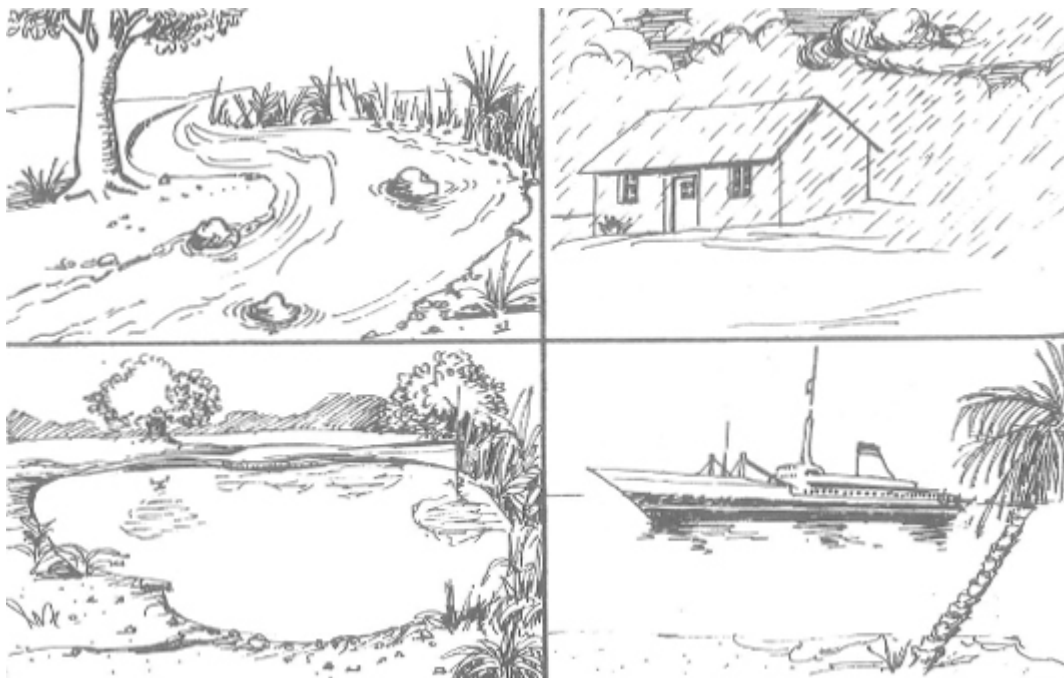


## 9. WATER AND SOLUTIONS

### 9.1 Introduction

Water abounds in the earth's crust, though mostly in an impure state. It covers four-fifths of the earth's surface and is found in oceans, rivers and lakes. In the Arctic region, it covers the surface of the whole land mass in the form of icebergs. Below the earth surface, water is trapped within rock formations, but its depth varies from place to place. In the air, it occurs as water vapour.



**Figure 9.1 Sources of water**

### Structure of water

A molecule of water contains two atoms of hydrogen and one atom of oxygen. The formula is thus,  $\text{H}_2\text{O}$ . The oxygen and hydrogen atoms are covalently linked together by each hydrogen atom forming a bond with each of the unpaired electrons of oxygen. The two lone pairs of electrons on oxygen are not used in bonding.

These non-bonding valence electrons are not symmetrically disposed, hence the water molecule is not linear, but is V-shaped as shown in Figure 9.2.

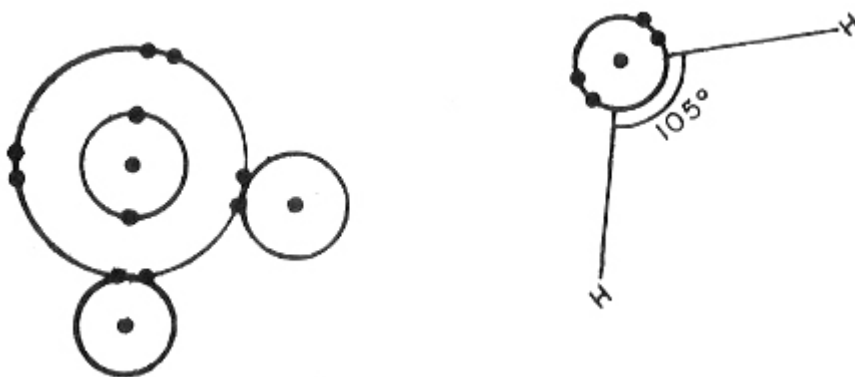


Figure 9.2 Shape of a water molecule

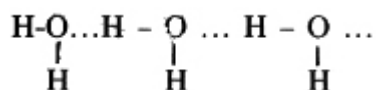
## 9.2 Properties of Water

A comparison of the physical properties of water with those of the hydrides of sulphur, selenium, and tellurium (i.e. elements in the same group of the Periodic Table as oxygen), shows some significant differences. Table 9.1 is a comparison of their physical properties.

**TABLE 9.1 SOME PHYSICAL PROPERTIES OF THE HYDRIDES OF GROUP VI ELEMENTS**

Hydride	Relative molecular mass	M.P. (°C)	B.P. (°C)
H <sub>2</sub> O	18	0.0	100
H <sub>2</sub> S	34	-85.5	-60.3
H <sub>2</sub> Se	82	-63.7	-41.3
H <sub>2</sub> Te	129	-51.0	-2.3

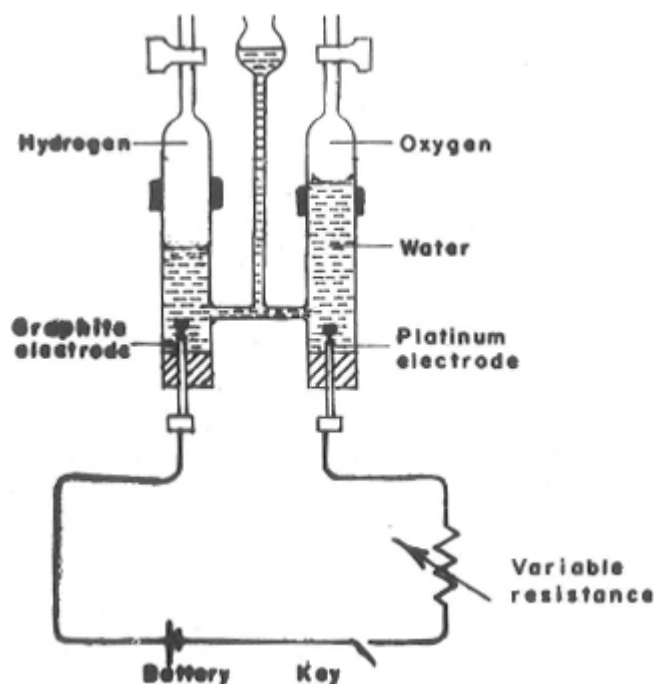
The higher figures for the melting and boiling points of water suggest that water molecules are held together by stronger forces than the molecules of the other hydrides. The higher electronegativity of oxygen, and the V-shape of the water molecule account for these higher forces, which are due to **hydrogen bonding**. Hydrogen bonding is a weak intermolecular force of attraction resulting from the attraction of a highly electronegative element in a polar molecule containing hydrogen, and the hydrogen atom of another molecule.



Pure water is a colourless and tasteless liquid. It has its highest density of 1g cm<sup>-3</sup> at 4°C.

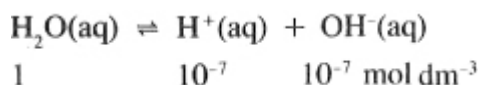
### 1. Electrolysis of water

*Experiment 9.1: To investigate the action of electric current on water*



**Figure 9.3 Electrolysis of water**

Set up the apparatus shown in Figure 9.3. Put distilled water into the voltameter, then switch on the current. Adjust the variable resistance to maximum resistance. The ammeter does not show a reading, that is, current does not flow through the circuit. This is because water is a poor conductor of electricity. It ionises only very slightly. In fact the hydrogen ion concentration in pure water has been shown to be only  $10^{-7} \text{ mol dm}^{-3}$ . That is,



The equilibrium lies far to the left. The amount of ions in water is therefore too small to carry current through the liquid.

Now, put a few drops of concentrated tetraoxosulphate(VI) acid into the water and again adjust the variable resistance to maximum reading. Current now flows as indicated by a movement of the pointer of the ammeter. Leave the set-up for some time. Bubbles of gas begin to appear above each of the electrodes. Within thirty minutes, a reasonable amount of gas is collected above each electrode.

Test the gas in the anode compartment with a glowing splint. The splint is rekindled, showing that the gas is oxygen. Test the gas in the cathode compartment with a lighted splint. There is a pop sound which indicates that the gas is hydrogen. The ratio of the volume of oxygen to hydrogen produced in the voltameter is 1:2. Applying Avogadro's hypothesis, we can thus deduce that one mole of oxygen combines with two mole of hydrogen to give one mole of water.

## **2. Action of metals on water**

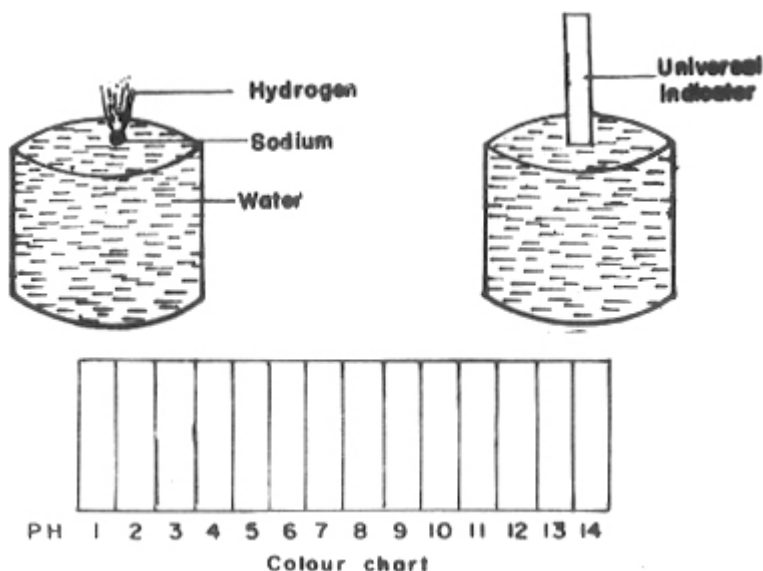
In Chapter 1, we performed experiments to show the action of metals on water. We noted that the alkali metals (sodium, potassium, etc), liberate hydrogen from cold water, the reaction becoming more vigorous from sodium to rubidium. The alkaline earth metal, magnesium, liberates hydrogen from steam, while calcium is more active and liberates hydrogen from cold water, though not vigorously. Iron and zinc also liberate hydrogen from steam. Copper, silver, mercury and gold have no action on water.

*Experiment 9.2: Investigating the pH of the solution formed by the action of metals on water*

Put a piece of sodium into about 50cm<sup>3</sup> of distilled water in a beaker placed in a fume cupboard. The sodium darts about with a hissing sound, liberating hydrogen. Watch till all the sodium dissolves, then add three drops of universal indicator to the resulting solution. Match the colour produced against the colour chart (Figure 9.4). A pH of about 13 is indicated.

Repeat with a small piece of calcium instead of sodium. The reaction is gentle and it takes a longer time for the calcium to dissolve completely.

The pH is about 12.5. The resulting solutions of the action of the alkali metals on water are stronger alkaline solutions than those of the action of the alkaline earth metals on water.



**Figure 9.4 Determining the pH of solution obtained from action of metals on water.**

**TABLE 9.2 SUMMARY OF THE ACTION OF METALS ON WATER**

Metal	Action with water
Na } K }	Liberate hydrogen from cold water vigorously; solution left is strongly alkaline.
Ca	Liberates hydrogen from cold water quietly. Solution left is weakly alkaline.
Mg } Al } Zn } Fe }	Liberate hydrogen from steam.
Pb } Cu } Hg } Ag } Au }	No action on cold water or steam.

## 9.3 Calculation of pH

That the concentration of hydrogen ions in water is  $10^{-7} \text{ mol dm}^{-3}$ , is the basis of the pH scale. When one mole of water ionizes, it produces only one mole of  $\text{H}^+$  and one mole of  $\text{OH}^-$  ions. Therefore the concentration of  $\text{OH}^-$  is also  $10^{-7} \text{ mol dm}^{-3}$ .

Since the concentration of  $\text{H}^+$  and  $\text{OH}^-$  are equal, water is neutral.

pH is defined as the logarithm of the reciprocal of hydrogen ion concentration.

$$\therefore \text{pH of water} = \log \frac{1}{[\text{H}^+]}$$

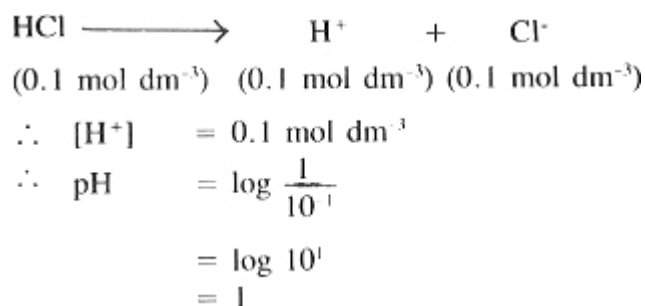
Where  $[\text{H}^+]$  is the molar concentration of the hydrogen ion.

$$\begin{aligned} \therefore \text{pH of water} &= \log \frac{1}{10^{-7}} \\ &= \log 10^7 \\ &= 7 \end{aligned}$$

An acidic solution contains more  $\text{H}^+$  ions than water, whereas an alkaline solution contains less  $\text{H}^+$  ions than water.

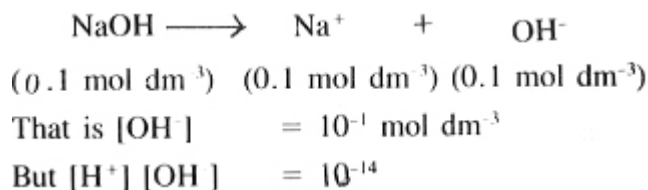
### pH of $0.1 \text{ mol dm}^{-3} \text{ HCl}$

A  $0.1 \text{ mol dm}^{-3} \text{ HCl}$  solution ionises completely to  $\text{H}^+$  and  $\text{Cl}^-$



### pH of 0.1 mol dm<sup>-3</sup> NaOH

Sodium hydroxide is completely ionised in water.



$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

$$\therefore \text{pH} = \log \frac{1}{[\text{H}^+]} = \log \frac{1}{10^{-13}}$$

$$= \log 10^{13} = 13$$

*Experiment 9.3: To determine the pH of solutions of electrolytes in water, using the universal indicator.*

Make solutions of the following electrolytes by dissolving the quantities indicated in Table 9.3 in water and making up to 100 cm<sup>3</sup> in a standard flask.

**TABLE 9.3**

Electrolyte	Quantity	Molarity	pH
HCl	1 cm <sup>3</sup> of conc.	0.1 mol dm <sup>-3</sup>	1
HNO <sub>3</sub>	0.63 cm <sup>3</sup> of conc.	0.1 mol dm <sup>-3</sup>	1
H <sub>2</sub> SO <sub>4</sub>	0.3 cm <sup>3</sup> of conc.	0.05 mol dm <sup>-3</sup>	1
Benzoic acid	Saturated solution		2.8
Ethanoic acid	3cm <sup>3</sup> glacial	0.1 mol dm <sup>-3</sup>	2.87
Tartaric acid	1.5 g	0.1 mol dm <sup>-3</sup>	2.0
NaOH	0.4 g	0.1 mol dm <sup>-3</sup>	13

KOH	0.56 g	0.1 mol dm <sup>-3</sup>	13
NH <sub>3</sub>	0.7 cm <sup>3</sup>	0.1 mol dm <sup>-3</sup>	11.3
Borax	2.35 g	0.3 mol dm <sup>-3</sup>	9.2

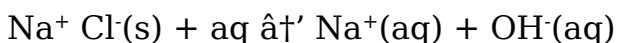
Put 10 cm<sup>3</sup> of each solution into a test-tube and add 3 drops of universal indicator. Match the colour produced with the chart of the universal indicator, to get the approximate pH value. The pH value expected are shown in Table 9.3.

The pH of 0.1 mol dm<sup>-3</sup> solutions of hydrogen chloride acid (hydrochloric acid) and trioxonitrate(V) acid is 1. They ionise completely in water, and so do strong acids. The pH of 0.1 mol dm<sup>-3</sup> solutions of ethanoic acid and benzoic acid are greater than one. These are weak acids which ionise only partially in water. Their 0.1 mol dm<sup>-3</sup> solutions produce less than 0.1 mole of hydrogen ion. They are thus weak electrolytes. Among the alkalis, sodium hydroxide and potassium hydroxide ionise completely in water, producing a high concentration of OH<sup>-</sup> ions. Their hydrogen ion concentrations are therefore low hence pH is high. Aqueous ammonia, on the hand, does not ionise completely. It is a weak base. Its pH though high, is less than the pH of the strong alkalis.

## 9.4 Solution Processes

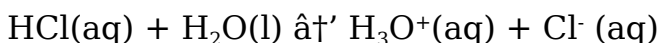
The polar nature of water accounts for its solvent action. It dissolves only ionic compounds. Dissolution occurs by the orientation of water molecules around the positive and negative ions of the compounds which have to first dissociate in water.

Sodium chloride, for example, dissolves in water by first dissociating into free sodium ions and chloride ions. Each sodium ion becomes surrounded by water molecules through the oxygen atom. Each chloride ion in turn is also surrounded by water molecules, through the hydrogen atoms. The energy released by this process, known as the **hydration energy**, supplies the energy for dissociating the sodium chloride into free ions.



The ions become independent of each other and homogeneously dispersed in the solvent, water.

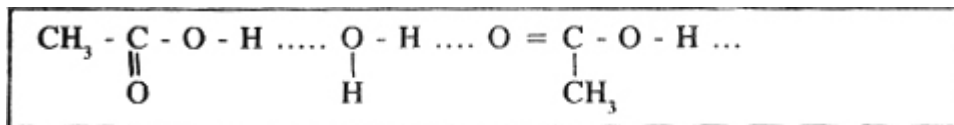
Some molecular compounds, such as hydrogen chloride, give out protons to water molecules.



The group ion, H<sub>3</sub>O<sup>+</sup>, which is formed, is responsible for the acidity of such solutions.

Organic compounds which dissolve in water are polar. Their

interaction with water molecules is through hydrogen-bonding. For example, ethanoic acid is miscible with water because hydrogen-bonding exists between the molecules of the acid and water.



Sugar also dissolves in water through hydrogen, bonding.

## 9.5 Solubility

Water is often described as a universal solvent. This is because practically every substance dissolves in it to some extent. Those that dissolve to an insignificant extent are said to be insoluble in water, while only those that dissolve to an appreciable extent are said to be soluble. Solubility is the term used to express the extent to which a substance dissolves in a solvent.

*Experiment 9.4: Investigation of the relative solubilities of common substances in water.*

Stir 1g of each of sodium chloride, sugar (sucrose), calcium trioxocarbonate(IV) and lead(II) chloride, in 25 cm<sup>3</sup> of distilled water, in separate test-tubes. The sodium chloride and sugar dissolve completely. Some calcium trioxocarbonate(IV) and lead(II) chloride solids remain undissolved. Warm the test-tubes containing the undissolved solids, and stir. The lead(II) chloride dissolves in the hot water, but some calcium trioxocarbonate(IV) still remains undissolved.

Experiment 9.4 suggests:

- (1) that at room temperature the same amount of water dissolves different quantities of different substances; and
- (2) that more solid solutes dissolve in hot water than in cold water. The maximum amount of a solute which will dissolve in a given amount of solvent at a given temperature is known as the solubility of the solute.

**The solubility of a substance is defined as the amount of it, in mole, that will dissolve in 1 dm<sup>3</sup> of solvent at a given temperature in the presence of some undissolved solute.**

The unit of solubility is mole per cubic decimeter (mol dm<sup>-3</sup>).

*Experiment 9.5: To determine the solubility of sodium chloride at different temperatures, and hence plot a solubility curve.*

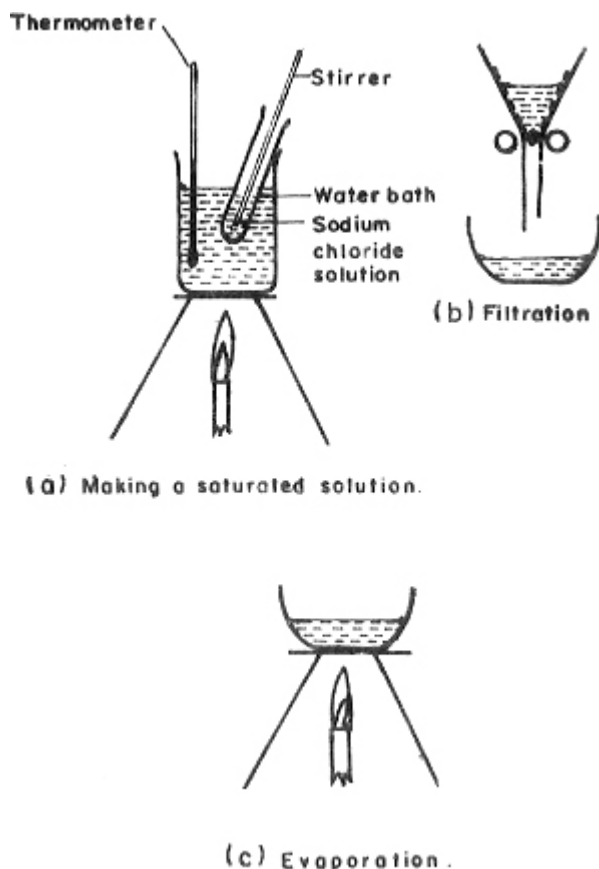
This experiment is to be performed as a group experiment. Each student or group of students is to determine the solubility of sodium chloride (or potassium chloride) at an assigned temperature. The



different results of all the groups are collected and used to plot a solubility curve.

Prepare a saturated solution of sodium chloride at about  $10^{\circ}\text{C}$  above your assigned temperature, by adding the salt to water in a test-tube immersed in a heated water bath carrying a thermometer (Figure 9.5a). Allow the solution to cool to  $1^{\circ}\text{C}$  above the assigned temperature, then filter it. Collect about  $10\text{ cm}^3$  of filtrate into a weighed evaporating dish. Weigh the dish and solution.

Evaporate the solution to dryness. Cool and weigh again. Heat, cool and weigh the dish until a constant mass is got. Calculate the solubility of sodium chloride at your assigned temperature.



**Figure 9.5 Determining the solubility of sodium chloride**

(**Note:** The temperature of the solution should fall to the exact assigned temperature during the period of filtering).

#### **SPECIMEN RESULTS AND CALCULATION**

Mass of empty evaporating dish = 132.6 g.  
 Mass of dish plus solution at  $30^{\circ}\text{C}$  = 146.1 g.  
 $\therefore$  Mass of solution at  $30^{\circ}\text{C}$  =  $(146.1 - 132.6)\text{ g}$   
 = 13.5 g

Constant mass of evaporating dish and salt after heating and cooling

$$= 136.1 \text{ g}$$

$$\hat{\wedge} \text{ Mass of salt} = (136.1 \hat{\wedge} 132.6) \text{ g} \\ = 3.5 \text{ g}$$

$$\hat{\wedge} \text{ Mass of water in 13.5 g of solution} = (13.5 \hat{\wedge} 3.5) \text{ g} \\ = 10 \text{ g.}$$

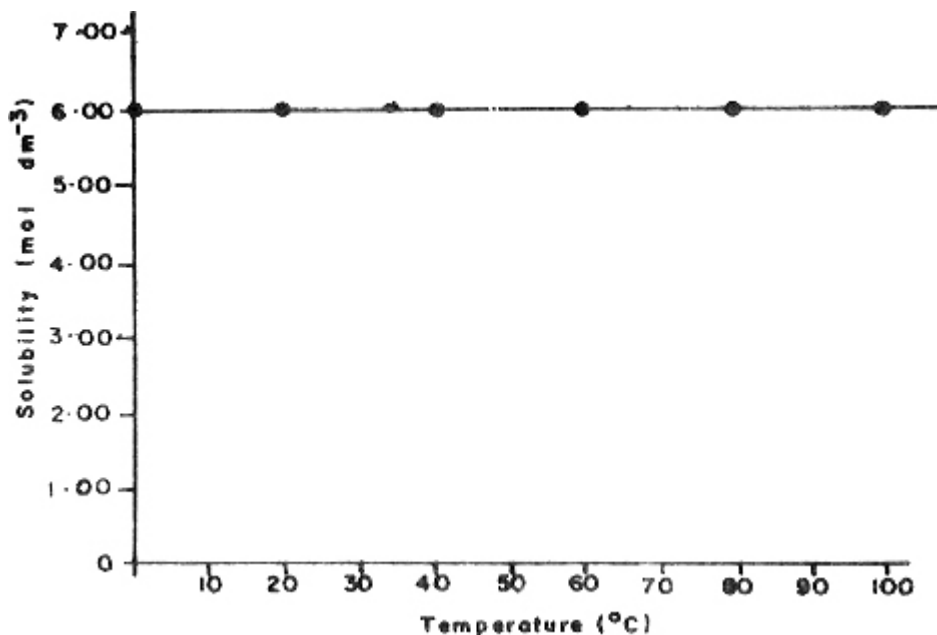
$\hat{\wedge}$  3.5g of salt dissolve in 10g of water at 30°C. Assuming that the density of the solution is the same as the density of water, i.e., 1g cm<sup>3</sup>, then 10g of the solution will occupy 10cm<sup>3</sup>.

$\therefore$  10 cm<sup>3</sup> of water dissolves 3.5g of salt at 30°C.

$$\therefore 1 \text{ dm}^3 \text{ of water will dissolve } \frac{3.5}{10} \times 1000 \text{ g} \\ = 350 \text{ g.}$$

$$\text{Relative molecular mass of sodium chloride, NaCl,} = (23 + 35.5) \\ = 58.5$$

$$\hat{\wedge} \text{ Solubility of sodium chloride at 30}^\circ\text{C} = \frac{350}{58.5} \text{ mol dm}^{-3} \\ = 5.98 \text{ mol dm}^{-3} \\ = 5.98 \text{ mol dm}^{-3}$$



**Figure 9.6 Solubility curve of sodium chloride**

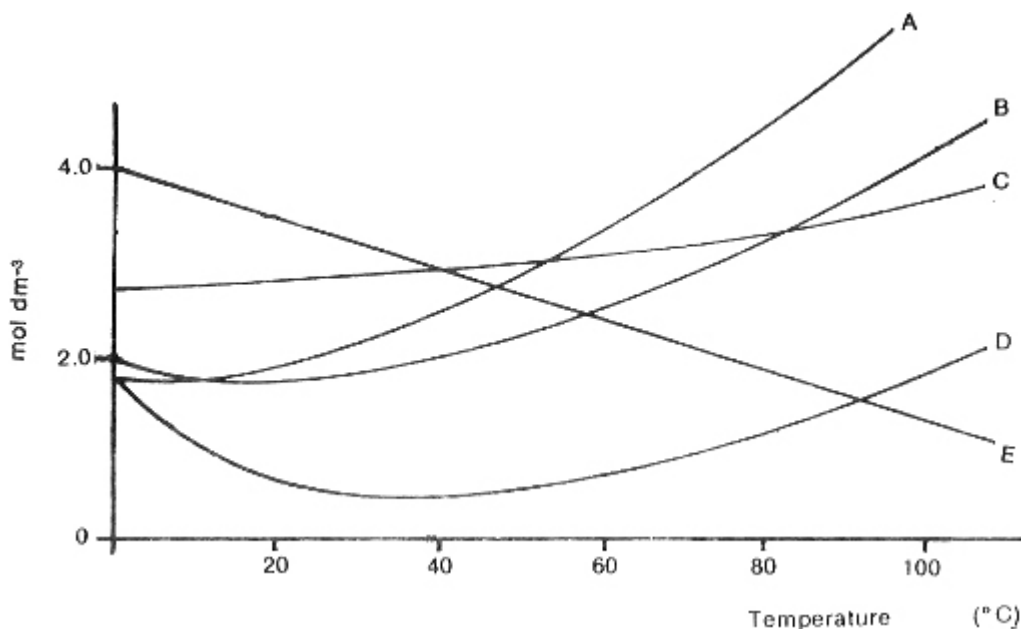
**Solubility curve** is a graph of solubility against temperature. The different solubilities are plotted on the y-axis against the temperatures on the x-axis. Plot such a curve with all the results from the different groups. Figure 9.6 is the expected curve.

From a solubility curve it is possible to

1. determine the solubility of a substance at any temperature covered in the graph. To do this, draw a line from the given temperature value vertically up to meet the curve, then extrapolate to the solubility axis and read the solubility at that temperature.
2. compare solubilities of two or more substances at a given temperature. If the solubilities of the two substances are plotted on the same graph, the one which has the higher solubility at the given temperature will have its curve higher up.
3. predict the possibility of separating two substances by fractional crystallisation. Substances with widely different solubilities can be so separated.

### WORKED EXAMPLES

1. Figure 9.7 represents the solubility curves of substances A, B, C, D and E.
  - (a) Which of these substances is the most soluble at  $18^{\circ}\text{C}$ ?
  - (b) At what temperature do substances A and E have the same solubility in  $\text{mol dm}^{-3}$ ?
  - (c) If a solution containing  $1.0 \text{ mole dm}^{-3}$  of each of A and D is allowed to cool from  $80^{\circ}\text{C}$ , which salt precipitates out first, and at what temperature?



**Figure 9.7 Solubility curves of A, B, C, D & E**

### SOLUTION

- (a) The most soluble substance is E. From the point,  $18^{\circ}\text{C}$ , on the temperature axis, draw a vertical line up. The highest graph up at that temperature is E.
- (b) At about  $45^{\circ}\text{C}$ .

From the point of intersection of the two curves draw a vertical line down to the temperature axis. Read off the temperature.

- (c) D precipitates out first at about  $40^{\circ}\text{C}$ .

From the  $1.0 \text{ mol dm}^{-3}$  point on the solubility axis draw a horizontal line. It meets the D curve at a point corresponding to  $40^{\circ}\text{C}$  on the temperature axis. That is the solubility of D is  $1.0 \text{ mol dm}^{-3}$  at  $40^{\circ}\text{C}$ . Above this temperature, the solubility of D is higher than  $1 \text{ mol dm}^{-3}$ . Therefore, the solution which contains  $1 \text{ mol dm}^{-3}$  can keep all that solute in solution only if the temperature does not fall below the critical  $40^{\circ}\text{C}$ .

2. From the same graph, if the relative molecular mass of B is 56, calculate the mass of B that precipitates on cooling  $100 \text{ cm}^3$  solution of B saturated at  $80^{\circ}\text{C}$ , to  $20^{\circ}\text{C}$ .

### SOLUTION

Determine the solubility of B at  $80^{\circ}\text{C}$  and at  $20^{\circ}\text{C}$  from the graph by drawing vertical lines from these temperatures and extrapolating to the solubility axis.

Solubility at  $80^{\circ}\text{C} = 3 \text{ mol dm}^{-3}$

Solubility at  $20^{\circ}\text{C} = 1.8 \text{ mol dm}^{-3}$ .

∧∧ The saturated solution at  $80^{\circ}\text{C}$  holds  $3 \text{ mol dm}^{-3}$ . At  $20^{\circ}\text{C}$  it holds  $1.8 \text{ mol dm}^{-3}$

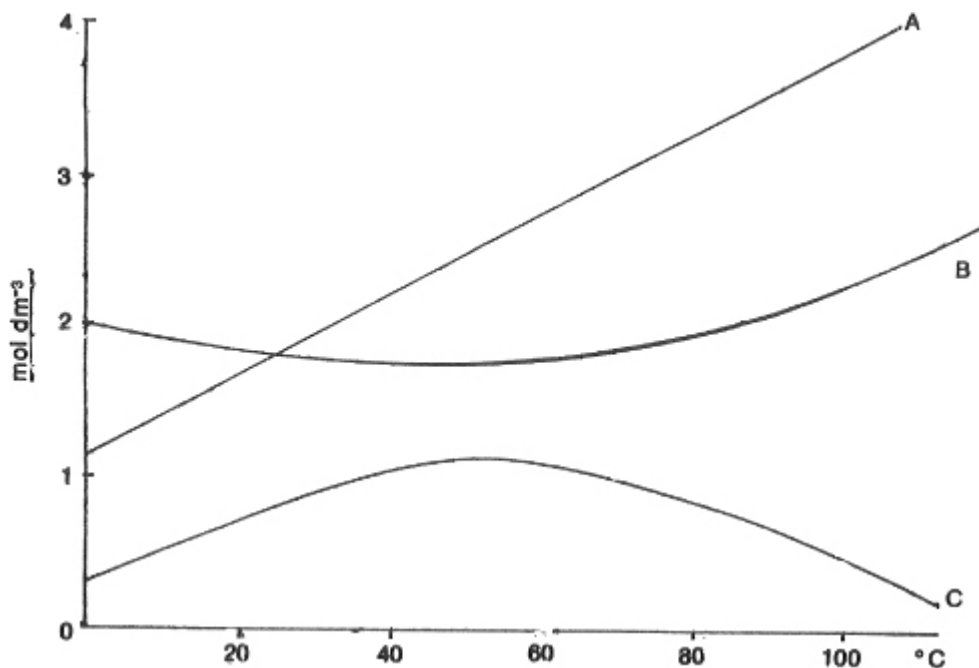
∧∧ Amount that precipitates when  $1 \text{ dm}^3$  of the solution cools from  $80^{\circ}\text{C}$  to  $20^{\circ}\text{C} = (3 - 1.8) \text{ mole} = 1.2 \text{ mole}$ . Since relative molecular mass of B is 56, mass that precipitates  $= (56 \times 1.2) \text{ g} = 67.2 \text{ g}$ . But only  $100 \text{ cm}^3$  was used.

$$\begin{aligned} \text{∧∧ Mass that precipitates when } 100 \text{ cm}^3 \text{ is cooled} &= \frac{67.2 \times 100}{1000} \\ &= 6.72 \text{ g.} \end{aligned}$$

3. (a) Define the following terms:

- (i) solubility,
- (ii) saturated solution,
- (iii) supersaturated solution.

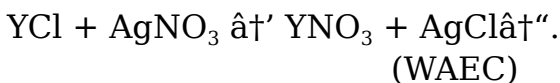
- (b) Consider the following solubility curves (Figure 9.8)



**Figure 9.8**

What can you deduce about the solubilities of A, B, and C?

- (c) 10.0 cm<sup>3</sup> of a metal chloride YCl solution saturated at 30°C required 64.96 cm<sup>3</sup> of 1.07 mol dm<sup>-3</sup> AgNO<sub>3</sub> for complete precipitation. Calculate the solubility of the salt YCl at 30°C. The equation for the precipitation is



**SOLUTION**

- (a) For the definitions, see text.
- (b) (i) The solubility of A increases as the temperature increases.
- (ii) The solubility of B does not change much with changes in temperature from 0-76°C.
- (iii) The solubility of C increases with temperature up to 50°C. Above 50°C it decreases with increase in temperature. A is therefore more soluble than C at all temperatures, and more soluble than B above 20°C. B is more soluble than C at all temperatures and C is the least soluble of the three.
- (c)  $\text{YCl(aq)} + \text{AgNO}_3\text{(aq)} \rightarrow \text{AgCl(s)} + \text{YNO}_3\text{(aq)}$   
 Number of mole of AgNO<sub>3</sub> required for complete reaction with  
 chloride =  $\frac{64.96 \times 1.07}{1000} = 0.0695$  mole  
 ∴ 10 cm<sup>3</sup> of the solution of YCl contained 0.0695 mole.  
 Hence, the solubility of YCl at 30°C

$$\begin{aligned}
 &= \frac{1000}{10} \times \frac{0.0695}{1} \text{ moles/dm}^3 \\
 &= 6.95 \text{ mole per dm}^3.
 \end{aligned}$$

## EXERCISE 9A

Which of the substances A, B, C, D, and E in Figure 9.7 shows an unusual solubility behaviour?

## 9.6 Types of Solutions

“Dilute” and “concentrated” are terms used to describe qualitatively the relative amounts of solute in a solvent. A **dilute solution** is one that does not contain much of solute, while a **concentrated solution** contains a large quantity of solute in a given volume of solution. But the exact amounts are not defined by these terms.

Other terms relating to amounts of solute in a solution include “unsaturated”, “saturated” and “supersaturated”.

**An unsaturated solution is one that can dissolve more of the solute at the given temperature.**

**A saturated solution cannot dissolve any more of the solute at the given temperature.**

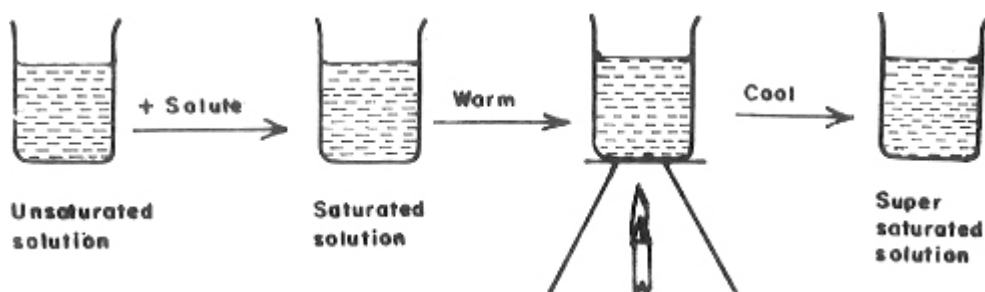
A saturated solution in fact contains some undissolved solute at the temperature under reference. Usually more solute dissolves on raising the temperature.

**A supersaturated solution is one that contains more solute than the saturated solution can hold at a given temperature.**

*Experiment 9.6: Investigating a supersaturated solution.*

Put 25 cm<sup>3</sup> of water into a beaker. Add crystals of sodium thiosulphate to the water in small amounts, with stirring till no more will dissolve. A saturated solution has been formed. Now warm the solution containing some undissolved solute, with stirring. The excess solute dissolves. Cool the solution carefully, without disturbing it, back to room temperature. The excess solute which dissolved on warming the saturated solution does not precipitate out. That solution is holding more solute than the saturated solution should at room temperature. It is supersaturated.

Drop a tiny crystal of sodium thiosulphate into the solution. The excess solute now precipitates out of solution, yielding a saturated solution once more.



**Figure 9.9 Preparation of a supersaturated solution of sodium thiosulphate**

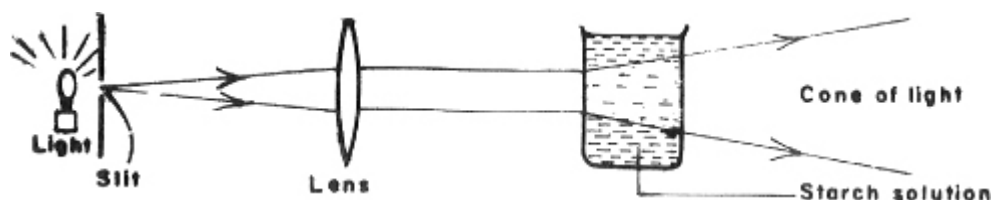
## Colloidal solution

Examples abound in nature of solutions such as milk, clay and barium chloride in water, where the very tiny particles of the solute never settle at the bottom. They are so tiny that the random movement of the water molecules keeps them in perpetual motion. Such solutions are called colloidal solutions.

*Experiment 9.7: Investigating the properties of colloidal solutions.*

Put some starch powder into water and stir. The starch does not dissolve. Filter the mixture through a filter paper folded the usual way. Warm the filtrate (do not boil it). A cloudy ‘œsolution’ is formed. Particles of the starch must have passed through the filter paper during filtration.

Focus a beam of light on the solution. A cone of light is seen to emerge from the opposite side of the beaker from which the light is focused. The starch particles in the solution scatter the beam of light into a cone. This light-scattering effect is known as **Tyndal effect**. (Figure 9.10). The particles of solute in a true solution do not cause Tyndal effect.



**Figure 9.10 Tyndal effect**

## 9.7 Hardness of Water

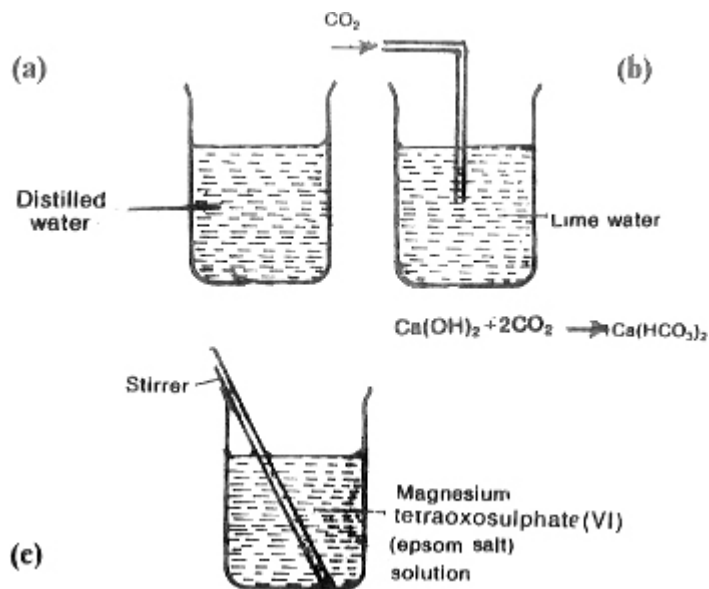
*Experiment 9.8: Investigating hardness of water.*

Select three clean beakers and label them A, B and C. Into beaker A, put 25 cm<sup>3</sup> of distilled water. Put 25 cm<sup>3</sup> of lime water into beaker B, then pass carbon(IV) oxide into the lime water. Into beaker C, put 0.5

g magnesium tetraoxosulphate(VI) and 25 cm<sup>3</sup> distilled water, then stir to dissolve (Figure 9.11).

Prepare soap solution by adding 5 g of soap shavings to 500 cm<sup>3</sup> of distilled water. Leave to stand till all the soap dissolves, then make up to 1 dm<sup>3</sup> with more distilled water.

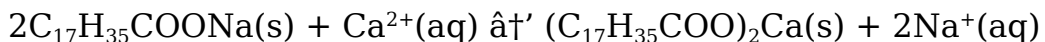
Add 1 cm<sup>3</sup> of the soap solution to each of the beakers labelled A, B and C. The water in beaker A lathers readily, whereas the water in beakers B and C do not.



**Figure 9.11 Identification of hard water**

Lime water (calcium hydroxide solution) reacts with carbon(IV) oxide to form calcium hydrogen trioxocarbonate(IV). Beaker B therefore is really a solution of calcium hydrogen trioxocarbonate(IV).

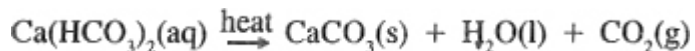
Water containing Ca<sup>2+</sup>, Mg<sup>2+</sup> or Fe<sup>2+</sup> ions does not lather readily with soap. Such water is said to be **hard**. The ions react with soap to precipitate the insoluble calcium, magnesium or iron(II) salts of the fatty acids in soap.



Soap does not lather until all the Ca<sup>2+</sup>, Mg<sup>2+</sup>, or Fe<sup>2+</sup> ions have been precipitated.

## Temporary and permanent hardness

Hardness due to hydrogen trioxocarbonates(IV) of calcium, magnesium or iron(II) can be removed by boiling, because these hydrogen trioxocarbonates(IV) salts precipitate their respective trioxocarbonates(IV) on heating.



Water containing hydrogen trioxocarbonates(IV) are said to be



temporarily hard.

Hardness due to the presence of tetraoxosulphates(VI) of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  cannot be removed by boiling, Water containing these salts is said to be permanently hard.

## Disadvantages of hard water

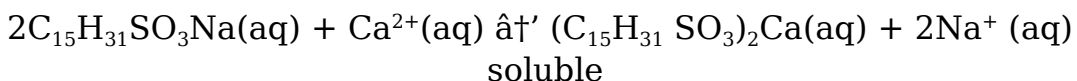
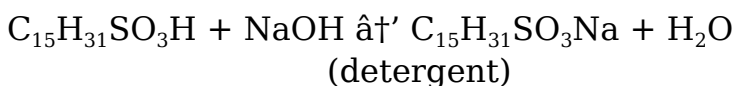
1. Using hard water for washing is uneconomical as it wastes soap. Large quantities of soap will be wasted before lather is formed.
2. Soap reacts with hard water to form insoluble scum (calcium stearate, for example). This is deposited on clothes and wash basins, which therefore become discoloured.
3. When hard water is used in boilers, a deposit of insoluble trioxocarbonate(IV), called boiler scale, forms on the bottom of the boiler. This scale prevents heat from passing quickly from the source of heat to the water. Fuel is therefore wasted.
4. Hard water reacts with some dyes to form insoluble compounds. This results in uneven dyeing of materials.

## Advantages of hard water

1. Hard water tastes better than pure water.
2. Hard water contains calcium ions which are good for healthy teeth and bones.
3. Beer seems to be better brewed if hard water is used.

## Detergents and hard water

Detergent such as Surf, Omo, etc, are metal alkylsulphonates. The calcium, magnesium or iron(II) alkylsulphonates are soluble in water. Detergents therefore do not form scum with hard water and are thus not wasted when used for washing in hard water.



## 9.8 Removal of Hardness in Water

There are various methods by which hardness can be removed. The removal of hardness from water is known as **softening**.

Distillation removes both temporary and permanent hardness. But it is a costly process and is therefore not employed on a large scale. Other methods of softening hard water involve the conversion of the

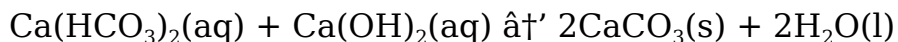
soluble salts which cause hardness into insoluble salts which can be filtered off.

## Softening temporary hardness

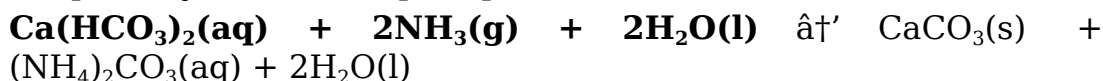
1. **Boiling:** Heat decomposes hydrogen trioxocarbonates(IV) to insoluble trioxocarbonates(IV). The insoluble salts precipitate out of water and so free it from hardness.



2. **Clark's process:** This method involves the addition of calculated quantities of calcium hydroxide to the hard water. Care is taken not to add too much calcium hydroxide, otherwise the  $\text{Ca}^{2+}$  ions from the calcium hydroxide may cause the very hardness they are intended to remove.

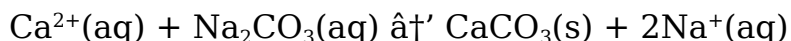


3. **Addition of aqueous ammonia:** Addition of aqueous ammonia to temporarily hard water precipitates calcium trioxocarbonate(IV).

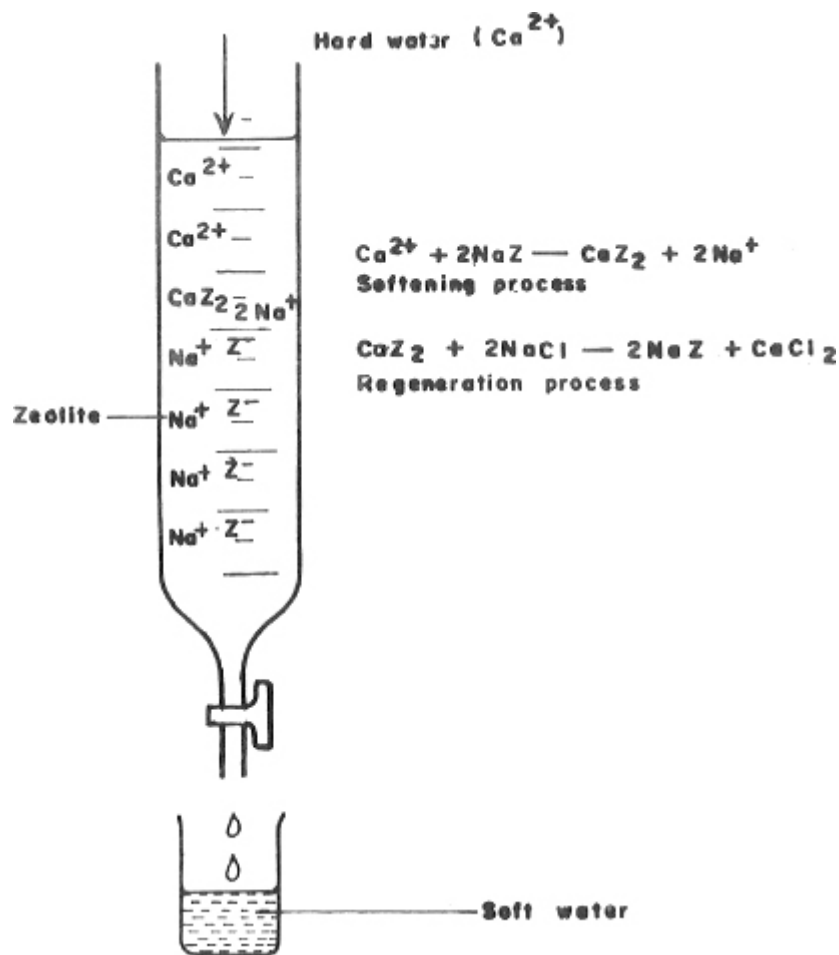


## Softening both forms of hardness

1. **By addition of sodium trioxocarbonate(IV):** Sodium trioxocarbonate(IV) removes calcium and magnesium ions as insoluble trioxocarbonate(IV)



2. **Use of ion exchange resins:** This is an exchange process. The hard water is passed through zeolites, which are naturally occurring forms of sodium aluminium trioxosilicates(IV). The sodium ions of the zeolite are exchanged with the calcium (or magnesium) of the hard water. Calcium (or magnesium) trioxosilicates(IV) are left behind. The water coming over is therefore free of the hardness-causing ions. After sometime, when the zeolite becomes spent (i.e. loses all its sodium ions), brine is run through it to regenerate sodium ions and make it active again.



**Figure 9.12 Ion exchange resin used for softening hard water**

### WORKED EXAMPLE

100 cm<sup>3</sup> of a sample of hard water requires 35 cm<sup>3</sup> of soap solution to produce a lather. After boiling the water, 100 cm<sup>3</sup> of it requires only 25 cm<sup>3</sup> of soap solution to produce a lather. What is the ratio of permanent to temporary hardness in the water sample?

### SOLUTION

Soap needed before boiling the sample of water removed both temporary and permanent hardness. After boiling the water before using soap, the soap removes only permanent hardness, because boiling removes the temporary hardness.

∧∧ Both forms of hardness are equivalent to 35 cm<sup>3</sup> of soap.  
Permanent hardness is equivalent to 25 cm<sup>3</sup> of soap.

∧∧ Temporary hardness is equivalent to (35 - 25) of soap = 10 cm<sup>3</sup>.

∧∧ Ratio of temporary to permanent hardness is  
10 : 25 or 2:5

## 9.9 Water Pollution

Rain water carries a variety of pollutants into bodies of water in rivers, lakes, seas and oceans. Industrial wastes and sewage may also be accidentally or intentionally discharged into these bodies of water. Oil spillage in oil exploration is another source of pollution. Table 9.4 is a classification of the impurities found in water from different sources.

Industrial wastes include chemicals from textile mills, petroleum refineries, canning industries, etc. Sewage includes man's waste products, both from his excretion and from his domestic solid wastes. Many of these pollutants, including the organic compounds which are derived from the use of detergents and agrochemicals (insecticides, herbicides, fertilizers), as well as dead plants and animals, are **biodegradable**. This means that they can be broken down by micro-organisms to harmless substances. If the breakdown process makes use of dissolved oxygen in water, it is said to be **aerobic**. If the oxygen content of the water is too low, the micro-organisms responsible for the break-down die off. The pollutants then decay **anaerobically** (without oxygen).

The pollutants are mostly compounds of carbon, nitrogen, phosphorus and sulphur. Their aerobic degradation products are carbon(IV) oxide ( $\text{CO}_2$ ), trioxonitrate(V) acid ( $\text{HNO}_3$ ), tetraoxophosphate(V) acid ( $\text{H}_3\text{PO}_4$ ), and tetraoxosulphate(VI) acid ( $\text{H}_2\text{SO}_4$ ) respectively. Their anaerobic decay products are methane ( $\text{CH}_4$ ), ammonia ( $\text{NH}_3$ ), phosphine ( $\text{PH}_3$ ), and hydrogen sulphide ( $\text{H}_2\text{S}$ ) respectively. All the products of anaerobic decay are foul-smelling. Therefore, a body of water containing a lot of organic waste products is foul-smelling due to the presence of such products.

**TABLE 9.4 WATER IMPURITIES**

Class	Source	Examples	Effect
Micro-organisms	Sewage	Bacteria, virus, protozoa, fungi.	Water-borne diseases.
Plant nutrients	Fertilizers, industrial wastes.	$\text{NO}_3^-$ , $\text{PO}_4^{3-}$	Growth of algae and other water plants.
Organic compounds	Detergents, insecticides, herbicides, sewage.	$\text{RSO}_3^-$ $\text{Na}^+$ , chlorinated hydrocarbons.	Use up dissolved oxygen for breakdown.
Minerals	Mine water, industrial wastes.	Acids, bases and salts.	Alter pH of water, poisonous.
Radio-isotopes	Mining, radio-active fall-outs.	Various radio-isotopes.	Damage body tissue of aquatic life and higher

Aquatic plants	Grown on water containing plant nutrients.	Sea weeds, algae.	animals via food chain. Use up dissolved oxygen for decay.
Suspended particles	Animals and plants on land.	Dead leaves, animal carcass, top-soil.	Decay uses up dissolved oxygen.
Heat	Cooling water from steam generators and steam-cooled engines.	Water used to cool nuclear reactors.	Cause death of aquatic life whose decay use up dissolved oxygen.

A body of water containing a lot of oxidizable matter will contain very little dissolved oxygen, whereas if there is little oxidizable matter in water, it will contain a reasonable amount of dissolved oxygen. A determination of the amount of oxidizable matter in a sample of water gives an indication of its purity.

*Experiment 9.9: To determine the amount of oxidizable matter in a sample of water from a local source.*

Reagents needed:

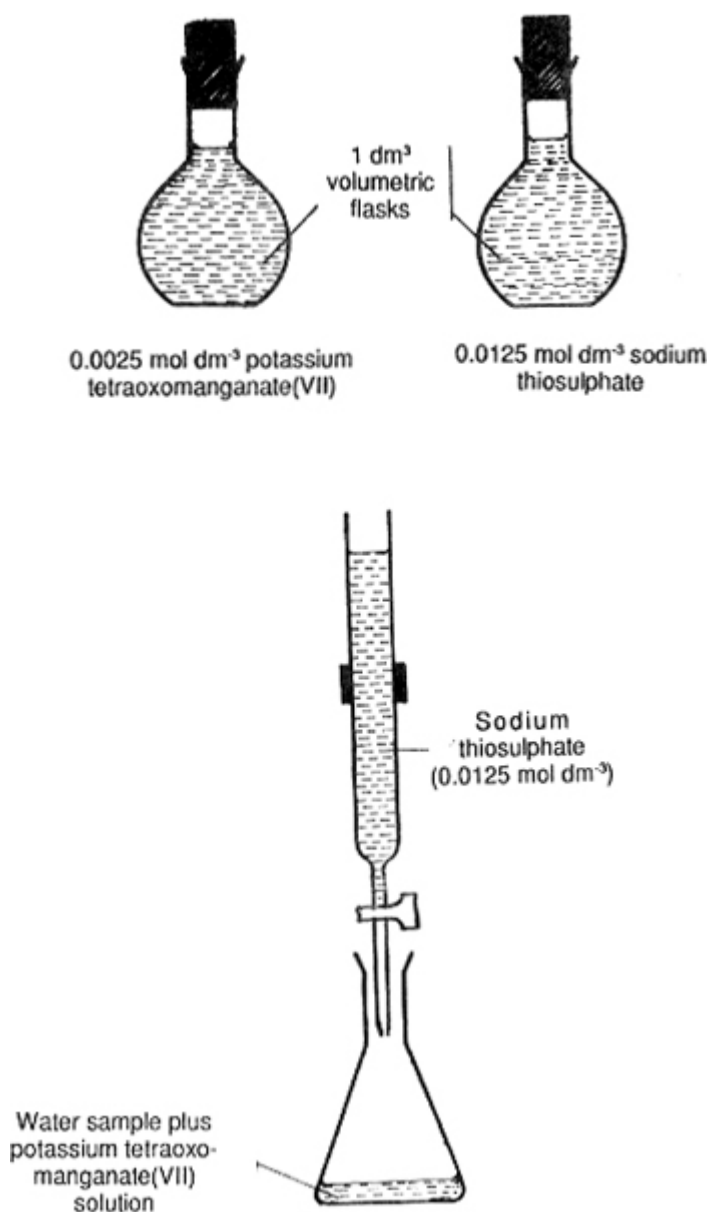
1. 10% potassium iodide solution: prepared by dissolving 10g of the salt in 100 cm<sup>3</sup> of water.
2. 0.0025 mol dm<sup>-3</sup> potassium tetraoxomanganate(VII) solution: prepared by dissolving 0.395g potassium tetraoxomanganate(VII) in water and making it up to 1 dm<sup>3</sup>
3. 0.0125 mol dm<sup>-3</sup> sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O prepared by dissolving 3.10g of the salt and 1g of sodium hydrogen trioxocarbonate(IV) in water, and making it up to 1 dm<sup>3</sup>.
4. Starch solution: Prepared by dissolving 20 g zinc chloride in 100 cm<sup>3</sup> of distilled water. Filter. Boil the filtrate. Add 4 g of starch powder into enough water to get a thin paste, then pour the hot zinc chloride solution into the paste with constant stirring. Dilute to 1 dm<sup>3</sup> with water.
5. 25% tetraoxosulphate(VI) acid: add 250 cm<sup>3</sup> of the concentrated acid to 700 cm<sup>3</sup> of distilled water, a little at a time. Cool, then make up to 1 dm<sup>3</sup> with distilled water.

## PROCEDURE

Collect the water sample when all the reagents are ready. If it is to be stored, fill the container to the brim with the water sample to avoid trapping atmospheric air which would cause oxidation during the period of storage.

Warm 250 cm<sup>3</sup> of water sample to 27°C in a 1000 cm<sup>3</sup> conical flask, and 250 cm<sup>3</sup> of distilled water in another flask. Add 10.0 cm<sup>3</sup> of the 0.0025 mol dm<sup>-3</sup> KMnO<sub>4</sub> solution and 10 cm<sup>3</sup> of the 25% H<sub>2</sub>SO<sub>4</sub> solution to both flasks. Shake to mix well. Stopper the flasks. Keep at 27°C for 4 hours. During this period, if the purple colour of the manganate(VII) solution tends to be discharged, add another 10.0 cm<sup>3</sup> of the 0.0025 mol dm<sup>-3</sup> solution. Excess of this solution must be maintained throughout the period.

At the end of the 4 hour period, add 1 cm<sup>3</sup> of the 10% potassium iodide solution to both flasks, and titrate with the sodium thiosulphate solution to a pale colour. Add two drops of starch and continue the titration until the blue colour is discharged. Repeat the titration with the second flask containing distilled water.



**Figure 9.13 Determination of Chemical Oxygen Demand (COD)**

#### **SPECIMEN RESULTS AND CALCULATION**

	Water sample (cm <sup>3</sup> )	Distilled water (cm <sup>3</sup> )
Final burette reading	1.40	13.50
Initial burette reading	0.00	4.00
Vol. of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.40	9.50

**Note:** Distilled water contains very little oxidizable matter. Hence the potassium tetraoxomanganate(VII) solution added to it is not used up. The mixture therefore requires a lot of sodium thiosulphate to react with all the manganate(VII) present. The sample of water contains a lot of oxidizable matter which the added potassium tetraoxomanganate(VII) oxidizes. Only a small amount of sodium thiosulphate is required to reduce the little excess manganate(VII) left in solution.

**The amount of oxidizable matter in water is known as its Chemical Oxygen Demand, COD.** It is calculated from the expression:

$$\begin{aligned}
 \text{COD} &= \frac{\left[ \begin{array}{c} \text{Vol. of Na}_2\text{S}_2\text{O}_3 \text{ required by excess KMnO}_4 \text{ in} \\ 10 \text{ cm}^3 \text{ distilled water} \end{array} \right] - \left[ \begin{array}{c} \text{Vol. of Na}_2\text{S}_2\text{O}_3 \text{ required by excess KMnO}_4 \\ \text{in } 10 \text{ cm}^3 \text{ water sample} \end{array} \right]}{\left[ \begin{array}{c} \text{Vol. of Na}_2\text{S}_2\text{O}_3 \text{ required by } 10 \text{ cm}^3 \text{ KMnO}_4 \end{array} \right] \times \left[ \begin{array}{c} \text{Vol. of water sample} \\ \text{used} \end{array} \right]} \times 1000 \text{ mg dm}^{-3} \\
 &= \frac{9.5 - 1.4}{10 \times 250} \times 1000 \text{ mg dm}^{-3} \\
 &= \frac{8.1}{2500} \times 1000 \text{ mg dm}^{-3} \\
 &= 3.24 \text{ mg dm}^{-3}
 \end{aligned}$$

#### EXERCISE 9B:

Three samples of water contain 2.1, 13.5 and 50.1 mg dm<sup>-3</sup> of oxidizable matter respectively. Which sample is the best for drinking? Which contains sewage? Which is spring water?

## 9.10 Treatment of Municipal Water Supply

Water, water everywhere, and none to drink. Seventy per cent of the earth's surface is covered by water. It is surprising therefore that we should have problems of scarcity of water. What we usually mean by such water scarcity, is the short supply of potable clean water. Sea water contains too much dissolved salt to be good for drinking. Water from rivers and streams are usually contaminated by

one pollutant or the other. Rain water is the purest form of water when it is collected from the open space, but it is not available all the time. Even when it is available, it may not contain certain minerals.

Domestic tap water is good for drinking because it is water that has undergone a number of purification processes, which include sedimentation, filtration, aeration and chemical treatment.

## Sedimentation

Water from its natural source (river or stream) is pumped into a storage tank, and from there into a mixing tank where alum is added to it to coagulate suspended particles. The larger particles settle down.

## Aeration

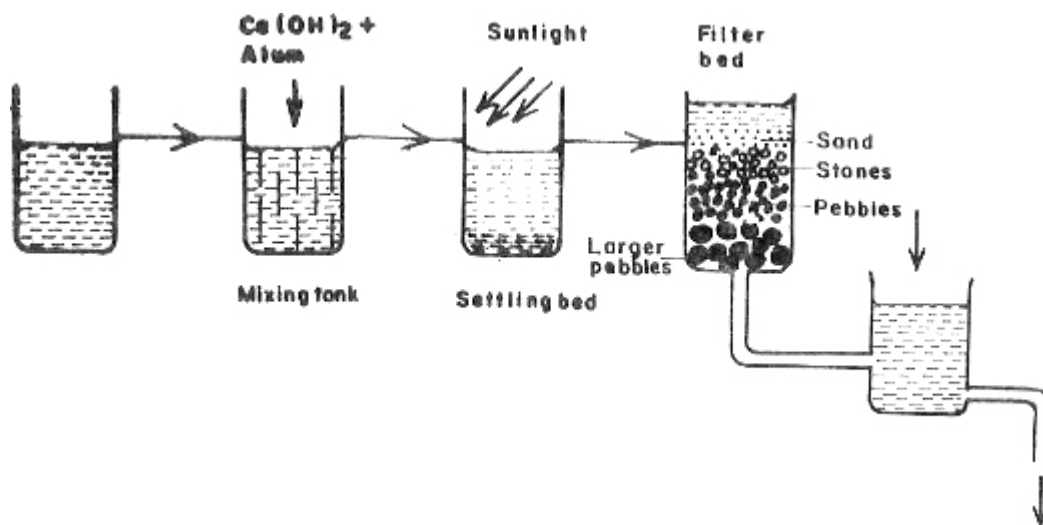
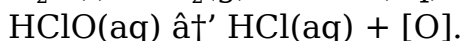
The water is exposed to sunlight to kill bacteria in it.

## Filtration

After exposure for about five days the water is made to pass through layers of sand, fine stones, gravels, and pebbles. These filter off the sediments and solid impurities in the water.

## Chemical Treatment

Addition of calculated quantities of calcium hydroxide corrects the pH of the water. It also removes temporary hardness. Addition of chlorine kills germs. When added to water, chlorine forms monooxochlorate(I) acid which decomposes readily, producing oxygen for disinfection.



**Figure 9.14 Water treatment plant**



## Chapter Summary

1. Water is a universal solvent in that it dissolves practically all substances, some to a large extent, others in minute amounts.  
Dissolved oxygen in water is essential for aquatic life.
2. When hydrogen burns in air or oxygen, water is formed.
3. Water which does not lather easily with soap is said to be hard.

Temporarily hard water	Permanently hard water
Contains $\text{HCO}_3^-$ of $\text{Ca}^{2+}$ or $\text{Mg}^{2+}$	Contains $\text{SO}_4^{2-}$ of $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ or $\text{Fe}^{2+}$
Softened by boiling	Not softened by boiling

Disadvantages of hard water

- (i) Wastage of soap in laundry.
  - (ii) Wastage of fuel in industrial boilers.
  - (iii) Formation of scum on washed fabric.
  - (iv) Difficulty in dyeing.
4. Purification of a town's water supply involves the following steps.
    - (i) Filtration.
    - (ii) Aeration.
    - (iii) Coagulation.
    - (iv) Filtration of coagulated particles.
    - (v) pH adjustment.
    - (vi) Chlorination.
  5. Solution = a homogeneous mixture of a solute in a solvent.

Unsaturated solution	Saturated solution	Supersaturated solution
Can dissolve more of the solute at the temperature of reference.	Cannot dissolve more of the solute and contains undissolved solute reference.	Contains more solute than a saturated solution can hold at the temperature of reference.

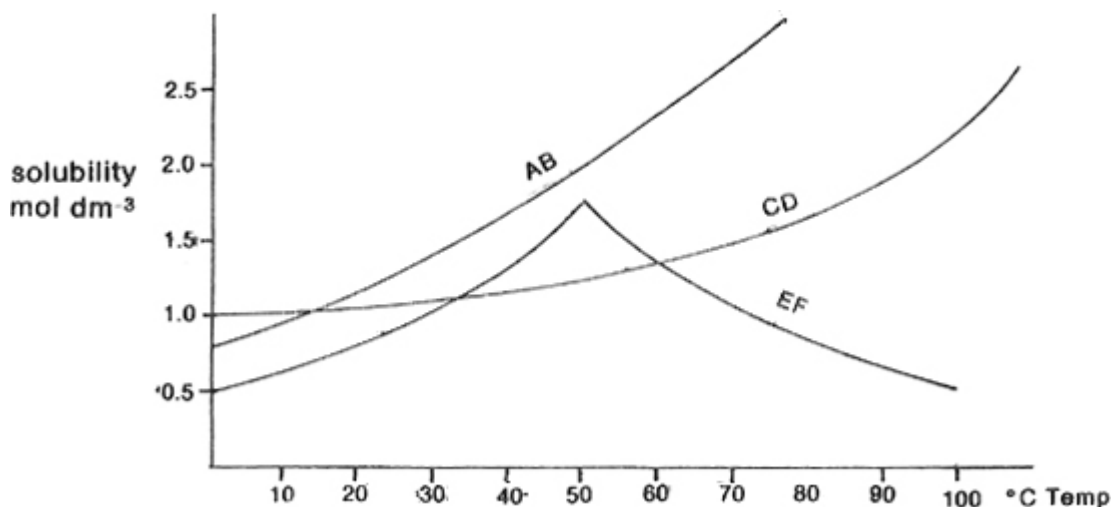
Solubility of a solute is the maximum amount of the solute which 1  $\text{dm}^3$  of a solvent can hold at a given temperature.

Unit:  $\text{mol dm}^{-3}$ .

6. Colloids are not true solutions. They contain particles which are not homogeneously dispersed in the solvent.

# Assessment

- What causes (i) temporary hardness, and (ii) permanent hardness in water?
  - What are the disadvantages of hardness in water?
  - How can both forms of hardness be removed?
- Define the term "solubility".  
 30 cm<sup>3</sup> of a saturated solution of a salt, NaX, at 25 °C was evaporated to dryness and only 2.5g of salt was left. Calculate the solubility of the salt at 25 °C in mol dm<sup>-3</sup>. Molar mass of NaX = 58.5 g
- Figure 9.15 represents the solubility curves of the salts indicated.



**Figure 9.15**

- Which is the least soluble salt, and the most soluble at 50 °C?
  - At what temperature are the solubilities of CD and EF equal?
  - If a saturated solution of AB (molar mass = 101 g) is cooled from 40 °C to 20 °C, what **mass** of salt precipitates?
- List the sources of water pollution.
    - Why do samples of water from different parts of the country taste differently even when they have undergone the same processes of purification?
    - What part do (i) chlorine (ii) alum, (iii) calcium hydroxide, play in the purification of a town's water supply?
  - Define the terms:
      - saturated solution.
      - dilute solution.
      - supersaturated solution.
    - Why is the boiling point of water (100 °C) much higher than that of hydrogen sulphide (≈60 °C)?
  - State the methods of solving the problems of pollution caused by

(a) solid wastes,

(b) non-solid wastes

Describe what happens when

(i) nitrogen(II) oxide is exposed to air,

(ii) sulphur(IV) oxide and hydrogen sulphide react in a gas jar.

7. You are given the following data:

Mass of dry empty dish = 7.16 g

Mass of dish + saturated solution of salt = 17.85 g

Mass of dish + dry salt = 9.30 g

Temperature of solution = 20°C

Molar mass of salt = 100 g

Density of solution of salt = 1.00 g cm<sup>-3</sup>

Calculate the solubility of the salt in

(i) g dm<sup>-3</sup>

(ii) mol dm<sup>-3</sup> of solution.

(WAEC)

8. The water from a new reservoir built to supply water to a village was found to waste a lot of soap when used to wash clothes. What is the possible cause of this? Explain.

(a) State and explain three ways by which you could improve the quality of the water. Would it be necessary to process the water as you have outlined, if all the villagers used detergents for washing? Give reasons for your answer.

(b) State briefly the part played by the addition of (i) chlorine, (ii) alum, in the large-scale purification of drinking water.