|  |
| --- |
| UNIT 8**SOLUBILITY AND PRECIPITATION REACTIONS**Teacher VersionSource: www.dynamicscience.com.au**Contents**1. Solubility and Solubility Curves
2. Solubility and Precipitation Reactions
3. Qualitative Analysis Part 3
4. Hard and Soft Water

Key words: aqueous solution, solvent, solute, concentration, molarity, strong electrolyte, weak electrolyte, soluble, solubility, saturated solution, sparingly soluble, insoluble, solubility curve, crystallisation, recrystallisation, precipitate, precipitation, hard water, soft water, limescale, sum, lather, ion exchange**Units which must be completed before this unit can be attempted:**Unit 1 – Atoms and the Periodic TableUnit 2 – Particles, Bonding and StructuresUnit 3 – Amount of Substance and MeasurementUnit 4 – Introduction to Physical ChemistryUnit 5 – Acids, Bases and SaltsUnit 6 – Redox Reactions**Estimated Teaching Time: 8 hours** |

**UNIT 8 SUMMARY AND SYLLABUS REFERENCE**

|  |  |
| --- | --- |
| **Lesson** | **Title and Syllabus Reference** |
| **1** | **Solubility and Saturated Solutions*****CA8a solubility – general principles*** *(saturated and unsaturated solutions, saturated solution as an equilibrium system, solubility expressed in moldm-3, solubility of sparingly soluble salts - complete dissociation of the portion that dissolves (qualitative treatment only));* ***CA13i General Skills and Principles - measurement of mass and volume****;* ***CA13aiii General Skills and Principles – filtration****;* ***CA13biii acid-base titrations - the use of standard solutions of acids and alkalis and the indicators methyl orange and phenolphthalein to determine the solubility of acids and bases*** |
| **2** | **Crystallisation and Solubility Curves*****CA8a solubility – general principles*** *(solubility curves and their uses, relationship between solubility and crystallisation, crystallisation as a method of purification);* ***CA13aiii General Skills and Principles – filtration and recrystallisation*** |
| **3** | **Precipitation*****CA4aiii chemical equations*** *(precipitation);* ***CA8b practical application of solubility*** *(generalisations of solubility of salts)* |
| **4** | **Preparation of Insoluble Salts*****CA13aiii filtration****;* ***CC4a methods of preparation of simple salts****;* ***ISA7.4 methods of preparation of salts*** *(preparation of salts using the following methods: precipitation)* |
| **5** | **Qualitative Analysis (Cations) – Precipitation Reactions*****CA8b practical application of solubility*** *(generalisations of solubility of salts and their applications in qualitative analyses));* ***CA13ci characteristic tests of the following cations with dilute NaOH(aq): Ca2+, Pb2+, Cu2+, Fe2+, Fe3+, Al3+ and Zn2+, confirmatory tests for these cations*** |
| **6** | **Qualitative Analysis (Anions) – Precipitation Reactions*****CA8b practical application of solubility*** *(generalisations of solubility of salts and their applications in qualitative analyses));* ***CA13cii confirmatory tests for the following ions: Cl-, SO32-, CO32-, SO42-****;* ***CA13civ characteristic test for the following gases: CO2 and SO2*** |
| **7** | **Hard and Soft Water*****CC7biii water and Solution - hardness of water: causes and methods of removing it*** *(advantages and disadvantages of hard water and soft water, experiments to compare the degree of hardness in different samples of water);* ***ISA9.2 hardness and softness of water*** *(advantages and disadvantages of hard and soft water, causes of hardness of water (Ca2+, Mg2+, Fe2+ ions), softening hard water (addition of washing soda, ion exchange, boiling and distillation))* |
| **8** | **Unit 8 Revision and Summary** |

****

***Lesson 1 – What is solubility and what are saturated solutions?***

1. **Solubility and Solubility Curves**
2. **Solubility and Saturated Solutions**

|  |
| --- |
| **Summary Activity 1.1: What is a solution?*** What do the terms “solution”, “solute” and “solvent” mean?
* What is the most common solvent? What is the name given to solutions containing this solvent?
* Can you give an example of a solution?
* What is molarity?
* What is an electrolyte? What is the difference between a strong and a weak electrolyte?
 |
| * Solution: mixture of two components, evenly distributed and in the same phase (usually liquid), solute = minor component of a solution; solvent = major component of a solution
* Water; aqueous solutions
* Sea water, brine, limewater
* Moles of solute per cubic decimetre of solution
* A substance which can form free ions in solution; strong electrolytes completely dissociate into ions in solution, weak electrolytes only partially dissociate
 |

* In SS1 (Unit 2 – Particles, Bonding and Structure) you learned that solutions consisted of a solute dissolved in a solvent
* **Solubility** is the ability of a solute to dissolve in a solvent; the solubility of a solute in a solvent is defined as the maximum possible **concentration** of the solute in that solvent; in this course we will consider only **aqueous solutions** (ie solutions in which the solvent is water)
* There are different ways to measure concentration, but the one we use in this course is the moles of solute per cubic decimetre of solution (moldm-3); this is also known as **molarity**
* The solubility of solutes varies with temperature, so when describing the solubility of a solute it is important to state the temperature; generally, the solubility of solids and liquids increases with increasing temperature but the solubility of gases decreases with increasing temperature

Eg The solubility of sodium chloride (NaCl) in water at 25 oC is 6.2 moldm-3.

 The solubility of glucose (C6H12O6) in water is 5.1 moldm-3 at 25 oC and 14 moldm-3 at 50 oC

 The solubility of ammonia (NH3) in water is 32 moldm-3 at 20 oC and 17 moldm-3 at 50 oC

* If the maximum possible molarity of a solution is low (ie below 0.2 moldm-3) the solute is described as slightly soluble; if the solubility is much lower than this the solute might be described as sparingly soluble or insoluble
* A solution which is at its maximum possible concentration at that temperature is said to be **saturated**; it is not possible to dissolve any more solute in a solution which is saturated; the solubility of a substance in water can also therefore be defined as the concentration of a saturated solution; if a solution is not saturated, its concentration is less than the maximum possible and it should be possible to dissolve more of the solute in it

|  |
| --- |
| **The solubility of a substance in a solvent is the concentration of a saturated solution of that substance in the solvent** |

|  |
| --- |
| **A saturated solution is a solution which is at its maximum possible concentration** |

* Solubility in water is generally restricted to ionic compounds and molecular substances; metals and giant structures will not dissolve in water unless there is a chemical reaction with the water
* Ionic compounds, if soluble, are strong electrolytes, which means that they dissociate completely to form ions in solution:

 eg NaCl(s) 🡪 Na+(aq) + Cl-(aq)

* Most molecular substances, if soluble, are usually weak electrolytes or non-electrolytes; weak electrolytes only dissociate slightly to form ions in solution:

 eg NH3(g) 🡪 NH3(g)NH4+(aq) + OH-(aq)

* non-electrolytes do not dissociate at all:

 eg C2H6O(l) 🡪 C2H6O(aq)

* a very small number of molecular substances are strong electrolytes:

 eg HCl(g) 🡪 H+(aq) + Cl-(aq)

* The process of dissolving a solute in a solvent is reversible; it is possible for the solute to separate itself from the solution and form the pure substance (usually as a solid, in which case it settles at the bottom of the container, or as a gas, in which case it escapes); a saturated solution is in a state of **dynamic equilibrium** (the solute is dissolving in the solvent at the same rate as it is separating it out from the solvent)

|  |
| --- |
| Image result for test icon**Test your knowledge 1.2: Understanding Solubility and Saturated Solutions**At 50 oC, it is possible to dissolve up to 244 g of glucose (C6H12O6) in 100 cm3 of water.1. What is the solubility of glucose in water (in moldm-3) at 50 oC?
2. What is the maximum mass of glucose which can dissolve in 25 cm3 of water at 50 oC?
3. A student attempts to dissolve 135 g of glucose in 60 cm3 of water at 50 oC. Will she succeed? Explain your answer.
4. Suggest two ways in which glucose could be crystallised from a solution.

A saturated solution of calcium hydroxide (Ca(OH)2) is known as limewater. At 25 oC, limewater has a molarity of 0.020 moldm-3. 1. Write an equation, using state symbols for the equilibrium which exists in limewater
2. Calculate the minimum mass of calcium hydroxide required to prepare 250 cm3 of limewater
3. A student attempts to dissolve 2.0 g of calcium hydroxide in 100 cm3 of water at 25 oC. Will he succeed? Explain your answer
4. Which is more soluble in water? Glucose or calcium hydroxide? Explain.
5. Are glucose and calcium hydroxide electrolytes? Explain your answer.
 |

|  |
| --- |
| 1. 13.6 moldm-3
2. 61.2 g
3. Yes, because the molarity would be 12.5 moldm-3 which is less than a saturated solution
4. By heating the solution until some of the water evaporates, or by cooling the solution
5. Ca(OH)2(s) 🡪 Ca2+(aq) + 2OH-(aq)
6. 0.37 g
7. No, because the molarity would be 0.27 moldm-3 which is greater than the solubility of Ca(OH)2
8. Glucose is more soluble because its saturated solution has a higher molarity than a saturated solution of calcium hydroxide
9. Calcium hydroxide is an electrolyte because when it dissolves it dissociates into its ions; glucose it not an electrolyte because it remains as molecules when it dissolves
 |

1. **Measuring the Solubility of Acids and Bases**
* It is possible to measure the solubility of an acid or base in water by carrying out an **acid-base titration**; firstly a saturated solution of the acid or base must be prepared; the concentration of the saturated solution, and hence the solubility of the acid/base, can be determined using an acid-base titration:

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 1.3: Determining the solubility of calcium hydroxide in water by titration**1. Use a weighing boat to weigh out 1 – 2 g of calcium hydroxide
2. Pour the calcium hydroxide into a 250 cm3 volumetric flask
3. Add distilled water, shaking continuously, until the base of the meniscus rests on the mark
4. Leave for a few days, shaking occasionally
5. Filter around 100 cm3 of the solution into a 250 cm3 beaker
6. Pipette two 25.0 cm3 portions of the filtrate into a conical flask, so a total of 50.0 cm3 of the Ca(OH)2 solution is in the conical flask
7. Add a few drops of phenolphthalein indicator to the conical flask
8. Prepare a burette for first use with 0.05 moldm-3 HCl and titrate the Ca(OH)2 solution against the HCl solution until the phenolphthalein decolorises
9. Repeat the titration until two concordant results have been obtained; note the average titre volume

**Write an equation for the reaction between Ca(OH)2 and HCl****Calculate the molarity of the Ca(OH)2 solution and hence the molar solubility of Ca(OH)2 in water** |
| **Equipment needed per group: spatula, weighing boat, funnel, filter paper, 250 cm3 volumetric flask, 250 cm3 beaker, 25.0 cm3 pipette with pipette filler, 50 cm3 burette, clamp, stand, boss, access to mass balance, access to distilled water, access to Ca(OH)2 (1 – 2 g per group), access to phenolphthalein (1 cm3 per group), access to 0.05 moldm-3 HCl (100 cm3 per group)*** **Ca(OH)2 + 2HCl 🡪 CaCl2 + 2H2O**
* **The solubility of Ca(OH) in water is 0.011 moldm-3; around 22 cm3 of HCl should be needed**
* **Using 22 cm3, moles of HCl = 22/1000 x 0.05 = 0.0011, so moles of Ca(OH)2 = 5.5 x 10-4, so molarity of solution = 2.2 x 10-4/0.05 = 0.011 moldm-3; this is the solubility of Ca(OH)2**
 |

# *Lesson 2 – What is crystallisation and what are solubility curves?*

1. **Crystallisation**

|  |
| --- |
| **Summary Activity 2.1: Preparing salts*** When you prepared salts in SS2 (Unit 5 – Acids, Bases and Salts and Unit 6 – Redox Reactions), how did you separate the pure salt from the solution? How does this technique work?
 |
| * We heated the salt solution gently until most of the water had evaporated off
* Some of the salt crystallises out during heating because the concentration of the solution increases as the water is removed
* Most of the salt crystallises out during cooling; the water continues to evaporate so the concentration increases, and the solubility decreases as the solution cools down
 |

* Salts and other solid solutes can usually be separated from their solutions by **crystallisation**:
* first heat the solution to evaporate off some of the water; as the water is removed the concentration of the solution increases; when the concentration becomes equal to the solubility of the solute (ie the solution becomes saturated) the solute will start to crystallise
* then allow the solution to cool; the water will to continue to evaporate, causing more solute to crystallise; also as the solution cools down the solubility decreases (most solids become less soluble at lower temperatures) so more solute crystallises
* don’t allow all the solvent to evaporate during heating; this will cause the temperature to rise rapidly and this may cause the solute to burn or decompose
* The technique of crystallisation (or recrystallisation) can also be used as a **purification** technique:
* the pure solid should dissolve in hot water but crystallise in cold water
* some impurities will not dissolve in water and so they can be filtered out after the solid dissolves in hot water
* other impurities dissolve even in cold water and remain in solution after the pure solid crystallises

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 2.2: Purify a sample of copper sulphate by recrystallisation**1. Pour 30 cm3 of distilled water into a 250 cm3 beaker
2. Add impure copper sulphate to the beaker using a spatula; stir the mixture gently so that the solid dissolves; keep adding the impure copper sulphate until it stops dissolving (you might need 10 g of copper sulphate or even slightly more
3. Add 3 cm3 of 1 moldm-3 H2SO4 and stir the mixture gently
4. Place some filter paper in a funnel; place the funnel over an evaporating dish and pour the copper sulphate solution into the funnel
5. Now place the evaporating dish containing the filtrate onto a gauze on a tripod above a Bunsen burner (or onto a sand bath); heat the solution until just over half of the liquid has evaporated
6. Allow the mixture to cool (it’s best to leave it for a few days in a fridge)
7. Carefully decant the excess solution and use a clean spatula to scrape any crystals onto a piece of filter paper
8. Transfer the crystals onto another piece of filter paper; fold the filter paper over the crystals and squeeze them gently

**At what point during this procedure are the insoluble impurities removed?****At what point during this procedure are the soluble impurities removed?** |
| **Equipment needed per group: 15 g of hydrated copper sulphate, spatula, 50 cm3 measuring cylinder; stirring rod, 250 cm3 beaker, 3 pieces of filter paper, funnel, evaporating dish, tripod, gauze and Bunsen burner OR sand bath, access to distilled water, access to fridge*** **The insoluble impurities are removed when the solid is filtered**
* **The soluble impurities are removed when the solid is decanted**
 |
| Can’t do this experiment? Watch this video instead: <https://www.youtube.com/watch?v=SAU-gptAFe0> |

1. **Solubility Curves**
* Most solids are more soluble in water at high temperatures than at low temperatures; it is useful to know the solubility of different solids at different temperatures and **solubility curves** are used for this purpose; the solubility curve for KNO3 in water is shown below:

|  |
| --- |
| Image result for test icon**Test your knowledge 2.3: Using solubility curves**1. What is the solubility of KNO3 at 55 oC?
2. What is the molarity of a saturated solution of KNO3 at 15 oC?
3. What mass of KNO3 can be dissolved in 50 cm3 of water at 25 oC?
4. What volume of water is required to dissolve 20 g of KNO3 at 70 oC?
5. 10 g of KNO3 is dissolved in 10 cm3 of boiling water at 100 oC and the solution is allowed to cool. At what temperature will crystals start to form?
6. What is the minimum temperature required to dissolve 15 g of KNO3 in 20 cm3 of water?
7. Is it possible to dissolve completely 30 g of KNO3 in 25 cm3 of water at 60 oC?
 |
| https://image.freepik.com/free-icon/plus-sign_318-54005.jpg**Extension 2.4: Using solubility curves**Completed Exercise 2.3? Use the solubility curves shown on the first page of this topic to set questions for each other to solve! |
| 1. Approx 9 moldm-3
2. Approx 2.5 moldm-3
3. Solubility = approx. 4 moldm-3 so n = 4 x 0.05 = 0.2 so m = 20 g
4. Solubility = approx. 14 moldm-3, n = 20/101 = 0.2 so V = n/C = 0.014 dm3 or 14 cm3
5. n = 10/101 = 0.1 so C = 0.1/0.01 = 10 moldm-3 so T = 55 - 57 oC
6. n = 15/101 = 0.15 so C = 0.15/0.02 = 7.5 moldm-3 so T = 46 - 48 oC
7. n = 30/101 = 0.3 so C = 0.3/0.025 = 12 moldm-3 but solubility = 11 moldm-3 so not all will dissolve
 |

# *Lesson 3 – What is precipitation and what is a precipitation reaction?*

1. **Solubility and Precipitation Reactions**
* In SS1 (Unit 2 – Particles, Bonding and Structure) you learned about why most, but not all, ionic compounds were soluble in water; in SS2 (Topic 5 – Acids, Bases and Salts) you learned about the solubility of a few common bases and salts

|  |
| --- |
| **Summary Activity 3.1: Solubility of Ionic Compounds*** What causes ionic compounds to dissolve in water?
* Why are some ionic compounds not soluble in water?
* Can you name any ionic compounds which are soluble in water?
* Can you name any ionic compounds which are not soluble in water?
 |
| * Ionic compounds dissolve in water because the positive ions are attracted to the electronegative O atom in water and the negative ions are attracted to the electropositive H atom in water
* The attraction between the ions and water has to be stronger than the attraction of the ions to each other; in some cases the ions are attracted to each other more strongly than they are attracted to water
* sodium chloride, ammonium sulphate, copper sulphate
* silver chloride, calcium carbonate etc
 |

**(i) Predicting the solubility of ionic compounds**

* Most common ionic compounds are soluble in water (ie have solubilities in water of 0.5 moldm-3 or greater at 25 oC); however there are a number of exceptions; by following a few general rules, it is possible to predict the solubility of most ionic compounds in water:
* Rule 1: All compounds containing the nitrate ion (NO3-) are soluble
* Rule 2: All compounds containing Group 1 ions (eg H+, Li+, Na+, K+ etc) and ammonium ions (NH4+) are soluble
* Rule 3: Most compounds containing halide ions (Cl-, Br-, I-) are soluble except the halides of lead (eg PbCl2) and silver (eg AgBr)
* Rule 4: Most compounds containing sulphate ions (SO42-) are soluble except the sulphates of lead, calcium, strontium and barium (PbSO4, CaSO4, SrSO4, BaSO4)
* Rule 5: Most compounds containing hydroxide ions (OH-) and carbonate ions (CO32-) are insoluble except those mentioned in Rule 2 (Rule 5); Ba(OH)2 and Sr(OH)2 are also soluble

|  |
| --- |
| Image result for test icon**Test your knowledge 3.2: Predicting the Solubility of Ionic Compounds**Give the formula of each of the following ionic compounds, and predict which will be soluble in water: |
| 1. magnesium nitrate
2. sodium sulphate
3. copper (II) chloride
4. silver chloride
5. lead (II) bromide
6. copper (II) sulphate
7. barium sulphate
8. magnesium sulphate
 | 1. barium carbonate
2. potassium carbonate
3. calcium carbonate
4. copper (II) hydroxide
5. lithium hydroxide
6. barium hydroxide
7. magnesium hydroxide
 |
| https://image.freepik.com/free-icon/plus-sign_318-54005.jpg**Extension 3.3: Predicting the Solubility of Ionic Compounds**Completed Exercise 3.2? Use the rules to predict the solubility of some more ionic compounds and test each other! |
| 1. Mg(NO3)2; soluble (Rule 1)
2. Na2SO4; soluble (Rule 2)
3. CuCl2; soluble (Rule 3)
4. AgCl; insoluble (Rule 3)
5. PbBr2; insoluble (Rule 3)
6. CuSO4; soluble (Rule 4)
7. BaSO4; insoluble (Rule 4)
8. MgSO4; soluble (Rule 4)
 | 1. BaCO3; insoluble (Rule 5)
2. K2CO3; soluble (Rule 2)
3. CaCO3; insoluble (Rule 5)
4. Cu(OH)2; insoluble (Rule 5)
5. LiOH; soluble (Rule 2)
6. Ba(OH)2; soluble (Rule 5)
7. Mg(OH)2; insoluble (Rule 5)
 |

**(ii) Precipitation**

* If one aqueous solution of an ionic compound is added to another, the cations in the first solution will come in to contact with the anions in the second solution, and the anions in the first solution will come into contact the cations in the second solution; in other words, two new ionic compounds will be created

Eg if NaCl(aq) and AgNO3(aq) are mixed together, the Na+ will come into contact with the NO3- (NaNO3) and the Ag+ will come into contact with the Cl- (AgCl)

* If both of these new compounds are soluble, the ions all mix together freely and no chemical reaction takes place; if either of the new compounds is insoluble, however, the two ions will join together to form a solid; this solid is called a **precipitate**; the formation of an insoluble ionic compound by mixing two different solutions together is called **precipitation**

Eg if NaCl(aq) and AgNO3(aq) are mixed together:

* NaNO3 and AgCl can be formed
* NaNO3 is soluble so the Na+ and NO3- ions remain in solution
* AgCl, is insoluble so the ions join together and a precipitate is observed
* the ionic equation for the reaction is **Ag+(aq) + Cl-(aq) 🡪 AgCl(s)**

|  |
| --- |
| Image result for test icon**Test your knowledge 3.4: Predicting Precipitation**Predict whether a precipitate will form when the following solutions are mixed. If precipitation occurs, write the ionic equation for the reaction taking place: |
| 1. barium chloride solution and sodium sulphate solution
2. lead nitrate solution and sodium chloride solution
3. copper sulphate solution and sodium hydroxide solution
4. sodium carbonate solution and ammonium nitrate solution
5. potassium carbonate solution and calcium chloride solution
6. magnesium chloride solution and sulphuric acid
7. silver nitrate solution and hydrochloric acid
8. sodium chloride solution and nitric acid
 |
| https://image.freepik.com/free-icon/plus-sign_318-54005.jpg**Extension 3.5: Predicting Precipitation**Completed Exercise 3.4? Use the rules to predict some other pairs of solutions which will form a precipitate when mixed together, and write ionic equations for the reactions taking place! |
| 1. precipitate: Ba2+(aq) + SO42-(aq) 🡪 BaSO4(s)
2. precipitate: Pb2+(aq) + 2Cl-(aq) 🡪 PbCl2(s)
3. precipitate: Cu2+(aq) + 2OH-(aq) 🡪 Cu(OH)2(s)
4. no precipitate
5. precipitate: Ca2+(aq) + CO32-(aq) 🡪 CaCO3(s)
6. no precipitate
7. precipitate: Ag+(aq) + Cl-(aq) 🡪 AgCl(s)
8. no precipitate
 |

# *Lesson 4 – How can we prepare insoluble salts?*

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 4.1: Observe precipitation reactions**You are provided with six bottles containing the following solutions:A is silver nitrate (AgNO3)B is hydrochloric acid (HCl)C is sulphuric acid (H2SO4)D is barium chloride (BaCl2)E is copper sulphate (CuSO4)F is sodium hydroxide (NaOH)Each bottle should come with its own 10 cm3 measuring cylinder1. Pour 5 cm3 of solution A into a test tube
2. Add 5 cm3 of solution B to the same test tube; note whether you see a precipitate or not
3. Write “precipitate” or “no precipitate” in the correct box of the table below
4. Repeat steps 2 – 3 using solutions C, D, E and F instead of B
5. Continue mixing the solutions until each combination has been mixed together once
6. Record your observations in the table below:

**Write ionic equations for any reactions taking place** |
| **Equipment needed per group: access to labelled bottles containing 0.05 moldm-3 AgNO3, and 0.1 moldm-3 HCl, H2SO4, BaCl2, CuSO4 and NaOH (25 cm3 per group), with one 10 cm3 measuring cylinder for each bottle, 15 x test tubes, one test tube rack*** **Expected observations:**

* **Equations:**

**AB: Ag+(aq) + Cl-(aq) 🡪 AgCl(s); AC: 2Ag+(aq) + SO42-(aq) 🡪 Ag2SO4(s); AD: Ag+(aq) + Cl-(aq) 🡪 AgCl(s);****AE: Ag+(aq) + Cl-(aq) 🡪 AgCl(s); AF: Ag+(aq) + OH-(aq) 🡪 AgOH(s); CD: Ba2+(aq) + SO42-(aq) 🡪 BaSO4(s); DE: Ba2+(aq) + SO42-(aq) 🡪 BaSO4(s); EF: Cu2+(aq) + 2OH-(aq) 🡪 Cu(OH)2(s)** |

**(iii) Preparing Insoluble Salts**

|  |
| --- |
| **Summary Activity 4.2: Preparation of soluble salts**In SS2 (Topic 5 – Acids, Bases and Salts and Topic 6 – Redox Reactions) you prepared some soluble salts.* Which salts did you prepare and how did you prepare them?
* What types of reaction were used to prepare each salt?
* How was the salt separated from the rest of the reaction mixture?
* Which of the reactants should be in excess?
 |
| * Copper sulphate was prepared by reacting excess copper oxide with sulphuric acid; this is an acid-base (or neutralisation) reaction; the excess copper oxide (which is insoluble) was removed by filtration and the soluble salt was extracted by crystallisation (the salt solution was heated and then allowed to cool)

CuO + H2SO4 🡪 CuSO4 + H2O* Ammonium sulphate was prepared by reacting ammonia with sulphuric acid in a 2:1 ratio; this is an acid-base (or neutralisation) reaction; both reactants are also soluble so the exact quantities were needed; the soluble salt was extracted by crystallisation (the salt solution was heated and then allowed to cool)

2NH3 + H2SO4 🡪 (NH4)2SO4* Zinc sulphate was prepared by reacting excess zinc with dilute sulphuric acid; this is a redox reaction; the excess zinc was removed by filtration and the soluble salt was extracted by crystallisation (the salt solution was heated and then allowed to cool

Zn + H2SO4 🡪 ZnSO4 + H2 |

* Soluble salts can be prepared by neutralisation reactions or by redox reactions; you learned about the preparation of soluble salts in SS2 (Topic 5 - Acids, Bases and Salts and Topic 6 – Redox Reactions); now you will learn about the preparation of **insoluble** salts
* Insoluble salts can be prepared very easily by precipitation reactions; if a solution containing the anion is added to a solution containing the cation, a precipitate of the insoluble salt is forms; a pure sample of the insoluble salt can be separated from the rest of the mixture by filtration

Eg the addition of lead nitrate solution to sodium chloride solution will result in the precipitation of the insoluble salt lead chloride

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 4.3: Prepare a sample of the insoluble salt lead chloride****(caution – lead compounds are toxic; wear gloves, wash your hands thoroughly after carrying out this experiment and do not pour the lead (II) nitrate solution down the sink)**1. Pour 5 cm3 of 1 moldm-3 lead (II) nitrate solution into a boiling tube
2. Pour 5 cm3 of 2 moldm-3 sodium chloride solution into the same boiling tube
3. Place a bung on the boiling tube and shake the contents thoroughly
4. Place a piece of filter paper into a funnel and pour the contents of the boiling tube into the funnel; allow the filtrate to run into a beaker
5. When the filtration is complete, pour a small quantity of cold distilled water into the funnel
6. Use a spatula to scrape the residue off the filter paper and onto another dry piece of filter paper
7. Fold the filter paper of the solid sample and squeeze gently

**Write an ionic equation for the reaction taking place during this preparation.****What type of reaction is taking place?****Does it matter which reactant is in excess? Explain your answer.** |
| **Equipment needed per group: 5 cm3 of 1 moldm-3 lead (II) nitrate solution, 5 cm3 of 2 moldm-3 sodium chloride solution; 2 x 10 cm3 measuring cylinders, boiling tube with bung; funnel, 2 x filter paper, small beaker (50 cm3), spatula, access to distilled water*** **Pb2+(aq) + 2Cl-(aq) 🡪 PbCl2(s)**
* **Precipitation**
* **It doesn’t matter; whichever reactant is in excess will be removed during the filtration process**
 |
| Can’t do this experiment? Watch this video instead: <https://www.youtube.com/watch?v=E1ODnGe9LnM> |

***Lesson 5 – How can we use precipitation reactions to identify cations in solution?***

1. **Qualitative Analysis Part 3 – Precipitation Reactions**
* Qualitative analysis is the experimental identification of a substance or of a particular species present in a substance; you learned about some simple qualitative tests for cations, anions and gases in Unit 5 – Acids, Bases and Salts and Unit 6 – Redox Reactions

|  |
| --- |
|  **Summary Activity 5.1: Qualitative Analysis of Cations*** Describe two different tests to confirm the presence of H+ ions in solution
* Describe a test to confirm the presence of NH4+ ions in solution
 |
| * Add blue litmus paper; it will turn red; add a sample of calcium carbonate; a gas will be given off which turns limewater milky
* Add sodium hydroxide solution and warm; a pungent gas should be given off which turns red litmus paper blue
 |

* Precipitation reactions are very useful in qualitative analysis – they are commonly used to identify particular cations and anions in solution:
* **Sodium hydroxide (NaOH)** solution can give characteristic precipitates with many common metal ions:

 Fe2+(aq) + 2OH-(aq) 🡪 Fe(OH)2(s) dark green precipitate

 Fe3+(aq) + 3OH-(aq) 🡪 Fe(OH)3(s) orange/brown precipitate

 Cu2+(aq) + 2OH-(aq) 🡪 Fe(OH)2(s) dark green precipitate

 Ca2+(aq) + 2OH-(aq) 🡪 Ca(OH)2(s) white precipitate

 Ag+(aq) + OH-(aq) 🡪 AgOH(s) beige precipitate

 In some cases, the hydroxide precipitates formed are amphoteric – this means that they react with alkali as well as acid, and dissolve in aqueous sodium hydroxide solution (see Topic 5 – Acids, Bases and Salts)

 Zn2+(aq) + 2OH-(aq) 🡪 Zn(OH)2(s); Zn(OH)2(s) + 2OH-(aq) 🡪 Zn(OH)42-(aq)

 white precipitate which dissolves in excess NaOH

 Pb2+(aq) + 2OH-(aq) 🡪 Pb(OH)2(s); Pb(OH)2(s) + 2OH-(aq) 🡪 Pb(OH)42-(aq)

 white precipitate which dissolves in excess NaOH

 Al3+(aq) + 3OH-(aq) 🡪 Al(OH)3(s) ; Al(OH)3(s) + OH-(aq) 🡪 Al(OH)4-(aq)

 white precipitate which dissolves in excess NaOH

 A small number of cations (NH4+, Na+, K+, Ba2+) do not give a precipitate with hydroxide ions

* **Hydrochloric acid (HCl)** solution can give characteristic precipitates with a small number of metal ions:

 Pb2+(aq) + 2Cl-(aq) 🡪 PbCl2(s) white precipitate

 Ag+(aq) + Cl-(aq) 🡪 AgCl(s) white precipitate

 Most other cations do not give a precipitate with chloride ions; this reaction allows Pb2+ to be distinguished from Zn2+ and Al3+

* **Summary: precipitation tests for cations**

|  |  |  |
| --- | --- | --- |
| Cation | Test | Observation |
| Fe2+ | Add NaOH | Dark green precipitate |
| Fe3+ | Add NaOH | Orange brown precipitate |
| Cu2+ | Add NaOH | Pale blue precipitate |
| Ca2+  | Add NaOH | White precipitate insoluble in excess NaOH |
| Zn2+ or Al3+ | Add NaOHAdd HCl | White precipitate soluble in excess NaOHNo precipitate |
| Pb2+ | Add NaOHAdd HCl | White precipitate soluble in excess NaOHWhite precipitate |

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 5.2: Use precipitation reactions to identify cations in solution**You are given eight solutions, labelled A, B, C, D, E, F, G and H; each solution contains one cation from the following: Pb2+, Ca2+, Fe2+, Fe3+, Zn2+, Cu2+, Al3+ and Na+1. Pour 2 cm3 of solution A into a test tube
2. Add a few drops of dilute NaOH, then add dilute NaOH until the test tube is almost full; note your observations
3. Repeat steps (a) to (b) using solutions B – H
4. Pour 2 cm3 of solution A into a test tube
5. Add a few drops of dilute HCl; record your observations
6. Repeat steps (d) to (e) using solutions B – H

Use your observations to identify which cation is in which solution; present your answers in a table similar to the one below:**Which two cations cannot be distinguished by this combination of tests?** |
| Chemicals needed: minimum 0.1 moldm-3 solutions of: FeSO4 (labelled A), Na2CO3 (labelled B), ZnSO4 (labelled C), CaCl2 (labelled D), CuSO4 (labelled E), Pb(NO3)2 (labelled F), Al2(SO4)3 (labelled G) and Fe2(SO4)3 (labelled H) - around 10 cm3 per group prepared in a single bottle, each with its own dropping pipette; also 0.5 - 1 moldm-3 of the following solutions: NaOH, HCl - up to 20 cm3 per group; each group needs its own bottle with its own dropping pipetteApparatus needed per group: 16 test tubes, 1 test tube rackExpected observations:* Zn2+ and Al3+ cannot be distinguished by this combination of tests
 |

**Lesson 6 – How can we use precipitation reactions to identify anions in solution?**

|  |
| --- |
|  **Summary Activity 6.1: Qualitative Analysis of Anions**1. Describe two different tests to confirm the presence of OH- ions in solution
2. Describe a test to confirm the presence of NO3- ions in solution
3. Describe a test to confirm the presence of CO32- ions in solution
4. Describe a test to confirm the presence of SO32- ions in solution
 |
| 1. Add red litmus paper; it will turn blue; add some ammonium chloride and warm; a pungent gas should be given off which turns red litmus paper blue
2. Add sodium hydroxide solution and aluminium powder and heat; a pungent gas should be given off which turns red litmus paper blue
3. Add HCl(aq); a gas will be given off which turns limewater milky
4. Add HCl(aq); a gas will be given off which turns blue litmus paper red and turns dichromate paper green
 |

* **Silver nitrate (AgNO3) solution** can give characteristic precipitates with most anions; however if these precipitates contain basic ions such as SO32-, CO32- or OH-, the precipitates will react with acids; Ag2SO3, AgOH and Ag2CO3 are all insoluble but react with acids; these precipitates therefore do not form if **dilute nitric acid (HNO3)** is added before the silver nitrate solution; the following precipitates form even in acidic conditions:

 Ag+(aq) + Cl-(aq) 🡪 AgCl(s) white precipitate

 Ag+(aq) + Br-(aq) 🡪 AgBr(s) cream precipitate

 Ag+(aq) + I-(aq) 🡪 AgI(s) yellow precipitate

* **Barium chloride (BaCl2) solution** can give characteristic precipitates with SO32-, SO42-and CO32-, some anions. BaSO3 and BaCO3 contain basic ions so react with acids. These precipitates therefore do not form if **dilute hydrochloric acid (HCl)** is added before the barium chloride solution. Under those conditions, only BaSO4 will form:

 Ba2+(aq) + SO42-(aq) 🡪 BaSO4(s) white precipitate

* **Summary: precipitation tests for anions**

|  |  |  |
| --- | --- | --- |
| Cation | Test | Observation |
| Cl- | Add HNO3 and then AgNO3 | white precipitate |
| Br- | Add HNO3 and then AgNO3 | cream precipitate |
| I- | Add HNO3 and then AgNO3 | yellow precipitate |
| SO42-  | Add HCl and then BaCl2 | white precipitate |
| SO32- | Add BaCl2Then add HCl | White precipitateDissolves in acid; gas evolved which turns blue litmus red and acidified dichromate paper green |
| CO32- | Add BaCl2Then add HCl | White precipitate soluble in excess NaOHDissolves in acid; gas evolved which turns limewater milky |

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 6.2: Use precipitation reactions to identify anions in solution**You are given six solutions, labelled A, B, C, D, E and F; each solution contains one anion from the following: NO3-, I-, SO42-, Cl-, SO32-, CO32-1. Pour 2 cm3 of solution A into a test tube
2. Add 2 cm3 of HNO3, and then a few drops of AgNO3; note your observations
3. Repeat steps (e) – (f) using solutions B – F
4. Pour 2 cm3 of solution A into a test tube
5. Add a few drops of BaCl2; note your observations
6. Repeat steps (e) – (f) using solutions B – F
7. Pour 2 cm3 of each solution which gave a precipitate with BaCl2 into separate test tubes
8. To each test tube, add 2 cm3 of HCl, and then a few drops of BaCl2; note your observations

Use your observations to identify which anion is in which solution; present your answers in a table similar to the one below:**Which two anions cannot be distinguished by this combination of tests? What test could be used to distinguish between these two anions?** |
| Chemicals needed: minimum 0.1 moldm-3 solutions of: FeSO4 (labelled A), Na2CO3 (labelled B), KI (labelled C), KNO3 (labelled D), CaCl2 (labelled E), Na2SO3 (labelled F) - around 10 cm3 per group prepared in a single bottle, each with its own dropping pipette; also access to 0.05 moldm-3 AgNO3, 0.1 moldm BaCl2, 1 moldm-3 HCl, 1 moldm-3 HNO3 - up to 50 cm3 per group; each bottle needs its own dropping pipetteApparatus needed per group: 17 test tubes, 2 test tube racksExpected observations:CO32- and SO32- cannot be distinguished by this combination of tests; they could be distinguished by adding CaCl2(aq) and then adding HCl(aq) to the resulting precipitate; the gas evolved from CO32- will turn limewater milky; the gas evolved from SO32- will turn blue litmus red and turn dichromate paper green |

|  |
| --- |
| Image result for test icon**Test your knowledge 6.3: Using precipitation to distinguish between different solutions**Describe a simple test to show how you would distinguish between the following solutions:1. sodium chloride and calcium chloride
2. zinc nitrate and calcium nitrate
3. iron (II) sulphate, copper sulphate and iron (III) sulphate
4. zinc nitrate and lead nitrate
5. sodium chloride and sodium nitrate
6. sodium chloride and sodium sulphate
7. sodium sulphate and sodium carbonate
 |
| 1. add NaOH (aq); no reaction with NaCl; white precipitate with Ca(OH)2
2. add NaOH (aq) dropwise and then in excess; white precipitate with Ca(NO3)2 is insoluble in excess NaOH; white precipitate with Pb(NO3)2 dissolves in excess NaOH
3. add NaOH (aq); dark green precipitate with FeSO4; pale blue precipitate with CuSO4: orange/brown precipitate with Fe2(SO4)3
4. add HCl (aq); no reaction with Ca(NO3)2; white precipitate with Pb(NO3)2
5. Add AgNO3 (aq); no reaction with NaNO3; white precipitate with NaCl
6. Add BaCl2 (aq); no reaction with NaCl; white precipitate with Na2SO4
7. Add BaCl2 (aq) then add HCl(aq); white precipitate with Na2SO4 is insoluble in HCl; white precipitate with Na2CO3 dissolves in HCl
 |
| https://image.freepik.com/free-icon/plus-sign_318-54005.jpg**Extension 6.4: Further qualitative analysis**Completed Exercise 6.3? Describe simple tests to distinguish between the following solutions: (these questions require you to use qualitative analysis from previous units)1. sodium nitrate and nitric acid
2. sodium hydroxide and sodium carbonate
3. sodium nitrate and ammonium nitrate
4. sodium nitrate and water
 |
| 1. add blue litmus paper; it turns red in nitric acid but not in sodium nitrate
2. add HCl; observe bubbles with sodium carbonate but not with sodium hydroxide, or add magnesium chloride solution (or any solution containing a +2 ion); a precipitate forms in both cases; with the carbonate, the precipitate will give off bubbles when it dissolves, but the hydroxide will dissolve without giving off bubbles
3. Add NaOH and heat; with ammonium nitrate, a pungent gas will be given off which turns red litmus blue; with sodium nitrate there will be no reaction
4. Add aluminium powder and sodium hydroxide and hear; with sodium nitrate, a pungent gas will be given off which turns red litmus blue; with water there will be no reaction
 |

***Lesson 7 – What is hard water?***

**d) Hard and Soft Water**

**(i) definition of hard water**

* Hard water is water which contains a high concentration of dissolved Ca2+, Mg2+ and Fe2+ ions; these ions are commonly found in rocks and can get into the water supply when water comes into contact with these rocks; the presence of these ions in water causes a number of precipitation reactions to take place which can cause problems; soft water is water which contains only a very low concentration of these ions

**(ii) disadvantages of hard water**

* The first problem caused by the presence of these ions is that when heated, these ions react with dissolved hydrogencarbonate ions (HCO3-) in water to form calcium carbonate, which is insoluble:

 Ca2+(aq) + 2HCO3-(aq) 🡪 CaCO3(s) + CO2(g) + H2O(l)

 Mg2+(aq) + 2HCO3-(aq) 🡪 MgCO3(s) + CO2(g) + H2O(l)

The compound CaCO3(s) is known as limescale and can form on the surface of heating elements, especially in kettles, washing machines, dishwashers and industrial water heaters; limescale reduces the efficiency heat transfer and it can also restrict the flow of water if it builds up in pipes

* The second problem caused by the presence of these ions is they react with the anions present in soap, such as C17H35COO- (stearate ions) to form a precipitate:

 Ca2+(aq) + C17H35COO-(aq) 🡪 Ca(C17H35COO)2(s)

This precipitate is known as scum and it removes the stearate ions from the water; as a result the lather which should be formed in water by the stearate ions does not form; so soap is less effective in hard water

* The structure of soap will be covered in more detail in Unit 11 – Further Organic Chemistry

**(iii) advantages of hard water**

* Ca2+, Mg2+ and Fe2+ are important minerals for the human body, and hard water can be a useful source of these minerals; if the concentration of these ions are very high, however, the disadvantages of hard water are judged to outweigh the benefits

**(iv) temporary and permanent hardness**

* The hardness of water is described as temporary if the main anion present in the water is HCO3-; when heated, HCO3- decomposes into CO32- which forms a precipitate with Ca2+, Mg2+ and Fe2+ ions;

Ca2+(aq) + 2HCO3-(aq) 🡪 CaCO3(s) + CO2(g) + H2O(l)

 Mg2+(aq) + 2HCO3-(aq) 🡪 MgCO3(s) + CO2(g) + H2O(l)

This precipitate can be removed by filtration and the resulting water is soft; temporary hardness can therefore be removed simply by heating the water

* The hardness of water is described as permanent if the main anion present in the water is not HCO3-; in such cases it is usually SO42- or Cl-; these ions do not form precipitation reactions on heating; permanent hardness therefore cannot be removed just be heating the water

**(v) softening water**

* Other than simply boiling (which only removes temporary hardness), there are three main techniques available for softening water (ie removing Ca2+, Mg2+ and Fe2+ ions):
* **Precipitation**: all of the ions responsible for water hardness form insoluble carbonates; the addition of a solution of sodium carbonate (Na2CO3) to the water will therefore remove all three of these ions as precipitates:

 Ca2+(aq) + CO32-(aq) 🡪 CaCO3(s)

 Mg2+(aq) + CO32-(aq) 🡪 MgCO3(s)

 Fe2+(aq) + CO32-(aq) 🡪 FeCO3(s)

The resulting water, when filtered, is soft

* **Distillation**: when water is boiled, any dissolved ions do not boil but remain in the residue (as ionic compounds have a high boiling point); when condensed again, the boiled water has lost its ions and is therefore soft
* **Ion Exchange**: ion exchange resins contain weakly attached sodium ions (Na+); when hard water is passed through these resins, the Ca2+ and Mg2+ ions attach more strongly to the resin and replace the Na+ ions; the Ca2+ and Mg2+ ions in the water are therefore replaced with Na+ ions and the water is now soft

**(vi) testing the hardness of water**

* The degree of hardness in different water samples can be compared simply by adding soap solution gradually until a lather is formed; the greater the quantity of soap solution required, the greater the levels of hardness in the water

|  |
| --- |
| cid:ii_jepnvfe00_1621fa54a497745d **Practical 7.1: Test the Hardness of Water**Collect four different samples of water from four different sources (such as tap water, rainwater, sea water and bottled water); you will need access to a solution of soap in ethanol1. Using a measuring cylinder, pour 10 cm3 of the first water sample into a conical flask
2. Fill a burette with the solution of soap in ethanol; record the initial burette reading
3. Add 1 cm3 of the soap solution to the conical flask and shake the flask well; observe whether or not a lather forms
4. If no lather forms, add a further 1 cm3 and shake the flask well; continue this process until a lather forms which lasts for 30 seconds
5. Once a lather has formed, record the final burette reading and calculate the volume of soap solution required
6. Rinse out your conical flask and repeat steps (a) to (e) for the other water samples
7. Record your results in a simple table

**Which water is the hardest?** |

|  |
| --- |
| Chemicals needed: water from different sources and a solution of soap in ethanol (around 50 cm3 per group)Apparatus needed per group: one conical flask, one measuring cylinder (10 cm3), one burette with clamp, boss and stand and one funnelThe seawater should be the hardest (need the greatest quantity of soap) and the rainwater should be the softest (need the least quantity of soap) |
| https://image.freepik.com/free-icon/plus-sign_318-54005.jpg**Extension 7.2: Testing for Temporary and Permanent Hardness in Water**Completed Exercise 7.1? How would you adapt Experiment 7.1 to determine how much of the hardness in each water sample was temporary and how much was permanent? |
| Take 10 cm3 of water from each source and boil them before adding the soap; then add the soap as in the original experiment; if less soap is required with the boiled sample, some of its hardness is temporary; the bigger the difference, the greater the amount of temporary hardness in the water |

|  |
| --- |
| Image result for test icon**Test your knowledge 7.3: Understanding the Difference Between Hard and Soft Water**1. Which ions are responsible for the hardness of water?
2. State two problems caused by hard water
3. State one advantage of hard water
4. Describe three ways of reducing the hardness of water
 |
| 1. Ca2+, Mg2+ and Fe2+ ions
2. Forms limescale when heated, forms scum instead of lather with soap
3. It is a good source of minerals for humans
4. Distillation, ion exchange, precipitation using sodium carbonate
 |

***Lesson 8 – How much have I learned about solubility and precipitation reactions?***

|  |
| --- |
| Image result for test icon**8.1 END-OF-UNIT QUIZ****UNIT 8 – SOLUBILITY AND PRECIPITATION REACTIONS**1. What is a saturated solution?
2. Explain how, in a saturated solution of NaCl, the solid NaCl and the aqueous NaCl form a dynamic equilibrium
3. Describe how the solubility of most solids varies with temperature
4. Describe how the solubility of most gases varies with temperature
5. Use graph paper to draw a solubility curve for NH4Cl given the following solubility data:

Use your graph to answer the following questions:1. What is the molarity of a saturated solution of NH4Cl at 25 oC?
2. What mass of NH4Cl can be dissolved in 50 cm3 of water at 45 oC?
3. What volume of water is needed to dissolve 10 g of NH4Cl at 55 oC?
4. At what temperature will a 10.0 moldm-3 solution of NH4Cl start to crystallise if it is cooled slowly from 90 oC?
5. Predict whether the following ionic compounds will be soluble in water:
6. copper sulphate
7. barium sulphate
8. sodium carbonate
9. copper carbonate
10. calcium chloride
11. Describe what you would observe if you mixed the following pairs of solutions together:
12. copper sulphate and sodium hydroxide
13. calcium nitrate and sodium chloride
14. lead nitrate and sulphuric acid
15. calcium chloride and sodium carbonate
16. silver nitrate and hydrochloric acid
17. Give a simple chemical test which would distinguish between the following solutions:
18. iron (II) sulphate and iron (III) sulphate
19. lead nitrate and zinc nitrate
20. sodium carbonate and sodium sulphate
21. (a) Which ions are responsible for the hardness of water

(b) Give two reasons why hardness of water is a problem(c) Describe three ways in which water can be softened(d) Describe a simple experiment to compare the hardness of different water samples |

|  |
| --- |
| 1. A solution which contains the maximum amount of dissolved solute which it is possible to dissolve in that quantity of solvent
2. The solid NaCl dissolves and the aqueous NaCl crystallises at equal rates
3. Solubility of solids usually increases with temperature
4. Solubility of gases usually decreases with temperature
5. 7.1 – 7.2 moldm-3 (b) solubility = 8.5 – 8.7 moldm-3 so mass = 23 – 24 g

(c) solubility = 10.0 – 10.2 moldm-3 so volume = 18 – 19 cm3 (d) around 54 oC1. (a) soluble; (b) insoluble; (c) soluble; (d) insoluble; (e) soluble
2. (a) pale blue precipitate; (b) no reaction; (c) white precipitate; (d) white precipitate; (e) white precipitate
3. (a) Add NaOH (aq); FeSO4 gives dark green precipitate, Fe2(SO4)3 gives orange/brown precipitate
4. Add HCl (aq); Pb(NO3)2 gives white precipitate; Zn(NO3)2 gives no reaction
5. Add HCl (aq) and then BaCl2(aq); Na2CO3 gives no reaction; Na2SO4 gives white precipitate
6. (a) Fe2+, Ca2+, Mg2+

(b) causes limescale when heated, causes scum instead of lather with soap(c) ion exchange, distillation, precipitation with sodium carbonate(d) Add soap from a burette to a fixed quantity of different water sample; measure how much is needed to form a lather; the more soap needed, the harder the water |