Without using the same solution twice, choose two pairs of solutions which would form a precipitate when mixed. | 1 |

- b** For one precipitate write a net ionic equation. 1
- c** For the other precipitate write a complete ionic equation. 1
- d** For one of the precipitation reactions name the spectator ions. 1
- 15** Describe an experiment you have performed to determine the heat of solution of a substance. List the quantities that you measured and explain how you used them to calculate the heat of solution. What were the main sources of error in your experiment and what steps did you take to minimise them? 7
- 16** 1.20×10^{-3} mol mercury(II) nitrate was dissolved in water and the volume made to 100.0 mL. 5.00 mL of this solution was diluted to 1.000 L to form Solution A.
- a** Calculate the molarity of solution A. 2
- b** Name and sketch the piece of glassware you would use:
- i** to measure out the 5.00 mL of solution
 - ii** for making up the 1.000 L of diluted solution 1
- 17** From the following list of substances:
- | | |
|---|-----------------------------------|
| hydrogen peroxide, H_2O_2 | tetrafluoromethane, CF_4 |
| sodium hydroxide | silicon dioxide |
| phosphorus trichloride | hydrogen sulfide |
- a** Choose *one* substance in which hydrogen bonding occurs. Draw a diagram (structure) including at least three molecules to show how it occurs. 2
- b** Name a substance from the list in which the only intermolecular forces are
- i** dispersion forces
 - ii** dipole–dipole interactions (excluding hydrogen bonds) plus dispersion forces 2
- 18 a** A saturated solution of calcium sulfate was prepared with a significant amount of solid calcium sulfate remaining in the bottom of the test tube. If 0.1 g calcium sulfate solid labelled with radioactive sulfur-35 were added and the mixture thoroughly shaken for many minutes:
- i** would the concentration of Ca^{2+} in the solution increase, decrease or remain the same?
 - ii** would any radioactivity be detected in the solution (after filtering off the solid)?
- Explain both of your answers fully. 3
- b** 100 mL 0.022 mol/L calcium chloride solution was mixed with 100 mL 0.022 mol/L sodium sulfate solution. The mixture was shaken thoroughly but remained clear (no precipitate formed). Calculate the concentration of calcium ions and sulfate ions in the mixed solution. (The effect on calcium ion concentration of mixing its solution with the sulfate ion solution is the same as mixing it with pure water: similarly for the sulfate ion.) 1
- c** 100 mL 0.026 mol/L calcium chloride solution was mixed with 100 mL 0.026 mol/L sodium sulfate solution. After shaking the mixture, it became turbid (a small amount of precipitate formed). Comparing results in **b** and **c**, what can you say about the magnitude of the solubility of calcium sulfate (in mol/L)? Explain your reasoning. 2
- 19** Compare the physical states and relative amounts of water in the atmosphere, hydrosphere, lithosphere and in living matter. 6

MODULE 3 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 3 of the New South Wales HSC Preliminary Course syllabus.

Syllabus content

The following table lists (for Module 3) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry Preliminary Course (CCPC)*.

Location of HSC syllabus Preliminary Course material in *Conquering Chemistry* for Module 3

Syllabus reference	Sections where found in CCPC
Students learn to:	
8.4.1 Water is distributed on Earth as a solid, liquid and gas	
■ define the terms, solute, solvent and solution	7.8
■ identify the importance of water as a solvent	7.8
■ compare the state, percentage and distribution of water in the biosphere, lithosphere, hydrosphere and atmosphere	Introduction to Chapter 7
■ outline the significance of the different states of water on Earth in terms of water as: <ul style="list-style-type: none">– a constituent of cells and its role as both a solvent and a raw material in metabolism– a habitat in which temperature extremes are less than in nearby terrestrial habitats– an agent of weathering of rocks both as liquid and as solid– a natural resource for humans and other organisms	7.1
8.4.2 The wide distribution and importance of water on Earth is a consequence of its molecular structure and hydrogen bonding	
■ construct Lewis electron-dot structures of water, ammonia and hydrogen sulfide to identify the distribution of electrons	7.3
■ compare the molecular structure of water, ammonia and hydrogen sulfide, the differences in their molecular shapes and in their melting and boiling points	7.3
■ describe hydrogen bonding between molecules	7.6
■ identify the water molecule as a polar molecule	7.4
■ describe the attractive forces between polar molecules as dipole–dipole forces	7.5
■ explain the following properties of water in terms of its intermolecular forces: <ul style="list-style-type: none">– surface tension– viscosity– boiling and melting points	7.2, 7.7

Syllabus reference Students learn to:	Sections where found in CCPC
8.4.3 Water is an important solvent in biological systems, transporting materials into and out of cells.	
<ul style="list-style-type: none"> ■ explain changes, if any, to particles and account for those changes when the following types of chemicals interact with water <ul style="list-style-type: none"> - a soluble ionic compound such as sodium chloride 7.9, 7.10 - a soluble molecular compound such as sucrose 7.11 - a soluble or partially soluble molecular element or compound such as iodine, oxygen or hydrogen chloride 7.11, 7.12 - a covalent network structure substance such as silicon dioxide 7.11 - a substance with large molecules, such as cellulose or polyethylene 7.11 ■ analyse the relationship between the solubility of substances in water and the polar nature of the water molecule 7.13 	
8.4.4 The concentration of salts in water will vary according to their solubility, and precipitation can occur when the ions of an insoluble salt are in solution together	
<ul style="list-style-type: none"> ■ identify some combinations of solutions which will produce precipitates, using solubility data 8.1, 8.2 ■ describe a model that traces the movement of ions when solution and precipitation occur 8.6 ■ identify the dynamic nature of ion movement in a saturated dissolution 8.6 ■ describe the molarity of a solution as the number of moles of solute per litre of solution using: $c = \frac{n}{V}$ ■ explain why different measurements of concentration are important 8.9 	
8.4.5 Water has a higher heat capacity than many other liquids	
<ul style="list-style-type: none"> ■ explain what is meant by the specific heat capacity of a substance 8.13 ■ compare the specific heat capacity of water with a range of other solvents 8.13 ■ explain and use the equation $\Delta H = -mC\Delta T$ ■ explain how water's ability to absorb heat is used to measure energy changes in chemical reactions 8.14 ■ describe dissolutions which release heat as exothermic and give examples 8.14 ■ describe dissolutions which absorb heat as endothermic and give examples 8.14 ■ explain why water's ability to absorb heat is important to aquatic organisms and to life on Earth generally 8.12, 8.15 ■ explain what is meant by thermal pollution and discuss the implications for life if a body of water is affected by thermal pollution 8.16 	

Compulsory experiments

The table below lists the compulsory experiments for Module 3 (from the right-hand column of the syllabus), along with places where you can find procedures for performing them (in *CCPC BLM*) and the location of relevant information in *CCPC*.

CCPC is an abbreviation for this book *Conquering Chemistry Preliminary Course*.

CCPC BLM is *Conquering Chemistry Preliminary Course Blackline Masters* by Debra Smith, McGraw-Hill Australia, Sydney, 2003.

Information about compulsory experiments for Module 3

Experiment	Location in CCPC BLM	Related material in CCPC
1 Determine the effect of anti-freeze or salt on the boiling point of water	Module 3 Worksheet 3 (page 113)	Chapter 7 exercise 4 Exam-style question 5
2 Demonstrate the surface tension and viscosity of water	Module 3 Worksheet 5 (page 117)	Sections 7.2, 7.7 Exam-style question 10
3 Investigate the solubilities in water of a range of substances that include ionic and molecular substances, covalent network solids and large molecules	Module 3 Worksheet 8 (page 127)	Sections 7.9, 7.11, 7.12, 7.13 Exam-style question 12
4 Determine the solubility or insolubility of salts of common metals using precipitation reactions	Module 3 Worksheet 10 (page 133)	Sections 8.1, 8.2, 8.3 Exam-style question 16
5 Prepare solutions of accurately known concentrations and carry out quantitative dilutions of them	Module 3 Worksheet 15 (page 150)	Chapter 8, Section 8.8 and Examples 5, 6, 7 Exam-style question 18
6 Measure temperature changes when substances dissolve in water and calculate a molar heat of solution	Module 3 Worksheet 18 (page 156)	Chapter 8, Section 8.12 and Example 13 Revision test question 15

Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

Location of material for other Module 3 activities

Syllabus item	Relevant material in CCPC
8.4.1	■ perform an investigation involving calculations of the density of water ... See also the experiment (not compulsory) in <i>CCPC BLM</i> Module 3 Worksheet 1 (page 106)
■ analyse information by using models to account for the differing densities of ice and liquid water ...	Figures 7.5, 7.6 and 7.9 may help Exam-style question 9
■ Experiment 1 (see above)	
8.4.2	■ process information ... to graph and compare the boiling and melting points of water ... Chapter 7, Figure 7.7 and Exercises 9, 10

Syllabus item	Relevant material in CCPC
■ identify data ... to model the structure of the water molecule and effects of forces between water molecules ...	Figures 7.1, 7.2, 7.3, 7.5, 7.6 may help
■ Experiment 2 (see above)	
8.4.3 ■ Experiment 3 (see above)	
■ process information ... to visualise the dissolution in water of various types of substances and solve problems by ...	Figures 7.9, 7.10, 7.11, 8.4 may help
8.4.4 ■ construct ionic equations ...	Sections 8.1, 8.4, 8.6
■ present information in balanced chemical equations and identify the appropriate phase descriptors ...	Section 8.4
■ Experiment 4 (see above)	
■ carry out simple calculations to describe the concentration of given solutions ...	Chapter 8, Section 8.8 and Examples 5, 6, 7
■ Experiment 5 (see above)	
■ calculate mass and concentration relationships in precipitation reactions ...	Chapter 8, Section 8.9 and Example 11
8.4.5 ■ Experiment 6 (see above)	
■ process ... information ... to assess the limitations of calorimetry experiments and design modifications ...	Chapter 8 Exercise 35 Revision test question 15

Prescribed focus areas

The five prescribed focus areas of the syllabus are listed on page 94.

The material of Module 3 (in this book and in the syllabus) relates almost exclusively to Areas 2 and 3, the nature and practice of chemistry and applications and uses of chemistry. There is some scope for discussing implications for society and the environment in treating the role of water in the Earth, the expansion of water as it freezes, thermal properties of water and thermal pollution, but very little scope for discussing history of chemistry or current issues, research and development. Topics where applications and uses of chemistry can be discussed include the effects of ethylene glycol and salt on the boiling and freezing points of water, the use of different measures of concentration (in commercial products) and the relevance of heat of solution to portable hot and cold packs used by athletes.