# SOLUBILITY

# I. CALCULATING SOLUBILITY AND ION CONCENTRATIONS

Once the mass of a substance present in 1 L of a solution has been experimentally measured, calculating the solubility of the substance is straightforward.

**EXAMPLE:** It is experimentally found that 1.00 L of saturated AgBrO<sub>3</sub>(aq) contains 1.96 g of AgBrO<sub>3</sub>. What is the **molar solubility** of AgBrO<sub>3</sub>? (That is, what is the solubility expressed in moles per litre?)

$$[AgBrO_3] = 1.96 \frac{g}{L} \times \frac{1mol}{235.8 g} = 8.31 \times 10^{-3} M$$

**EXAMPLE:** The molar solubility of Pbl<sub>2</sub> is  $1.37 \times 10^{-3}$  M. Express this value in grams per litre.

Solubility (g/L) = 
$$1.37 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times \frac{461.0 \text{ g}}{1 \text{ mol}} = 0.632 \frac{\text{g}}{\text{L}}$$

**EXAMPLE:** It is experimentally found that 0.250 L of saturated CaCl<sub>2</sub> contains 18.6 g of CaCl<sub>2</sub> at  $20^{\circ}$ C. What is the molar solubility of CaCl<sub>2</sub>?

$$[CaCl_2] = \frac{18.6 \text{ g}}{0.250 \text{ L}} \times \frac{1 \text{mol}}{111.1 \text{ g}} = 0.670 \text{ M}$$

#### Note: Unless otherwise indicated, assume all solutions are at a temperature of 25°C.

#### EXERCISES:

- 1. Aluminum fluoride,  $AIF_3$ , has a solubility of 5.59 g/L at 20<sup>o</sup>C. Express this solubility in moles per litre.
- Lead (II) chloride, PbCl<sub>2</sub>, has a solubility of 0.99 g/100.0 mL at 20<sup>o</sup>C. Calculate the molar solubility of PbCl<sub>2</sub>.
- 3. The molar solubility of MgCO<sub>3</sub> is  $1.26 \times 10^{-3}$  M at  $25^{\circ}$ C. Express this value in grams per litre.
- 4. The molar solubility of  $Ag_2CO_3$  is 1.2 x  $10^{-4}$  M at  $25^{\circ}C$ . Express this value in grams per 100.0 mL.
- 5. Chromium (VI) oxide, CrO<sub>3</sub>(s), has a solubility of 92.6 g in 150.0 mL of solution at 0<sup>o</sup>C. Calculate the molar solubility of CrO<sub>3</sub>.
- 6. Silver chlorite, AgClO<sub>2</sub>, has a molar solubility of 0.014 M at 25<sup>o</sup>C. What mass of AgClO<sub>2</sub> is contained in 50.0 mL of saturated AgClO<sub>2</sub>?
- 7. Manganese (II) chloride, MnCl<sub>2</sub>, has a molar solubility of 5.75 M at 0<sup>o</sup>C. If 125 mL of saturated MnCl<sub>2</sub> is evaporated to dryness, what mass of MnCl<sub>2</sub> will be left?
- 8. A chemistry student is assigned the task of determining the solubility of potassium chloride, KCI. She adds an excess of solid KCI to water, stirs, and lets the solution sit overnight. The next day, she pipets a 25.00 mL portion of the saturated solution into a pre–weighed evaporating dish, determines the combined mass, carefully boils off the water present, allows the residue to cool and re–determines the mass of the evaporating dish and residue. The data obtained is given below.

temperature of solution	= 22.5 <sup>°</sup> C
mass of evaporating dish	= 54 <b>.</b> 87 g
mass of solution and evaporating dish	= 84 <b>.</b> 84 g
mass of residue and evaporating dish	= 62 <b>.</b> 59 g

#### Calculate:

- a) the mass of 25.00 mL of the solution.
- b) the mass of KCl in 25.00 mL of solution.
- c) the mass of water in 25.00 mL of solution.
- d) the mass of KCl which can dissolve in 100.0 g of water at  $22.5^{\circ}$ C.
- e) the molar solubility of KCI, expressed in moles of KCI per litre of solution.
- 9. The following data is obtained when a saturated solution of aqueous ammonium sulphate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>(aq), is poured into a beaker and evaporated to dryness.

temperature of solution	= 25°C
volume of solution used	= 70.0 mL
mass of beaker	= 87.23 g
mass of original solution and beaker	= 147 <b>.</b> 42 g
mass of beaker and dried (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	= 104.08 g

Calculate:

- a) The mass of the solution.
- b) The mass of ammonium sulphate in the solution.
- c) The mass of water in the solution.
- d) The mass of ammonium sulphate which could be dissolved in 100.0 g of water.
- e) The molar concentration of the ammonium sulphate solution.

# **II. PREDICTING THE SOLUBILITIES OF SALTS**

This section examines some of the general rules for predicting the solubilities of salts and uses a *Solubility Table* to predict whether a given salt is soluble in water.

First, let's establish what is meant when a salt is said to be "SOLUBLE" or to have "LOW SOLUBILITY."

Strictly speaking, nothing is INSOLUBLE in water. For example, glass dissolves to an extremely small extent in water. Normally, the amount of glass that dissolves in water can be NEGLECTED and glass is said to have **NEGLIGIBLE SOLUBILITY** in water.

Some compounds may dissolve SLIGHTLY, such that the amount that dissolves is extremely small but cannot be neglected. Such a substance is said to have **LOW SOLUBILITY**. For example, lead (II) chloride, PbCl<sub>2</sub>, has low solubility in water, but the amount which dissolves cannot always be neglected: the small amount of Pb<sup>2+</sup> ion present in saturated PbCl<sub>2</sub>(aq) is toxic if swallowed.

Now the problem is: When has a compound dissolved to a sufficient extent that you cannot say it has LOW SOLUBILITY? This is like asking: "What is the least amount of money you need in order to be RICH?" All that can be done is to set an *arbitrary value*.

**Definition:** A substance is said to have **LOW SOLUBILITY** if a saturated solution of the substance has a concentration of less than 0.1 M.

**Note:** The phrase "having a solubility of less than 0.1 M" is often used to indicate low solubility. You will often see something like the following statement in a problem:

### "Equal volumes of 0.2 M compound A and 0.2 M compound B are mixed."

After dilution, both compounds A and B are present as 0.1 M solutions. If a precipitate forms when A and B are mixed, the precipitate qualifies as having low solubility.

Let us illustrate how to use the table "SOLUBILITY OF COMMON COMPOUNDS IN WATER" (found on the last page of this Unit) by starting with the following small section of the table. (In the future, this table will be referred to as the "Solubility Table" or simply the "Table.")

Note that the term "Alkali ions" refers to the <u>family</u> of ions: Li<sup>+</sup>, Na<sup>+</sup>, etc. DO NOT FORGET THIS FACT when reading the Table.

**EXAMPLE:** Determine whether FeCO<sub>3</sub>(s) is soluble or has low solubility.

Using the Solubility Table, find the compound's negative ion ( $CO_3^{2-}$  in this case) and locate it in the "NEGATIVE ION" column (first column). Note that negative ions are written last in the chemical formula.

On the immediate right of  $CO_3^{2-}$ , find the other ion,  $Fe^{2+}$ , in the "POSITIVE ION" column. Since  $Fe^{2+}$  is not explicitly listed, it must be included in the category "**All Others**."

Finally, look in the "SOLUBILITY OF COMPOUNDS" column (last column) to see that FeCO<sub>3</sub>(s) has "LOW SOLUBILITY".

When two ions form a compound having "LOW SOLUBILITY," the mixing of the two ions will cause a **PRECIPITATE** to form.

**EXAMPLE:** Will a precipitate form when equal volumes of 0.2 M solutions of CaS and Na<sub>2</sub>SO<sub>4</sub> are mixed?

First, look for combinations of ions that might form a precipitate:

The ions present are:

$$CaS = Ca^{2+} + S^{2-}$$
  
Na<sub>2</sub>SO<sub>4</sub> = 2 Na<sup>+</sup> + SO<sub>4</sub><sup>2-</sup>

Ignore the combinations  $Ca^{2+} + S^{2-}$  and  $Na^+ + SO_4^{2-}$ . (They must be soluble in order to allow us to obtain a 0.2 M solution of them.)

Examine the "cross-combinations" shown above:

 $Na^{+} + S^{2-}$ : the Solubility Table indicates that this mixture is "Soluble"  $Ca^{2+} + SO_{4-}^{2-}$ : the Solubility Table indicates that this mixture has "Low Solubility"

Therefore, mixing the solutions produces a precipitate of CaSO<sub>4</sub>.

#### SPECIAL NOTES:

1. Copper forms TWO different ions:  $Cu^+$  and  $Cu^{2+}$ .

 $Cu^{+}$  has "LOW SOLUBILITY" when combined with Cl<sup>-</sup>, Br<sup>-</sup> or l<sup>-</sup>.  $Cu^{2+}$  is "Soluble" when combined with Cl<sup>-</sup>, Br<sup>-</sup> or l<sup>-</sup>.

**No** simple compounds exist which contain the  $Cu^+$  ion and are soluble. (Copper(I) nitrate does not exist.) Therefore, you can only be asked if a compound containing  $Cu^+$  is or is not soluble. You cannot be asked if a precipitate of CuCl, say, is formed when two solutions are mixed because there is no easy way to get sufficient concentrations of  $Cu^+$  ion into solution.

2. It will be assumed that you either have memorized the formulae and charges of the common ions or will be using the table "Names, Formulae, and Charges of Some Common Ions", found on page 341 of *Hebden: Chemistry 11, A Workbook for Students.* You MUST be able to write the chemical formula of a compound formed from two ions.

#### EXERCISES:

10. Determine the solubility of the following ionic compounds from the table "SOLUBILITY OF COMMON COMPOUNDS IN WATER".

a)	AgCl	C)	FeS	e)	Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	g)	Na <sub>3</sub> PO <sub>4</sub>	i)	CuCl <sub>2</sub>
b)	NaOH	d)	FeSO <sub>4</sub>	f)	Fe(NO <sub>3</sub> ) <sub>3</sub>	h)	Cul	j)	PbBr <sub>2</sub>

- 11. Determine whether 0.2 M solutions of the following form a precipitate when equal volumes are mixed, and give the formula of any precipitate formed.
  - a) AgNO<sub>3</sub> and NH<sub>4</sub>Br c) KOH and AlCl<sub>3</sub>
  - b) SrBr<sub>2</sub> and NaNO<sub>3</sub> d) Nal and Pb(NO<sub>3</sub>)<sub>2</sub> f) CaS and NH<sub>4</sub>Cl
- 12. Look at the following two "Facts".
  - Fact: Many barium compounds are extremely poisonous, yet barium sulphate is swallowed routinely by patients in order to get clearer X-ray pictures of their lower intestines. Why doesn't barium sulphate poison these patients?

e) BaS and Na<sub>2</sub>SO<sub>4</sub>

Fact: It is possible to saturate a swimming pool with silver bromide and kill off all the nasty little microorganisms such as algae and bacteria, so that the pool water remains clean and sparkling, yet the water is as pure as drinking water and harmless to people. Since silver ion is a heavy metal ion and hence dangerous to our health in large doses, how is it possible that water **saturated** with silver bromide doesn't harm us?

Suggest answers to the questions asked.

The Solubility Table allows us to make an important generalization:

Compounds containing alkali metals,  $H^+$ ,  $NH_4^+$  or  $NO_3^-$  will be soluble in water.

This generalization has two important consequences:

1. It is difficult (or impossible) to precipitate alkali metal ions,  $H^+$ ,  $NH_4^+$  or  $NO_3^-$  from solution.

- 2. If you have to write the formula for a **soluble compound** containing a specific ion, you should include an alkali metal ion,  $NH_4^+$  or  $NO_3^-$  to help ensure the compound will be soluble. (We will omit H<sup>+</sup> from further consideration because it represents a more complicated situation which will be discussed in more detail in Chemistry 12.)
  - a) If you need to get a particular anion into solution, it is strongly suggested that you choose Na<sup>+</sup> to combine with your anion; salts containing sodium are very common.

**Example:** A soluble salt containing  $CO_3^{2-}$  would be Na<sub>2</sub>CO<sub>3</sub>.

b) If you need to get a particular cation into solution, it is strongly suggested that you choose  $NO_3^-$  to combine with your cation; salts containing nitrate are very common.

**Example:** A soluble salt containing  $Fe^{3+}$  would be  $Fe(NO_3)_3$ .

#### EXERCISE:

13. You wish to make some precipitates. You will make up 0.2 M solutions of certain soluble salts, mix equal volumes of the solutions and filter off the resulting precipitates. Give the complete chemical formulae for the soluble salts you would select to make up the necessary solutions for the following precipitates.

a)  $PbCl_2$  b) AgBr c)  $Cr_2S_3$  d)  $SrSO_4$ 

In this unit, every reaction that produces a precipitate is a **DOUBLE REPLACEMENT REACTION**. (If you can't remember how to balance double replacement reactions, refer back to page 115 of "*Chemistry 11: A Workbook for Students*" because you will need this skill in the following and later exercises.)



## EXERCISE:

- 14. For each of the following combinations of equal volumes of 0.2 M aqueous solutions,
  - identify the possible products by formula. i)
  - ii) state which (if any) product has a low solubility.
  - iii) if there IS a precipitate, write the equation for the reaction and indicate which compounds are aqueous and which are solids.
  - a) MgS + Sr(OH)<sub>2</sub>
- g) silver nitrate and sodium phosphate
- b)  $CuBr_2 + Pb(NO_3)_2$
- h) zinc sulphate and iron (II) chloride
- c) FeBr<sub>3</sub> + Srl<sub>2</sub> i) cobalt (II) sulphate and lithium carbonate
- d)  $Ba(NO_3)_2 + Li_2SO_4$ e)  $K_3PO_4 + CuCl_2$

f)  $(NH_4)_2SO_3 + AI_2(SO_4)_3$ 

- j) iron (III) nitrate and magnesium sulphide
- k) beryllium sulphate and ammonium carbonate e)  $K_3PO_4 + CuCl_2$ 
  - I) magnesium sulphate and strontium hydroxide

# **III. SEPARATING MIXTURES OF IONS BY PRECIPITATION METHODS**

One important use of solubility is in the field of QUALITATIVE ANALYSIS. Qualitative analysis involves the use of experimental procedures to determine which elements, molecules or ions are present in a substance. Let's see how solubility differences can help to analyze a solution.

Here is the basic idea:

- Assume that an aqueous solution contains only one or both of the cations: Ag<sup>+</sup> and Sr<sup>2+</sup>.
- Try to find some anion that can form a precipitate with only one of the two cations. If a precipitate forms, you can assume that the ion being looked for is present; if no precipitate forms, the ion is absent.

The table below shows the reactions between the cations possibly present in solution (on the left of the table) and the possible anions that could be added (along the top of the table). The five columns correspond to the five groups of ions in the first column of the Solubility Table that can produce a precipitate. A "-" indicates that no precipitate forms; "ppt" indicates that a precipitate forms when the ions are mixed.

	Cl (*)	SO <sub>4</sub> <sup>2-</sup>	S <sup>2–</sup>	OH_	PO <sub>4</sub> <sup>3-</sup> (*)
$Ag^+$	ppt	ppt	ppt	ppt	ppt
Sr <sup>2+</sup>		ppt		—	ppt

\* Only one member, say Cl<sup>-</sup>, of the halide group (Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup>) and only one member, say  $PO_4^{3-}$ , of the group  $PO_4^{3-}$ ,  $CO_3^{2-}$  and  $SO_3^{2-}$  needs to be used.

As can be seen, no anion can precipitate **ONLY**  $\text{Sr}^{2+}$ . For example, if  $\text{SO}_4^{2-}$  is added to the solution, then both  $\text{Ag}^+$ and Sr<sup>2+</sup> will form precipitates and you cannot be certain which ion causes the precipitate.

On the other hand, if  $CI^-$ ,  $S^{2-}$ , or  $OH^-$  is added, then only  $Ag^+$  can be present if a precipitate forms. Assume that sufficient  $CI^-$  is added to the solution so that any  $Ag^+$  present is precipitated out of solution. Now, one of  $SO_4^{2-}$  or  $PO_4^{3-}$  can be added. If one of these ions causes a precipitate to form, then  $Sr^{2+}$  must be present. Otherwise,  $Sr^{2+}$ is absent.

NOTE: After a precipitate has formed, filter off the precipitate (or put the test tube containing the solution being analyzed into a centrifuge to separate the solid precipitate and pour or pipette off the liquid) before adding more anions to the remaining solution.

**EXAMPLE:** A solution contains one or more of Ag<sup>+</sup>, Ba<sup>2+</sup> and Ni<sup>2+</sup>. What ions could be added, and in what order, to determine which of these cations are present?

Set up a table of solubilities:

	Cl	SO <sub>4</sub> <sup>2-</sup>	S <sup>2–</sup>	OH_	PO <sub>4</sub> <sup>3-</sup>
$Ag^+$	ppt	ppt	ppt	ppt	ppt
Ba <sup>2+</sup>	-	ppt	-	ppt	ppt
Ni <sup>2+</sup>	-	-	ppt	ppt	ppt

Only  $Ag^+$  can be precipitated if  $CI^-$  is added. Therefore, first see if there is any  $Ag^+$  present by adding  $CI^-$  and filtering off any precipitate formed. If no precipitate forms, you can conclude that  $Ag^+$  is absent.

At this point, virtually no Ag<sup>+</sup> will be in solution. Cross out the horizontal line for Ag<sup>+</sup>.

	CI	SO <sub>4</sub> <sup>2-</sup>	S <sup>2–</sup>	OH_	PO <sub>4</sub> <sup>3-</sup>
Ag⁺	<del>ppt</del>	<del>ppt</del>	<del>ppt</del>	<del>ppt</del>	<del>ppt</del>
Ba <sup>2+</sup>	_	ppt	_	ppt	ppt
Ni <sup>2+</sup>	-	—	ppt	ppt	ppt

Now a choice exists: either  $SO_4^{2-}$  or  $S^{2-}$  can be added.

- If SO<sub>4</sub><sup>2-</sup> is added, any Ba<sup>2+</sup> that is present will precipitate. Any Ni<sup>2+</sup> that is present can then be precipitated by adding one of S<sup>2-</sup>, OH<sup>-</sup> or PO<sub>4</sub><sup>3-</sup>.
- If  $S^{2-}$  is added, any Ni<sup>2+</sup> that is present will precipitate. Any Ba<sup>2+</sup> that is present can then be precipitated by adding one of SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup> or PO<sub>4</sub><sup>3-</sup>.

The previous example can be re-written in the form of an experimental procedure:

**Step 1**: To 1 mL of a solution that might contain Ag<sup>+</sup>, Ba<sup>2+</sup> and/or Ni<sup>2+</sup>, add a few drops of 1 M NaCl solution.

If there is NO PRECIPITATE, then  $Ag^+$  is absent. Proceed to Step 2. If a PRECIPITATE FORMS, then  $Ag^+$  is present. Filter off and discard the precipitate. Proceed to Step 2 to test the rest of the solution.

**Step 2:** To the solution from Step 1, add a few drops of 1 M Na<sub>2</sub>SO<sub>4</sub> solution (to arbitrarily precipitate any Ba<sup>2+</sup> first).

If there is NO PRECIPITATE, then **Ba<sup>2+</sup> is absent**. Proceed to Step 3.

If a PRECIPITATE FORMS, then  $Ba^{2+}$  is present. Filter off and discard the precipitate. Proceed to Step 3 to test the rest of the solution.

Step 3: To the solution from Step 2, add a few drops of 1 M NaOH.

If there is NO PRECIPITATE, then Ni<sup>2+</sup> is absent. If a PRECIPITATE FORMS, then Ni<sup>2+</sup> is present.

The above model can be used to write up similar procedures. Notice that quite concentrated test solutions were used (1 M) to precipitate any metal cations as completely as possible with the few drops of added solution.

**NOTE:** The summary said to add Cl<sup>-</sup> to precipitate any Ag<sup>+</sup> but the experimental procedure had to specify a complete compound (NaCl), not just Cl<sup>-</sup>.

## EXERCISES:

- 15. When adding a salt to precipitate a cation from a mixture of ions, why must the salt be soluble?
- 16. What ions could be present in a solution if separate samples of it gave a precipitate when:
  a) either SO<sub>4</sub><sup>2-</sup> or OH<sup>-</sup> is added?
  b) SO<sub>4</sub><sup>2-</sup> is added, but none when OH<sup>-</sup> is added?
- 17. A solution contains only one of Ag<sup>+</sup> or Pb<sup>2+</sup>. Is it possible to use a precipitation procedure based on your Solubility Table to determine which ion is present? If so, how? If not, why?
- 18. A solution contains Al<sup>3+</sup> and Ag<sup>+</sup>. What compounds could be added, and in what order, to separate these ions? You must specify the complete compound that will be added, not just the anion contained in the compound. Do not write out a complete experimental procedure.
- 19. A solution contains Sr<sup>2+</sup>, Ca<sup>2+</sup> and Ag<sup>+</sup>. What compounds could be added, and in what order, to separate these ions?
- 20. A solution contains Mg<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>. What compounds could be added, and in what order, to separate these ions?
- 21. A solution contains Fe<sup>3+</sup>, Ca<sup>2+</sup>, Ag<sup>+</sup> and Be<sup>2+</sup>. What compounds could be added, and in what order, to separate these ions?
- 22. Using your results from Exercise 18, write an experimental procedure for analyzing a solution which can only contain Ag<sup>+</sup> and Al<sup>3+</sup>, but might contain one, both or neither of these ions.
- 23. Using your results from Exercise 19, write an experimental procedure for analyzing a solution which can only contain Sr<sup>2+</sup>, Ca<sup>2+</sup> and Ag<sup>+</sup>, but might contain any number of these ions.
- 24. You are asked to identify the ions present in a particular solution. The ions which **may** be present are:  $\overline{I}$ ,  $SO_4^{2-}$  and  $OH^-$ .
  - a) What is the name given to the process of identifying the chemical substances in a sample?
  - b) You are to perform the identification using *only* the following reagents (that is, test chemicals): AgNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>. Which reagent must be added first? Explain why.
  - c) How would you complete the analysis of the solution?
- 25. A solution is known to contain one or more of the ions:  $S^{2-}$ ,  $OH^-$ ,  $CI^-$  and  $CO_3^{2-}$ . You are to identify the ions present using **only** the reagents: AgNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and Sr(NO<sub>3</sub>)<sub>2</sub>. Briefly describe a procedure which can be used to analyze the anions in the solution.

The next exercises show how precipitation methods are used to find the actual concentration of ions in solution experimentally. Assume a solution contains  $Ba^{2+}$ . The Solubility Table shows that  $SO_4^{2-}$  forms a low solubility compound with  $Ba^{2+}$ . Precipitating the  $Ba^{2+}$  from solution in the form of  $BaSO_4$ , drying the precipitate and determining its mass, allows the  $[Ba^{2+}]$  in the original solution to be calculated.

#### EXERCISES:

26. You have a sample of a solution containing  $Ba^{2+}$ . You add  $Na_2SO_4$  to the sample until no more  $BaSO_4(s)$  precipitates, then filter, dry and weigh the precipitate. Your results are as follows.

volume of sample	= 25.0 mL
mass of filter paper	= 1.21 g
mass of filter paper + BaSO <sub>4</sub> (dry)	= 3.75 g

Calculate: a) the moles of BaSO<sub>4</sub> produced.

b) the concentration of  $Ba^{2+}$  in the original solution.

- 27. A solution contains an unknown amount of  $Pb^{2+}$ . If 4.28 g of  $PbSO_4(s)$  are obtained from 100.0 mL of the solution, what is the  $[Pb^{2+}]$  in the solution?
- 28. Addition of phosphate ions to a 25.00 mL sample of a solution containing  $Ag^+$  ions produces 1.57 g of  $Ag_3PO_4(s)$ . What is the  $[Ag^+]$  in the original solution?

# IV. SOME CHEMICAL ANALYSIS TECHNIQUES

Chemical analysis has two main branches: **qualitative** analysis (determining the **identity** of the chemicals present) and **quantitative** analysis (determining the **amounts** of the chemicals present). In the previous section we saw how to perform a qualitative analysis. Now we will look at how quantitative analysis can be used.

Some modern chemical analysis involves sophisticated techniques and equipment that are beyond the scope of Chemistry 11 and 12. However, there are still numerous "classical" methods that are used. As an example, we shall examine four analysis procedures that are concerned with measuring the biological health of a lake.

# A. Measuring Dissolved Oxygen

Lakes must contain dissolved oxygen in order to have a thriving ecosystem. The **B**iological **O**xygen **D**emand (BOD) is a measurement of the dissolved oxygen required by microorganisms to break down organic contaminants such as decaying leaves, plants and human-introduced pollutants. If the BOD is too high, the bacterial action required to break down the organic contaminants leaves too little remaining oxygen to support a healthy ecology containing aquatic plants, fish, etc.

Dissolved oxygen concentrations typically vary between 0-15 mg/L. There are a number of factors affecting concentration: the depth at which a water sample is taken, the temperature of the water, the elevation of the lake, the time of day, and the degree of mixing with the air due to wind and stream inflow.

The most common method of measuring dissolved oxygen in a water sample is Winkler's method. (There are actually numerous modifications of the Winkler method; a simple version is discussed here.) Because oxygen can easily enter or leave a water sample, water samples are collected and stored in special Winkler bottles having a known volume and a close-fitting stopper. In addition, samples must be handled carefully to minimize exposure to atmospheric oxygen and must be processed quickly.

Samples for analysis are prepared by adding MnSO<sub>4</sub>, NaOH and NaI to water containing dissolved oxygen. The initial reaction is:

$$MnSO_4(aq) + 2 NaOH(aq) + \frac{1}{2} O_2(aq) \rightarrow MnO(OH)_2(s) + Na_2SO_4(aq).$$

Sulphuric acid is then added to allow the MnO(OH)<sub>2</sub> to convert the iodide ion to iodine:

$$MnO(OH)_{2}(s) + 2 NaI(aq) + 2 H_{2}SO_{4}(aq) \rightarrow MnSO_{4}(aq) + I_{2}(aq) + 3 H_{2}O(I) + Na_{2}SO_{4}(aq)$$

The above two reactions can be combined as follows. The  $MnO(OH)_2(s)$  produced in the first reaction is used up in the second reaction, so that is doesn't appear in the combined reaction equation (below). In addition, both the first and second reactions each produce one  $Na_2SO_4$ , so that the combined equation involves  $2 Na_2SO_4$  in the products. Finally, the  $MnSO_4$  consumed in the first reaction is produced again in the second reaction and the combined effects "cancel" each other.

2 NaOH(aq) + 
$$\frac{1}{2}O_2(aq)$$
 + 2 NaI(aq) + 2 H<sub>2</sub>SO<sub>4</sub>(aq)  $\rightarrow$  I<sub>2</sub>(aq) + 3 H<sub>2</sub>O(I) + 2 Na<sub>2</sub>SO<sub>4</sub>(aq) ... (1)

At this point, the solution is ready to be analyzed. The iodine is titrated with a solution of sodium thiosulphate,  $Na_2S_2O_3$ , using starch as an indicator:

$$2 \operatorname{Na}_2 S_2 O_3(aq) + I_2(aq) \rightarrow \operatorname{Na}_2 S_4 O_6(aq) + 2 \operatorname{Na}(aq).$$
 ... (2)

(Starch solution turns blue in the presence of iodine; when the last of the dissolved  $I_2$  has reacted, the blue colour disappears.)

**EXAMPLE:** A 60.0 mL sample of lake water is treated with MnSO<sub>4</sub>, NaOH, NaI and H<sub>2</sub>SO<sub>4</sub>. The resulting solution is titrated to an endpoint with 6.17 mL of 0.0100 M sodium thiosulphate. What is the sample's dissolved oxygen concentration, expressed in milligrams per litre?

We work backwards from the titration results, using equation (2):

$$2 \operatorname{Na}_2 S_2 O_3(aq) + I_2(aq) \rightarrow \operatorname{Na}_2 S_4 O_6(aq) + 2 \operatorname{Na}(aq).$$

First, find the moles of  $I_2$  titrated with the  $Na_2S_2O_3$ :

moles 
$$I_2 = 6.17 \times 10^{-3} L \times \frac{0.0100 \text{ mol} \text{Na}_2 \text{S}_2 \text{O}_3}{L} \times \frac{1 \text{ mol} \text{I}_2}{2 \text{ mol} \text{Na}_2 \text{S}_2 \text{O}_3} = 3.085 \times 10^{-5} \text{ mol}$$

Next, use the combined reaction equation to find the moles of O<sub>2</sub> in the original sample:

2 NaOH(aq) + 
$$\frac{1}{2}$$
 O<sub>2</sub>(aq) + 2 NaI(aq) + 2 H<sub>2</sub>SO<sub>4</sub>(aq)  $\rightarrow$  I<sub>2</sub>(aq) + 3 H<sub>2</sub>O(I) + 2 Na<sub>2</sub>SO<sub>4</sub>(aq)

moles 
$$O_2 = 3.085 \times 10^{-5} \text{ mol } I_2 \times \frac{0.5 \text{ mol } O_2}{1 \text{ mol } I_2} = 1.543 \times 10^{-5} \text{ mol}$$

Finally, calculate the concentration of O<sub>2</sub>, in milligrams per litre, in the original sample:

concentration 
$$O_2 = \frac{1.543 \times 10^{-5} \text{ mol}}{60.0 \times 10^{-3} \text{ L}} \times \frac{32.0 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mg}}{10^{-3} \text{ g}} = \frac{8.23 \text{ mg}}{\text{L}}$$

#### EXERCISES:

- In a two-step process, MnSO<sub>4</sub>, NaOH and NaI are added to a 150.0 sample of water from the bottom of a pond, followed by the addition of H<sub>2</sub>SO<sub>4</sub>. The subsequent titration reaction requires 3.61 mL of 0.0122 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to reach an end point with starch solution. Calculate the concentration of dissolved oxygen, in mg/L, in the original water sample.
- 30. Analysis of a 300.0 mL sample of lake water for dissolved oxygen by the Winkler method requires 11.57 mL of 0.00948 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to completely react the I<sub>2</sub> produced in the reaction that consumed the dissolved oxygen. Calculate the concentration of dissolved oxygen in the lake water sample. Express your answer in milligrams per litre.

### B. Measuring pH

The health of a lake's ecosystem is directly affected by the pH of the lake's water. A lake's pH is a measurement of the acid or base concentration in the water. The pH scale is shown below (the concentrations are in mol/L).

Note the following:

- pH changes slightly when temperature changes; a pH of 7 indicates neutral conditions when the temperature is 25°C.
- Water always contains some of both H<sup>+</sup>(aq) and OH<sup>-</sup>(aq).
- In an acidic solution, there is more H<sup>+</sup> present than OH<sup>-</sup>, and in basic solutions the reverse is true.
- In a neutral solution:  $[H^+] = [OH^-]$ .
- a change of 1 unit on the pH scale represents a tenfold change in the [H<sup>+</sup>] and [OH<sup>-</sup>]
- pH values can theoretically be more than 14 or less than 0, but there is no practical value in referring to a pH outside the range 0-14.

To help you better relate to the concept of pH, some typical pH values are shown in the following table. (The values are approximate.)

Substance	рН	Substance	рН
Stomach acid	1.5-3.5	Human blood	7.41 (arterial);
			7.36 (venous)
Lemon juice	2.2-2.4	Sea water	7.5 – 8.4
Vinegar	2.5-3.5	Egg whites	7.6-8.0
Tomato juice	4.0-4.4	Baking soda solution	8.5
Black coffee	5	Household ammonia	12
Cow's milk	6.5-6.7	Household bleach	12.5

Measuring pH is a simple technique involving a pH meter. The meter has a probe which is partially immersed in the solution to be tested and allows a direct reading of pH to be made.

The pH of healthy lakes usually lies in the range 6.5-8.5, depending on the time of year and whether water at the surface or near the bottom is being sampled. A range of 7.5-8.5 is found near the surfaces of lakes during the warmer months.

**EXAMPLE:** The pH of a water sample near the bottom of a lake is 7 and the pH at the surface is 8. This means the water near the bottom is neutral and the water near the surface is very slightly basic. The  $[H^+]$  becomes 10 times less going from the bottom (pH =7 means  $[H^+] = 10^{-7}$  M) to the surface (pH = 8 means  $[H^+] = 10^{-8}$  M). The  $[OH^-]$  becomes 10 times greater going from the bottom to the surface: at the bottom (pH = 7 means  $[OH^-] = 10^{-7}$  M and pH = 8 near the surface means  $[OH^-] = 10^{-6}$  M).

#### EXERCISES:

- 31. A bottle contains 0.10 M HCl. What are the [H<sup>+</sup>] and [OH<sup>-</sup>] in the solution? What is the acid's pH?
- 32. When pH decreases, what happens to  $[H^+]$ ? What happens to  $[OH^-]$ ?
- 33. According to the table above, is black coffee's [OH<sup>-</sup>] greater or smaller than that of stomach acid?
- 34. Distilled water dissolves some of the CO<sub>2</sub> in the air contacting the water's surface. The reaction between water and carbon dioxide is: CO<sub>2</sub>(aq) + H<sub>2</sub>O(I) → H<sup>+</sup>(aq) + HCO<sub>3</sub><sup>-</sup>(aq).
   Does the dissolving of carbon dioxide in water create a solution having a pH more than, less than, or equal to 7?
- 35. How many times greater or smaller is the [H<sup>+</sup>] when the pH changes:
  (a) from 7 to 9?
  (b) from 6 to 2?
  (c) from 14 to 7?
  (d) from 0 to 3?
- 36. A solution has a  $[H^+] = 1 \times 10^{-5}$  M. What is the pH of the solution?
- 37. Solution A = 0.1 M NaCl. Solution B = 0.1 M NaOH. Solution C = 0.1 M HNO<sub>3</sub>. Which solution has the highest pH? Which solution has the lowest pH?

### C. Analysis of Nitrates

Unlike most other ions which can be removed from solution by precipitation methods, nitrate is extremely soluble. This high solubility makes detection and analysis of nitrate relatively difficult.

#### a) Analyzing Samples Having Substantial Amounts of Nitrate

As an example of a sample containing substantial amounts of nitrate, we consider how to analyze a fertilizer containing nitrate.

A sample of fertilizer having a known mass is dissolved in water. Some finely divided Devarda's alloy (consisting of copper, aluminum and zinc) and an excess of sodium hydroxide solution are then added to the solution. Heating the mixture causes the following reaction:

The solution is heated and distilled into a receiving flask. The distilling process causes the dissolved ammonia to rapidly pass into a known excess volume of hydrochloric acid having a known concentration. (This reaction is necessary to prevent the ammonia gas from escaping.) The reaction between the ammonia and hydrochloric acid is:

$$NH_3 + HCI \rightarrow NH_4CI.$$

Finally, the remaining, unreacted hydrochloric acid in the receiving flask is titrated with a sodium hydroxide solution having a known concentration:

 $HCI (aq) + NaOH(aq) \rightarrow NaCI(aq) + H_2O(I)$ 

**EXAMPLE:** A 2.51 g sample of nitrate-containing fertilizer is placed in a flask containing about 250 mL of distilled water. A few grams of Devarda's alloy and about 10 mL of 20 % NaOH are added to the solution and a distillation apparatus is attached to the flask. The mixture is heated gently at first and then more strongly until the dissolved ammonia in the flask completely distills over. The distillate is collected in a receiving flask containing 25.0 mL of 0.203 M HCI. The unreacted HCI solution in the receiving flask is then titrated with 7.49 mL of 0.196 M NaOH. What is the percentage of nitrate in the fertilizer?

Note: The only solutions that are used in the calculations are the HCl and NaOH put in the receiving flask.

total moles HCl added =  $25.0 \times 10^{-3} L \times 0.203 \text{ mol/L} = 0.005075 \text{ mol}$ 

moles NaOH =  $7.49 \times 10^{-3} L \times 0.196$  mol/L = 0.001468 mol = excess moles HCl = moles unreacted by NH<sub>3</sub>

moles HCl reacted by  $NH_3$  = total moles HCl added – excess moles HCl = 0.005075 mol – 0.001468 mol = 0.003607 mol = moles  $NH_3$  reacted

Using the original reaction equation: moles  $NO_3^-$  = moles  $NH_3$  = 0.003607 mol

Percentage nitrate in sample =  $\frac{0.003607 \text{ mol } \text{NO}_3^-}{2.51 \text{ g sample}} \times \frac{62.0 \text{ g } \text{NO}_3^-}{\text{mol } \text{NO}_3^-} \times 100 \% = 8.91 \%$ 

#### EXERCISES:

38. A 1.25 g fertilizer sample is placed in a 500 mL flask about half-full of water, followed by the addition of Devarda's alloy and sodium hydroxide solution. The resulting mixture is heated and distilled into a receiving flask containing 25.0 mL of 0.153 M HCI. The remaining excess HCI in the receiving flask is neutralized by the addition of 12.4 mL of 0.200 M NaOH. What is the percentage of nitrate in the fertilizer sample?

39. A technician for a mining company analyzes a sample of crude sodium nitrate using the Devarda method. The receiving flask contains 100.0 mL of 0.2006 M HCI. A 1.02 g sample of the crude material requires 28.4 mL of 0.199 M NaOH to neutralize the excess HCI in the receiving flask. Calculate the percentage of sodium nitrate in the sample.

### b) Analyzing Samples Having Very Small Concentrations of Nitrate

The nitrate ion is an essential nutrient for the growth of aquatic plants. Typical nitrate concentrations in healthy lakes are 0.1-0.2 mg/L. Most of this nitrate is used by algae to assist their growth; limited amounts of nitrate will limit the growth of algae (algae is at the bottom of the aquatic food chain). If nitrate levels increase to as little as 0.5 mg/L as a result of pollution from sewage, industrial waste or fertilizer runoff, algae growth becomes unchecked and soon the water can look like pea soup. High nitrate and phosphate concentrations can lead to **eutrophication**. Eutrophication is a situation where excess nutrients cause excessive bacterial and algae growth that eventually lead to almost total depletion of dissolved oxygen and the destruction of animal and plant life. Nitrates in lakes and rivers can cause more problems than just rampant algae growth. Drinking water having nitrate concentrations in excess of 10 mg/L can be toxic to infants. However, nitrate consumption is not necessarily a problem: dietary intake of nitrates in limited quantities is considered to be beneficial. The main source of nitrates in most diets is vegetables and, in addition, our bodies produce nitrates as a result of normal metabolism.

The most common ways to determine the concentration of nitrates in water involve the use of a spectrophotometer. The water sample is treated with a variety of chemicals that eventually produce a distinctive colouration. The intensity of the colour is measured in the spectrophotometer and compared to the colours produced by samples with known nitrate concentrations.

**EXAMPLE:** The concentration of nitrate in a sample of lake water is analyzed as follows:

Note: the details of the reaction are presented as background information only.

A 25.00 mL sample of lake water is transferred to a 100 mL volumetric flask. The nitr<u>a</u>te ions present are converted to nitr<u>i</u>te ions by reacting the nitrate with zinc metal in an acidic solution:

$$Zn(s) + NO_{3}^{-}(aq) + 2 H^{+}(aq) \rightarrow Zn^{2+}(aq) + NO_{2}^{-}(aq) + H_{2}O(l)$$

Next, the nitrite produced in the above reaction is reacted with solutions containing sulfanilic acid,  $HO_3S-C_6H_4-NH_2$ , and 1-naphthylamine,  $C_{10}H_7-NH_2$ , to produce a large molecule having an intense red colour.

After the red colour has developed, the contents of the flask are diluted to exactly 100 mL and some of the red solution is poured into a spectrophotometer cuvette (a special test tube), placed in the spectrophotometer and the **absorbance** is measured. (See the diagram below. The diffraction grating acts like a prism and breaks up the incoming white light into the colours of the rainbow.) Absorbance measures the proportion of the incoming light that is absorbed by the sample and therefore does not pass through and strike the photoelectric cell. The more concentrated the red molecules, the greater the colour intensity and the greater the absorbance of light.



DIAGRAM OF A SIMPLE SPECTROPHOTOMETER

A series of standard samples having a known concentration of nitrite ions are also treated with sulfanilic acid and 1-naphthylamine and the absorbances of these samples are recorded. The results of the experiment are summarized below. *Note:* Absorbance has no units because it is a ratio between similar quantities.

Concentration of nitrite (mg/L)	Absorbance
0.100	0.09
0.300	0.26
0.500	0.43
0.700	0.61
0.900	0.78
unknown	0.37

The results are plotted on the following graph.



Plotting the known nitrite concentration/absorbance values on the graph allows us to draw a best straight line through the points, also known as a **calibration curve**. Reading the absorbance for the unknown from the straight line on the graph allows us to find the concentration: 0.43 mg/L. Since the original sample of lake water is diluted from 25.00 mL to a volume of 100.0 mL, and since 1 mole of nitrite is produced for every mole of nitrate originally present, the original concentration of nitrate in the water is calculated as follows:

This is a dilution calculation, so we use the equation:  $c_{\text{CONC}} \times V_{\text{CONC}} = c_{\text{DIL}} \times V_{\text{DIL}}$ 

Original concentration = 
$$c_{\text{CONC}} = \frac{c_{\text{DIL}} \times V_{\text{DIL}}}{V_{\text{CONC}}} = \frac{0.43 \text{ mg}}{\text{L} \text{ (diluted)}} \times \frac{100.0 \text{ mL (diluted)}}{25.00 \text{ mL (original)}} = 1.7 \text{ mg/L}$$
.

#### EXERCISES:

- 40. A water sample has a nitrate concentration of 0.150 mg/L. Express this value in moles per litre.
- 41. A 50.0 mL sample of highly-polluted, nitrate-containing lake water is transferred to a 250.0 mL volumetric flask, reacted to create a red-coloured solution, diluted to 250.0 mL and analyzed using a spectrophotometer. The following data is obtained.

Concentration of nitrite (mg/L)	Absorbance
4.00	0.16
8.00	0.32
12.00	0.48
16.00	0.64
20.00	0.80
unknown	0.36

Use the following graph to find the concentration of nitrate, in mg/L, in the lake water sample.



## D. Analysis of Phosphorus

Phosphorus is never found as an element in nature so we will examine how to analyze a sample for phosphates, the most commonly-occurring phosphorus compounds.

There are two separate methods in common use, depending on whether there are substantial amounts of phosphate in the sample or very small concentrations.

#### a) Analyzing Samples Having Substantial Amounts of Phosphate

Phosphates in solution are largely present in the form of  $HPO_4^{2-}$  (aq). If the phosphate is part of a fertilizer, for example, we can use the following precipitation procedure.

A known amount of fertilizer is dissolved in water. A solution of magnesium sulphate heptahydrate (also known as "Epsom salts") is then added to the fertilizer solution, followed by the addition of ammonia solution. The reaction which occurs is:

 $NH_4^+(aq) + Mg^{2+}(aq) + HPO_4^{2-}(aq) + OH^-(aq) + 5 H_2O(I) \rightarrow NH_4MgPO_4 \cdot 6H_2O(s)$ 

Note that when ammonia is dissolved in water, some of the ammonia reacts with the water:

 $NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$ ,

which explains the presence of the ammonium and hydroxide ion in the previous reaction equation.

After the precipitation reaction is complete, the solid is filtered off, washed, dried and weighed. The percentage of phosphorus in the fertilizer sample is then calculated.

**EXAMPLE:** A 2.50 g sample of fertilizer is dissolved and reacted with magnesium sulphate heptahydrate and ammonia solution to produce 1.73 g of dry NH<sub>4</sub>MgPO<sub>4</sub>•6H<sub>2</sub>O. Calculate the percentage of phosphorus in the fertilizer.

mass of P in product = 1.73 g NH<sub>4</sub>MgPO<sub>4</sub>•6H<sub>2</sub>O x  $\frac{1 \text{mol NH}_4 \text{MgPO}_4 \cdot 6\text{H}_2\text{O}}{245.3 \text{ g NH}_4 \text{MgPO}_4 \cdot 6\text{H}_2\text{O}} \text{ x}$  $\frac{1 \text{mol P}}{1 \text{mol NH}_4 \text{MgPO}_4 \cdot 6\text{H}_2\text{O}} \text{ x} \frac{31.0 \text{ g P}}{1 \text{mol P}} = 0.2186 \text{ g}$ Percentage P in sample =  $\frac{\text{mass P in product}}{\text{mass of sample}} \text{ x } 100 \% = \frac{0.2186 \text{ g}}{2.50 \text{ g}} \text{ x } 100 \% = 8.75 \%$ 

#### EXERCISES:

- 42. Brand X fertilizer is advertised as having 13 ± 1 % phosphorus content. To test this claim, a student dissolves a 2.00 g sample of the fertilizer in water and reacts the solution with magnesium sulphate heptahydrate and ammonia solution. After filtering off and drying the precipitate, the student records a mass of 1.61 g of NH<sub>4</sub>MgPO<sub>4</sub>•6H<sub>2</sub>O. Is the student's result for the percentage within the range claimed?
- 43. A 5.27 g sample of bat guano (a type of fertilizer) produces 1.55 g of NH<sub>4</sub>MgPO<sub>4</sub>•6H<sub>2</sub>O as a result of a phosphorus analysis procedure. What is the percentage of phosphorus in this fertilizer?

## b) Analyzing Samples Having Very Small Concentrations of Phosphate

Lake waters contain some naturally-occurring phosphorus compounds, but the concentrations are typically so low (0.01-0.03 mg/L, depending on environmental factors) that precipitation methods are not practical. Phosphorus in unpolluted lakes comes from decay of plant and animal sources, and from leaching of phosphate-containing minerals in the surrounding environment.

Plant growth in unpolluted lakes is limited by the amount of available phosphate, so that a natural balance will occur as organisms consume the available phosphorus, die and release the phosphorus for eventual re-use. However, if sewage, agricultural runoff or industrial discharge enters the water system, then increased phosphate levels can cause unrestrained algae growth. During the 1960s and early 1970s the use of phosphates in detergents was identified as the cause of thousands of lakes having such extensive eutrophication that their fish populations were either in serious decline or entirely absent. Government legislation that limited the amount of phosphate allowed in detergents eventually reversed the worst effects of the previous phosphorus pollution.

There are numerous spectrophotometric methods to analyze phosphate in water. The following method is typical. A solution of ammonium molybdate,  $(NH_4)_2MoO_4$ , is added to a water sample followed by the addition of a tin(II) chloride solution. The result is a blue solution of unknown composition. Similar to the procedure we saw with analysis of nitrate in water samples, a series of standard solutions having known phosphate concentration are prepared in addition to preparing the unknown. All the samples are placed in a spectrophotometer and their absorbances are determined. A graph of absorbance versus concentration is then prepared to find the concentration of the unknown sample.

#### EXERCISE:

44. A 25.0 mL sample of water is placed in a 100.0 mL volumetric flask and treated with ammonium molybdate and tin(II) chloride solution. After the blue colour develops, the mixture is diluted to 100.0 mL. A set of standard solutions with known phosphate concentrations is prepared. The absorbance readings for all the samples are determined by placing the solutions in a spectrophotometer. The following data are obtained:

Concentration of phosphate (mg/L)	Absorbance
0.300	0.14
0.600	0.28
0.900	0.40
1.200	0.55
1.500	0.68
unknown	0.52

Use the graph below to find the concentration of phosphate, in mg/L, in the lake water sample.



# V. ENVIRONMENTAL IMPACTS OF NON-METAL OXIDE SOLUTIONS

There are 17 non-metallic elements. Oxygen is a highly reactive non-metal that forms oxides with other non-metals to create compounds having great benefits and great problems in the environment, depending on their concentrations. Hydrogen forms the most abundant non-metal oxide: dihydrogen oxide, also known as water. Water is essential to life on our planet and, except in a few circumstances such as flooding, is considered universally beneficial.

Of the 15 remaining non-metals, the 6 noble gases do not form oxide solutions, and oxides of phosphorus and oxides of the 5 halogens do not exist in nature as isolated molecules. The oxides of the remaining three non-metals – carbon, nitrogen and sulphur – are examined in this section for their impacts on the environment.

## a) Carbon

Carbon forms two oxides: carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>.

Normal air contains only trace amounts of carbon monoxide and, in addition, CO is only slightly soluble in water. As a result, CO solutions have little to no environmental impact.

Carbon dioxide solutions, on the other hand, create significant environmental impact. As we saw previously, in Exercise 34, CO<sub>2</sub> dissolves in water to create a slightly acidic solution:

$$CO_2(aq) + H_2O(I) \rightarrow H^+(aq) + HCO_3^-(aq)$$
.

The pH of pure water is 7.0 (at  $25^{\circ}$ C), but normal rainwater has a pH of about 5.6 as a result of atmospheric CO<sub>2</sub> dissolving in water. Although atmospheric concentrations of CO<sub>2</sub> are steadily increasing, the acidity of normal rainwater is not affected to a great extent by these increasing concentrations and therefore CO<sub>2</sub> is not considered a major contributor to **acid rain**. Any rainfall having a pH < 5.6 is considered to be acid rain.

However, from the middle 1700s to present day, the oceans' pHs have dropped by about 0.1, which represents an increase of about 25 % in the [H+] of ocean waters, and the rate of this acidification is increasing. The increased acidity of the oceans has already resulted in a decrease in the concentration of available carbonate ions in many regions. The loss of available carbonate ions is due to the reaction:

$$CO_2(aq) + H_2O(l) + CO_3^{2-}(aq) \rightarrow 2 HCO_3^{-}(aq)$$

Marine organisms that rely on an abundance of carbonate ion in their surroundings, such as corals, clams, oysters, and many types of plankton, are having their abilities to produce their shells affected. The shells of these creatures are produced when calcium and carbonate ions are combined to form a type of calcium carbonate called *aragonite*:

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

Since plankton lie at the bottom of the ocean food chain, the seriousness of this problem is hard to overstate. Without sufficient plankton, the entire marine food chain could collapse and huge numbers of people who depend on ocean products for food could face starvation.

Carbon dioxide creates a problem not directly associated with solutions: atmospheric warming. Carbon dioxide is an example of a **greenhouse gas**. Greenhouse gases, such as carbon dioxide, methane, ozone, nitrous oxide (N<sub>2</sub>O) and water, absorb high-energy radiation from incoming sunlight and re-emit lower-energy infrared radiation; that is, they emit heat. As the concentration of greenhouse gases increases, the Earth's atmosphere is warmed proportionally. This atmospheric warming causes warming of the surface of the oceans, which in turn increases the rate of evaporation from their surfaces and increases the potential for increased storm and hurricane activity. Increased evaporation also means there is more cloud cover and still more trapping of heat below the cloud layers. Another effect of heat being trapped in the atmosphere is the melting of glaciers and sea ice. This melting effect has been observed, with great concern, for many years, and the rate of melting is accelerating. An additional concern is the warming of the permafrost in arctic regions. Permafrost contains vast amounts of methane trapped in cage-like ice structures called **clathrates**. As clathrates melt, the trapped methane is released and, being a greenhouse gas, further accelerates atmospheric warming.

If there were no life on Earth, climate change would be of no particular consequence, but organisms of all sizes, from microbes to elephants and whales, are finely-tuned and highly adapted to their chemical and physical environments. Even slight changes in average temperature, pH, sunlight, and gas concentrations, for example, can upset adaptation to an environment – and for many organisms, non-adaptation to an environment can lead to extinction.

## b) Nitrogen and Sulphur

Nitrogen oxides are produced in combustion reactions such as those occurring in automobile engines:

$$N_2 + O_2 \rightarrow 2 \text{ NO}$$
$$N_2 + 2 O_2 \rightarrow 2 \text{ NO}_2.$$

Some nitrogen dioxide, NO<sub>2</sub>, further reacts with water vapour to produce a mixture of nitrous and nitric acids:

$$2 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3.$$

A large amount of dinitrogen monoxide (nitrous oxide, N<sub>2</sub>O) is produced by soil bacteria, acting on naturally-occurring soil components, animal manure or soil enriched by human-made fertilizers. Industrial processes and combustion reactions also add to N<sub>2</sub>O gas emission. Besides the fact that N<sub>2</sub>O is a greenhouse gas, it also has a destructive effect on the ozone layer.

Most combustible fuels, including coal and oil, contain sulphur or sulphur compounds. When such fuels are burned, sulphur dioxide is produced:

$$S + O_2 \rightarrow SO_2$$
,

and some of the SO<sub>2</sub> reacts further with air to produce sulphur trioxide:

$$2 \operatorname{SO}_2 + \operatorname{O}_2 \twoheadrightarrow 2 \operatorname{SO}_3.$$

When SO<sub>2</sub> and SO<sub>3</sub> react with water vapour, acidic solutions are produced:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4.$$

This mixture of HNO<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> creates *acid rain*. Although the activities of people largely contribute to acid rain, lightning, volcanic eruptions and rotting vegetation also contribute significant amounts to the production of acid rain.

Acid rain affects more than just the oceans. The ecosystems of lakes can be harmed or destroyed if sufficiently acidic rainfall occurs. Acidification of forest soils by acid rain causes trees to sicken and die. When acidic rain falls on rocks and soils, poisonous elements can be leached out of the rocks and beneficial nutrients can be leached out of topsoils into subsoils, where the nutrients are no longer available to plant roots. In addition, many food crops are sickened or destroyed by acid rain.

When sufficient amounts of pollutants such as nitrogen oxides, sulphur oxides, smoke from forest fires and coal-burning power plants, unburned petroleum fuels and petroleum combustion products exist in the atmosphere, ultraviolet light causes the production of obnoxious smells and fine airborne particles that create the yellow-brown haze called **smog**.

# SOLUBILITY OF COMMON COMPOUNDS IN WATER

(A compound is listed as "soluble" if its solubility is > 0.1 mol/L at  $25^{\circ}$ C)

NEGATIVE (Anions	POSITIVE (Cations	SOLUBILITY COMPOUND
All	Alkali ions: Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , Fr <sup>+</sup>	Soluble
All	Hydrogen ion, H+	Soluble
All	Ammonium, $NH_4^+$	Soluble
Nitrate, $NO_3^-$	All	Soluble
Chloride, CI <sup>-</sup> or Bromide, Br-	All others	Soluble
or lodide, I <sup>-</sup>	Ag <sup>+</sup> , Pb <sup>2+</sup> , Cu <sup>+</sup>	LOW SOLUBILITY
$\alpha$ $\alpha$	All others	Soluble
Supriate, SO <sub>4</sub>	Ag+, Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Pb <sup>2+</sup>	LOW SOLUBILITY
Sulphido S2-	Alkali ions, H+,NH <sub>4</sub> +, Be <sup>2+</sup> Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup>	Soluble
	All others	LOW SOLUBILITY
	Alkali ions, H <sup>+</sup> , NH <sup>+</sup> <sub>4</sub> , Sr <sup>2+</sup>	Soluble
Hydroxide, OH	All others	LOW SOLUBILITY
Phosphate, $PO_4^{3-}$ or	Alkali ions, H+, NH <sub>4</sub>	Soluble
or Sulphite, $SO_3^2$	All others	LOW SOLUBILITY