chapter

8

Chemical Analysis

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One of the earliest chemical technologies was the control of fermentation—the production of ethanol (ethyl alcohol) from plant sugars. In the human body, this alcohol induces chemical reactions that affect the coordination and judgment of the drinker. In turn, these changes can contribute to serious car accidents. This is why Canada has laws stipulating limits to the concentration of ethanol allowed in the blood of a motorist.

When a driver is asked to breathe into a breathalyzer, the device measures the alcohol content in the exhaled air. The reading from the device indicates the result as a concentration of alcohol in the blood (**Figure 1**). For example, a reading of 0.08 on a breathalyzer means that the blood alcohol content is 0.08%, or 80 mg of alcohol in 100 mL of blood. A police officer takes a breath sample for on-the-spot analysis. Because of the possibility of challenges in court, the officer must be prepared to defend the reliability and accuracy of the reading. If the breathalyzer test indicates an alcohol concentration above the legal limit (in Canada, the legal limit is 0.08), a blood sample may be analyzed more precisely in a laboratory. This test uses a technique called titration, which you will learn about in this chapter.

Chemical analysis involves knowledge of chemical reactions, an understanding of diverse experimental designs, and practical skills to apply this knowledge and understanding. In this chapter, you will have opportunities to develop all of these using the skills you developed in Chapter 7.

Chemical analysis is also closely tied to technology, using specialized equipment and techniques to detect and measure substances with ever-increasing accuracy and precision. Understanding the function and handling of such equipment is also part of your experience in this chapter.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. Does the colour of a solution indicate which solutes it contains?
2. Do calculated quantities of a product necessarily predict how much product actually forms in a reaction?
3. Can the amount of a second reactant required for a reaction be determined without a stoichiometric calculation?
4. When an acidic solution is slowly poured into a sample of basic solution, how does the solution's pH change?

Figure 1
A breath sample is quickly analyzed for ethanol concentration by this compact technological device.

Exploration Test Your Drinking Water

Canadian government agencies routinely analyze our drinking water. The increasing sales of bottled water purified by reverse osmosis or distillation testify to public awareness and concern in this area. Government labs, of course, have access to high technology and highly trained and skilled personnel. The chemistry knowledge you have acquired, however, will let you make some informed statements about tap water with just a couple of simple tests.

Materials: tap water sample, pure water sample (distilled or filtered by reverse osmosis), dropper bottles of sodium carbonate solution, dropper bottles of silver nitrate solution, four small test tubes

- To each of the two water samples in separate test tubes, add a few drops of $Na_2CO_3(aq)$.
- Carefully observe each sample for signs of precipitate formation.
- To each of the two water samples in new separate test tubes, add a few drops of $AgNO_3(aq)$.
- Carefully observe each sample for signs of precipitate formation.

(a) Referring to a table of ionic compound solubility generalizations, state which ions are *not* present in significant concentration in the tap water sample.
(b) If you have evidence of precipitation, state which ions, according to the evidence, *may* be present in the tap water sample.
(c) List some ions that cannot be analyzed and identified by these two tests.
(d) Water purification usually involves some degree of chlorination to kill microorganisms. Given this fact, what common ion might you expect to be present in most municipally treated tap water?

8.1 Introduction to Chemical Analysis

Analysis of an unknown chemical sample can include both *qualitative* analysis—the identification of a specific substance present—and *quantitative* analysis—the determination of the quantity of a substance present.

While there are many analytical technologies and procedures used, three methods predominate:

- **colorimetry**, or analysis by colour, which uses light emitted, absorbed, or transmitted by the chemical (Section 8.1)
- **gravimetric analysis**, which uses stoichiometric calculations from a measured mass of a reagent (Section 8.2)
- **titration analysis**, which uses stoichiometric calculations from a measured solution volume of a reagent (Section 8.4)

Table 1 Colours of Solutions

Ion	Solution colour
Groups 1, 2, 17	colourless
$Cr^{2+}(aq)$	blue
$Cr^{3+}(aq)$	green
$Co^{2+}(aq)$	pink
$Cu^{+}(aq)$	green
$Cu^{2+}(aq)$	blue
$Fe^{2+}(aq)$	pale green
$Fe^{3+}(aq)$	yellow-brown
$Mn^{2+}(aq)$	pale pink
$Ni^{2+}(aq)$	green
$CrO_4^{2-}(aq)$	yellow
$Cr_2O_7^{2-}(aq)$	orange
$MnO_4^{-}(aq)$	purple

Colorimetry

First, consider the colours of aqueous solutions. Observation shows that most aqueous solutions are colourless. As **Table 1** shows, ions of elements in Groups 1, 2, and 17 impart no colour at all to solutions. Some other ions, not listed in the table, are also colourless. However, many solutions containing monatomic and polyatomic ions of the transition elements do have a visible colour.

Aqueous ion colour is due to the ion's interference with visible light. Ions absorb specific wavelengths, which makes analysis possible. A specific colour identifies a particular ion. The percentage of light that is absorbed depends on how many ions are in the light path, that is, on the concentration of that ion.

For example, in the reaction of copper with silver nitrate solution that you studied in Chapter 7, you observed that silver and nitrate ions are both colourless (and, thus, invisible) in solution. Copper(II) ions, however, are a characteristic blue colour, making it easy to tell when they are forming in the reaction. The blue colour becomes more intense as the reaction proceeds because the concentration of the copper(II) ions is increasing.

Figure 1
Which solution is which?

COMMUNICATION example

According to the evidence in **Figure 1**, which is organized in **Table 2**, which solution is potassium dichromate, sodium chloride, sodium chromate, potassium permanganate, nickel(II) nitrate, and copper(II) sulfate? (Refer to **Table 1**.)

Table 2 Colours of the Unknown Solutions

Solution	1	2	3	4	5	6
Colour	purple	colourless	green	yellow	blue	orange

Solution

According to the evidence and **Table 1**, the solutions are (1) potassium permanganate, (2) sodium chloride, (3) nickel(II) nitrate, (4) sodium chromate, (5) copper(II) sulfate, and (6) potassium dichromate.

Aqueous ions can sometimes be identified qualitatively by eye, but for more precise identification or for quantitative measurement, technology must be used. A standard spectrophotometer is a device that measures the quantity of light absorbed at any desired visible wavelength when a light beam is passed through a solution sample. A spectrophotometer, like the one in **Figure 2**, can measure the concentration of any desired coloured ion, even in a solution that has several different mixed colours, because it can be adjusted to "see" only the precise colour (wavelength) selected.

We can also use flame tests to detect the presence of several metal ions, such as copper(II), calcium, and sodium (see the Selected Ion Colours table on the inside back cover). In a flame test, a clean platinum or nichrome wire is dipped into a test solution and then held in a nearly colourless flame (**Figure 3**). There are other ways to conduct flame tests: You could dip a wood splint in the aqueous solution and then hold it close to a flame; you could hold a tiny solid sample of a substance in the flame; or you could spray the aqueous solution into the flame.

Robert Wilhelm Bunsen and Gustav Robert Kirchhoff took the idea of the flame test and developed it into a technique called spectroscopy. Bunsen had previously invented an efficient gas laboratory burner that produced an easily adjustable, hot, nearly colourless flame. Bunsen's burner made better research possible—a classic example of technology leading science—and made his name famous. Bunsen and Kirchhoff soon discovered two new elements, cesium and rubidium, by examining the spectra produced by passing the light from flame tests through a prism.

Flame tests are still used for identification today. Of course, the technology has become much more sophisticated. An atomic absorption spectrophotometer (**Figure 4**) analyzes the light absorbed by samples vaporized in a flame. It can even detect wavelengths not visible to humans, which means that it can "see" and measure the concentrations of ions that are invisible to us, such as silver ions. This type of spectrophotometer can detect minute quantities of substances, in concentrations as tiny as parts per billion. By measuring the quantity of light absorbed, this device can also do quantitative analysis—measuring the concentrations of various elements precisely and accurately. Similar technology is used in a completely different branch of science: astronomy. Astronomers study the light spectra from distant stars to find out what elements make up the stars.

The Northern Lights (**Figure 5**) often create beautiful displays of moving colour in the sky in the Canadian North. Spectroscopy indicates that the various colours are due to high-energy charged particles from the Sun colliding with different molecules in the atmosphere at different altitudes. For example, a reddish colour is emitted by oxygen atoms at altitudes over 300 km, and greenish yellow (the most common) is from oxygen atoms at altitudes from 100 to 300 km.

Figure 2

Solutions of different colour intensity absorb light to different degrees, so the concentration of a coloured product can be measured by light absorbence.

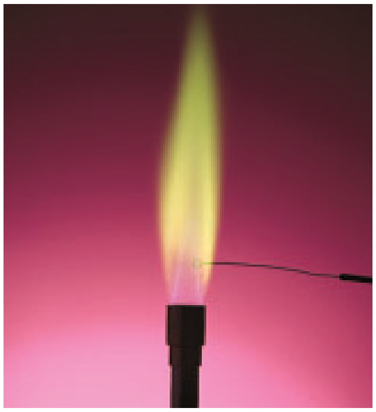

Figure 3

Copper(II) ions impart a green colour to this flame. This green flame and the characteristic blue colour in aqueous solution can be used as diagnostic tests for copper(II) ions.

Figure 4

The atomic absorption spectrophotometer is a valuable tool, essential for precise qualitative and quantitative analyses in many areas of science.

Figure 5

Inuit nearly all share a common legend about the aurora, that the moving streamers of light are the spirits of their ancestors playing a game involving kicking a walrus skull around the sky, just as they did to while away the long winter darkness when they were living. The Innu word "aqsalijaat" can be loosely translated as "the trail of those playing soccer."

WEB Activity

Web Quest: Is Your Classroom Putting You to Sleep?

The air we breathe is invisible, so we cannot always tell if it is pure and healthy for us. Sometimes, pollutants can build up in the air and affect our health and our performance. How can you tell if the air you breathe has poisons in it? What are the signs of bad air? What is the impact on the individuals who breathe it? This Web Quest explores the dangers of toxins in the air, how they impact the people who breathe them, and what can be done to improve the situation.

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Section 8.1 Questions

1. Describe the fundamental difference between quantitative and qualitative analysis.
2. What is the expected colour of solutions that contain the following? (Refer to **Table 1**.)
   (a) $Na^+(aq)$
   (b) $Cu^{2+}(aq)$
   (c) $Fe^{3+}(aq)$
   (d) $Cr_2O_7^{2-}(aq)$
   (e) $Cl^-(aq)$
   (f) $Ni^{2+}(aq)$
3. What colour is imparted to a flame by the following ions? Refer to the Selected Ion Colours table on the inside back cover.
   (a) calcium
   (b) copper(II)
   (c) Na^+
   (d) K^+
   (e) H^+
4. Flame tests on solids produce the same results as flame tests on solutions. These tests may be used as additional evidence to support the identification of precipitates. What colour would the following precipitates give to a flame?
   (a) $CaCO_3(s)$
   (b) $PbCl_2(s)$
   (c) $SrSO_4(s)$
   (d) $Cu(OH)_2(s)$
5. Complete the Analysis and Evaluation (Design only) of the following report.

Problem

What ions are present in the solutions provided?

Design

The solution colour is noted and a flame test is conducted on each solution.

Evidence

Table 3 Solution and Flame Colours

Solution	Solution colour	Flame colour
A	colourless	violet
B	blue	green
C	colourless	yellow
D	colourless	yellow-red
E	colourless	bright red

6. Artificial fire logs for home fireplaces are commonly available in supermarkets and hardware stores. Along with the combustible ingredients, the fire logs often have chemicals deliberately added to colour the flames. If such a fire log has copper(II) chloride near its core, sodium nitrate in layers farther out from the centre, and strontium chloride near the surface, describe how the flames will look over the normal three-hour burning period.

Extension

7. Identifying ions in an aqueous solution can be very important. Nitrate ions in well water, for example, must be identified because they may be harmful to health (especially for children) if the concentration is too high. Assume you have a solution containing several common cations and anions, which may or may not contain strontium ions. Write an experimental design for an analysis to determine whether strontium ions are present. Use two precipitation reactions followed by filtrations, and then a flame test. Use your Solubility of Ionic Compounds table (inside back cover) to decide what solutions you might use for the precipitation reactions. You may assume that no ions are present that are not listed in this table. *Hint:* Plan your first precipitation to remove most cations that are *not* strontium ions from the solution. Explain the logic you apply to each step of your design, in particular, why a flame test is required as a final step.
8. Forensic chemists with the RCMP and other forensic laboratories use flame emission spectroscopy to analyze glass and paint chips found at crime scenes.
   (a) Describe a scenario in which such an analysis would be useful.
   (b) What roles do you think science, society, and technology played in the development of this technology?

Gravimetric Analysis 8.2

Quantitative Analysis

The chemistry and the technology of quantitative analysis are closely related; knowledge and skills in both areas are essential for chemical technologists in medicine, agriculture, and industry.

In one type of chemical analysis, precipitation is part of the experimental design. As you know, precipitation occurs when a reaction forms a slightly soluble product. In a quantitative analysis involving precipitation, the sample under investigation is combined with an excess quantity of another reactant to ensure that all the sample reacts.

BIOLOGY CONNECTION

Quantitative Analysis

Chemistry is not the only science in which quantitative analysis is important. If you are studying biology, you may quantitatively analyze oxygen consumption of germinating seeds.

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LAB EXERCISE 8.A

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

Chemical Analysis Using a Graph

Lab technicians sometimes perform the same chemical analysis on hundreds of samples every day. For example, in a medical laboratory, blood and urine samples are routinely analyzed for specific chemicals such as cholesterol and sugar. In many industrial and commercial laboratories, technicians read the required quantity of a chemical from a graph that has been prepared in advance. This saves the time and trouble of doing a separate stoichiometric calculation for each analysis performed. By completing the Analysis of the investigation report, you will be illustrating this practice. Use graphics or spreadsheet software, if available, to create your graph.

Purpose

The purpose of this lab exercise is to use a graph of a precipitation reaction's stoichiometric relationship to determine the mass of lead(II) nitrate present in a sample solution.

Problem

What mass of lead(II) nitrate is in 20.0 mL of a solution?

Design

Samples of two different lead(II) nitrate solutions are used. Each sample is reacted with an excess quantity of a potassium iodide solution, producing lead(II) iodide, which has a low solubility and settles to the bottom of the beaker (**Figure 1**). After the contents of the beaker are filtered and dried, the mass of lead(II) iodide is determined. The reference data supplied in **Table 1**, relating the mass of $Pb(NO_3)_2$ to the mass of PbI_2 for this reaction, are graphed. The analysis is completed by reading the mass of lead(II) nitrate present in each solution from the graph.

Figure 1
When lead(II) nitrate reacts with potassium iodide, a bright yellow precipitate forms.

Table 1 Reaction of Lead(II) Nitrate and Potassium Iodide

Mass of PbI_2 produced (g)	Mass of $Pb(NO_3)_2$ reacting (g)
1.39	1.00
2.78	2.00
4.18	3.00
5.57	4.00
6.96	5.00

Evidence

Table 2 Two Different $Pb(NO_3)_2$ Solutions

	Solution 1	Solution 2
Volume used (mL)	20.0	20.0
Mass of filter paper (g)	0.99	1.02
Mass of dried paper plus precipitate (g)	5.39	8.57

Precipitation Completeness

In Lab Exercise 8.A, the Design states that an excess of potassium iodide solution is used, but no mention is made about how to determine that the quantity you choose to add is, in fact, an excess. In a gravimetric analysis where a precipitation reaction is used, it is not possible to predict the quantity of excess reagent required, because you do not initially *know* the amount of the limiting reagent; that is why you are doing an analysis. For such reactions, use the following *trial-and-error* procedure to verify that a sample of limiting reagent has completely reacted:

1. Precisely measure a sample volume of the solution containing the limiting reagent.
2. Add (while stirring) an approximately equal volume of the excess reagent solution.
3. Allow the precipitate that forms to settle, until the top layer of solution is clear.
4. With a medicine dropper, add a few more drops of excess reagent solution. Allow the drops to run down the side of the container, and watch for any cloudiness that may appear when the drops mix with the clear surface layer (**Figure 2(a)**).
5. If any new cloudiness is visible, the reaction of the limiting reagent sample is not yet complete. Repeat steps 2 to 4 of this procedure as many times as necessary, until no new precipitate forms during the test in step 4 (**Figure 2(b)**).
6. When no new cloudiness is visible (the test does not form any further precipitate), the reaction of the sample of limiting reagent is complete.

Recall from Chapter 7 that for stoichiometric calculations to provide useful information about any reaction done for purposes of chemical analysis, we must assume that the reaction will be spontaneous, rapid, quantitative, and stoichiometric. The precipitation reaction you will use in Investigation 8.1 (to provide evidence for the analysis of sodium carbonate) is a good example of a reaction that meets all four of these requirements.

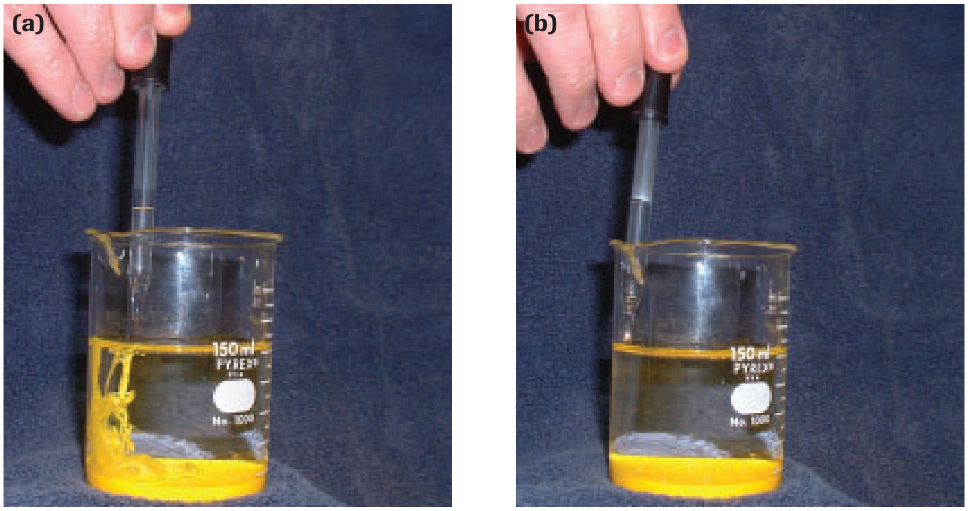

Figure 2
When the precipitate has settled enough so that the top layer of solution is clear, you can test for completeness of reaction.
(a) If cloudiness forms, more of the excess reagent will have to be added.
(b) If no cloudiness forms, the reaction of limiting reagent is complete.

Practice

1. Explain, in terms of cations, anions, and collision–reaction theory, what completeness of reaction actually means for the reaction in Lab Exercise 8.A. Write a net ionic equation to illustrate your answer.
2. Is the trial-and-error procedure a scientific or a technological procedure?
3. Write a procedure for how you could make sure that a precipitation reaction "goes to completion" if the sample is filtered after the first precipitation, *without* testing for completeness before filtering. Explain what solution would be added, where, and why.

INVESTIGATION 8.1 *Introduction*

Analysis of Sodium Carbonate

Sodium carbonate has been used for all of recorded history in a variety of applications, from glassmaking to detergent manufacture to water treatment. A common name for sodium carbonate is soda ash, an appropriate name because it can easily be extracted from wood ashes. Sodium carbonate is one of the ten highest-volume chemicals produced in North America.

In this investigation, you will use techniques and equipment common to gravimetric analysis to analyze a sodium carbonate solution.

Purpose

The purpose of this investigation is to use the stoichiometric method as part of a gravimetric analysis.

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
○ Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
● Evaluation (1, 3)

Problem

What is the mass of solute in a 50.0 mL sample of sodium carbonate solution?

Design

The mass of sodium carbonate present in the sample solution is determined by having it react with an excess quantity of a calcium chloride solution. The mass of calcium carbonate precipitate formed is used in stoichiometric calculation to determine the mass of sodium carbonate that reacted.

To perform this investigation, turn to page 340.

Section 8.2 Questions

1. A student wants to precipitate all the toxic lead(II) ions from 2.0 L of solution containing 0.34 mol/L $Pb(NO_3)_2(aq)$. The purpose of this reaction is to make the filtrate solution nontoxic. If the student intends to precipitate lead(II) sulfate, suggest an appropriate solute, and calculate the minimum required mass of this solute.
2. A chemical analyst wants to determine the concentration of a solution of copper(II) sulfate that is used for treating wood, to prevent decay. A large strip of zinc metal is placed in a 200 mL sample of this solution. When the reaction shows no further change, much of the zinc strip remains. The originally blue solution is now colourless. A brownish layer of fine copper particles has formed, which when filtered and dried, has a mass of 1.72 g. What is the amount concentration of the sample solution?
3. Only quantitative reactions are suitable for use in a chemical analysis. Complete the Prediction, Analysis, and Evaluation (of the Design and Prediction) of the investigation report.

   Purpose
   The purpose of this investigation is to use the stoichiometric method to determine whether a reaction is quantitative.

   Problem
   What mass of precipitate is produced by the reaction of 20.0 mL of 0.210 mol/L sodium sulfide with an excess quantity of aluminium nitrate solution?

   Design
   The two solutions provided react with each other, and the resulting precipitate is separated by filtration and then dried. The mass of the dried precipitate is determined.

   Evidence
   A precipitate formed very rapidly when the solutions were mixed.

   A few additional drops of the aluminium nitrate solution added to the clear layer above the settled precipitate produced no additional cloudiness.

   mass of filter paper = 0.97 g

   mass of dried filter paper plus precipitate = 1.17 g
4. Many industries recycle valuable byproducts, such as silver nitrate solution. You are an industry technician who needs to determine the amount concentration of a solution. Complete the Analysis of the investigation report.

   Purpose
   The purpose of this investigation is to use the stoichiometric method to analyze a solution for its amount concentration.

   Problem
   What is the amount concentration of silver nitrate in the solution to be recycled?

   Design
   A sample of the silver nitrate solution reacts with an excess of sodium sulfate in solution. The precipitate is filtered and the mass of dried precipitate is measured.

   Evidence
   A white precipitate formed in the reaction.

   No further precipitate formed when a few extra drops of sodium sulfate were added to the clear solution layer above the settled precipitate.

   volume of silver nitrate solution = 100 mL

   mass of filter paper = 1.27 g

   mass of dried filter paper plus precipitate = 6.74 g

8.3 Stoichiometry: Limiting and Excess Reagent Calculations

Calculating Mass of Excess Reagents

For reaction situations other than analysis, you usually know (have measured values for) the quantities of one or more reagents. In these situations, it is often desirable to know in advance how much excess reagent will be required to ensure that the reaction goes to completion. When you know the quantity of more than one reagent, you also need to know which of those reagents will limit the reaction. Stoichiometric calculation can provide this kind of useful information.

For reacting a precisely measured quantity of one reagent with an excess of another, we use a "rule of thumb," a general but inexact guideline that works for most situations. For questions in this textbook, assume that a *reasonable quantity of excess reagent to use is 10% more than the quantity required for complete reaction*, as determined in a stoichiometric calculation. There are exceptions to this rule in practice, especially in industrial and commercial chemistry. When the excess reagent is inexpensive or free, using a larger excess is normal. For example, the burner on a propane barbecue is designed to supply a huge excess of oxygen to the reaction zone (the flame). The amount of propane is limited by the size of the hole in the burner supply pipe. In this case, not only is the oxygen free, but it is also extremely important that the reaction be complete, to minimize production of highly toxic carbon monoxide.

SAMPLE problem 8.1

You decide to test the method of stoichiometry using the reaction of 2.00 g of copper(II) sulfate in solution with an excess of sodium hydroxide in solution. What would be a reasonable mass of sodium hydroxide to use?

To answer this question, you need to calculate the minimum mass required and then add 10%. The first part of this plan follows the usual steps of stoichiometry:

$CuSO_4(aq)$	+	$2\,NaOH(aq)$	→	$Cu(OH)_2(s)$	+	$Na_2SO_4(aq)$
2.00 g		m				
159.62 g/mol		40.00 g/mol				

$$n_{CuSO_4} = 2.00\,\cancel{g} \times \frac{1\text{ mol}}{159.62\,\cancel{g}}$$
$$= 0.0125\text{ mol}$$

$$n_{NaOH} = 0.0125\text{ mol} \times \frac{2}{1}$$
$$= 0.0251\text{ mol}$$

$$m_{NaOH} = 0.0251\,\cancel{\text{mol}} \times \frac{40.00\text{ g}}{1\,\cancel{\text{mol}}}$$
$$= 1.00\text{ g}$$

or $$m_{NaOH} = 2.00\,\cancel{\text{g CuSO}_4} \times \frac{1\,\cancel{\text{mol CuSO}_4}}{159.62\,\cancel{\text{g CuSO}_4}} \times \frac{2\,\cancel{\text{mol NaOH}}}{1\,\cancel{\text{mol CuSO}_4}} \times \frac{40.00\text{ g NaOH}}{1\,\cancel{\text{mol NaOH}}}$$
$$= 1.00\text{ g NaOH}$$

Now add 10% to this value: 1.00 g + 0.10 g = 1.10 g

Learning Tip

Remember to keep the unrounded values in your calculator for further calculation until the final answer is reported. The values for intermediate calculation are rounded when written down. Follow the calculation process for the Sample Problems on your calculator to review how to do this.

WEB Activity

Canadian Achievers—Ursula Franklin

In addition to a distinguished career in research, Ursula Franklin (**Figure 1**) has been a tireless advocate for the responsible use of scientific knowledge and an active member of Science for Peace.

1. Describe two fields of scientific research where Franklin did pioneering work.
2. Summarize briefly the objectives of the Science for Peace organization.

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Figure 1
Ursula Franklin (1921–)

Practice

1. A chemistry teacher wishes to have students perform a precipitation reaction, to practise filtration techniques and to test a stoichiometric prediction. Vials containing precisely measured 1.50 g samples of barium chloride are given to each student group. A stock supply of pure solid sodium sulfate is available in the laboratory. Both reagents are colourless in aqueous solution.
   (a) What would be a reasonable mass of sodium sulfate for each group to use to ensure complete reaction of their barium chloride sample?
   (b) When the precipitate is filtered, which aqueous ion should not be present in the filtrate?
   (c) Describe a procedure that students could use to test the filtrate to see whether the limiting reagent has all reacted.
   (d) What should the students do if the test shows the limiting reagent has not all reacted?

2. In a laboratory gas generator, zinc and an aqueous solution of hydrogen chloride are combined to produce hydrogen. If a 2.00 g sample of zinc is to react completely with an excess of 2.00 mol/L HCl(aq), what would be a reasonable volume of the acid to use?

Identifying Limiting and Excess Reagents

Another application of stoichiometry is the identification of limiting and excess reagents in a chemical reaction, when two known quantities of chemicals react. Which one is the limiting reagent? This is determined using the same stoichiometric principles as before. Like all stoichiometry problems, the mole ratio from the balanced chemical equation is the key part of the solution.

SAMPLE problem 8.2

If 10.0 g of copper is placed in a solution of 20.0 g of silver nitrate, which reagent will be the limiting reagent?

$$\begin{array}{llll} \mathrm{Cu(s)} & + \; \mathrm{2\,AgNO_3(aq)} & \rightarrow \mathrm{2\,Ag(s)} + \mathrm{Cu(NO_3)_2(aq)} \\ 10.0\text{ g} & 20.0\text{ g} & \\ 63.55\text{ g/mol} & 169.88\text{ g/mol} & \end{array}$$

According to the balanced equation, 1 mol of copper reacts completely with 2 mol of silver nitrate. To determine which reagent is limiting (and therefore which is in excess), convert the reactant quantities given into chemical amounts:

$$\begin{aligned} n_{\mathrm{Cu}} &= 10.0\ \cancel{\text{g}} \times \frac{1\text{ mol}}{63.55\ \cancel{\text{g}}} \\ &= 0.157\text{ mol} \end{aligned}$$

$$n_{AgNO_3} = 20.0\ \cancel{g} \times \frac{1\ mol}{169.88\ \cancel{g}}$$

$$= 0.118\ mol$$

You now need to test one of these values using the mole ratio from the chemical equation. In other words, assume that one chemical is completely used up and see if a sufficient amount of the second chemical is available. If copper is the limiting reagent, then the amount of silver nitrate required is calculated as follows:

$$n_{AgNO_3} = 0.157\ mol \times \frac{2}{1}$$

$$= 0.315\ mol$$

Obviously, this value (0.315 mol) is much greater than the amount we actually have available (0.118 mol). Therefore, the assumption is incorrect—copper cannot be the limiting reagent; it must be present in excess. Silver nitrate must be the limiting reagent.

Learning Tip

For any stoichiometric reaction:

aA + bB → product(s)

you can select either reactant for a calculation check to determine which reagent is actually limiting. If you assume that A is limiting, you use the mole ratio b/a to calculate the amount of B required to react with the amount of A that is present.

- If the amount of B present is enough, then A is limiting, and B is in excess.
- If the amount of B is not enough, then B is limiting, and A is in excess.

Notice that it does not matter which chemical you initially assume to be limiting. You will be able to identify both the limiting and excess reagents no matter which chemical you first choose to assume as the limiting reagent.

Once you have identified the limiting and excess reagents, you can immediately answer a number of other questions. How much of the excess reagent will remain after the reaction? How much product will be obtained? *It is important to note that all predictions made from a balanced chemical equation must be based on the limiting reagent.*

SAMPLE problem 8.3

In the reaction of a 10.0 g sample of copper with 20.0 g of silver nitrate in solution in Sample Problem 8.2, what mass of copper will be in excess (left over when the reaction is complete)? What mass of silver will be produced?

Write and balance the reaction equation.

$$Cu(s) + 2\,AgNO_3(aq) \rightarrow 2\,Ag(s) + Cu(NO_3)_2(aq)$$

To find the excess quantity of copper, find the mass of copper required to react with the 20.0 g of silver nitrate and compare that with the starting mass of copper. From Sample Problem 8.2, you know that the 20.0 g of silver nitrate is equivalent to 0.118 mol, and the chemical equation shows that the mole ratio of copper to silver nitrate is 1:2. Therefore, the chemical amount of copper that reacts can be calculated as follows:

$$n_{Cu} = 0.118\ mol \times \frac{1}{2}$$

$$= 0.0589\ mol$$

This can now be converted, using the molar mass of copper, to a mass of copper:

$$m_{Cu} = 0.059\ \cancel{mol} \times \frac{63.55\ g}{1\ \cancel{mol}}$$

$$= 3.74\ g$$

The excess quantity of copper is 10.0 g − 3.74 g, or 6.3 g.

To find the yield of silver product expected, use the chemical amount of the limiting reagent, $AgNO_3$, to predict the mass of this product:

$$\begin{aligned} n_{Ag} &= 0.118\ \text{mol} \times \frac{2}{2} \\ &= 0.118\ \text{mol} \\ m_{Ag} &= 0.118\ \cancel{\text{mol}} \times \frac{107.87\ \text{g}}{1\ \cancel{\text{mol}}} \\ &= 12.7\ \text{g} \end{aligned}$$

According to the stoichiometric method, the predicted (theoretical) yield of silver product is 12.7 g.

▶ COMMUNICATION *example*

In an experiment, 26.8 g of iron(III) chloride in solution is combined with 21.5 g of sodium hydroxide in solution. Which reactant is in excess, and by how much? What mass of each product will be obtained?

Solution

$$\begin{array}{lllllll} FeCl_3(aq) & + & 3\ NaOH(aq) & \rightarrow & Fe(OH)_3(s) & + & 3\ NaCl(aq) \\ 26.8\ \text{g} & & 21.5\ \text{g} & & m & & m \\ 162.20\ \text{g/mol} & & 40.00\ \text{g/mol} & & 106.88\ \text{g/mol} & & 58.44\ \text{g/mol} \end{array}$$

$$\begin{aligned} n_{FeCl_3} &= 26.8\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{162.20\ \cancel{\text{g}}} \\ &= 0.165\ \text{mol} \\ n_{NaOH} &= 21.5\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{40.00\ \cancel{\text{g}}} \\ &= 0.538\ \text{mol} \end{aligned}$$

If $FeCl_3$ is the limiting reagent, the amount of NaOH required is

$$\begin{aligned} n_{NaOH} &= 0.165\ \text{mol} \times \frac{3}{1} \\ &= 0.496\ \text{mol} \end{aligned}$$

The sodium hydroxide is in excess. The excess amount and mass are

$$\begin{aligned} n_{NaOH} &= 0.538\ \text{mol} - 0.496\ \text{mol} \\ &= 0.042\ \text{mol} \\ m_{NaOH} &= 0.042\ \cancel{\text{mol}} \times \frac{40.00\ \text{g}}{1\ \cancel{\text{mol}}} \\ &= 1.7\ \text{g} \end{aligned}$$

The mass of the two products is

$$\begin{aligned} m_{Fe(OH)_3} &= 0.165\ \cancel{\text{mol}\ FeCl_3} \times \frac{1\ \cancel{\text{mol}\ Fe(OH)_3}}{1\ \cancel{\text{mol}\ FeCl_3}} \times \frac{106.88\ \text{g}\ Fe(OH)_3}{1\ \cancel{\text{mol}\ Fe(OH)_3}} \\ &= 17.7\ \text{g}\ Fe(OH)_3 \\ m_{NaCl} &= 0.165\ \cancel{\text{mol}\ FeCl_3} \times \frac{3\ \cancel{\text{mol}\ NaCl}}{1\ \cancel{\text{mol}\ FeCl_3}} \times \frac{58.44\ \text{g}\ NaCl}{1\ \cancel{\text{mol}\ NaCl}} \\ &= 29.0\ \text{g}\ NaCl \end{aligned}$$

According to the stoichiometric method, sodium hydroxide is in excess by 1.7 g, the mass of iron(III) hydroxide produced is 17.7 g, and the mass of sodium chloride produced is 29.0 g.

Figure 2

If tap water contains iron ions, and is also slightly basic, precipitation of iron inside water pipes becomes a real problem. Ideally, tap water should be very slightly acidic, so it will keep any iron in solution. Neither copper nor the plastics normally used for water supply pipes are corroded by acids.

Practice

3. For each of the following combinations of reagents, identify the limiting and excess reagents, and find the chemical amount of excess reagent that will remain unreacted:
   (a) 10.0 mol of methane and 10.0 mol of oxygen
   (b) 2.20 mol of magnesium and 3.30 mol of hydrochloric acid
   (c) 0.44 mol of copper(II) nitrate in solution and 0.55 mol of sodium phosphate in solution
   (d) 2.41 mmol of sodium hydroxide in solution and 6.66 mmol of sulfuric acid

4. For each of the following combinations of reagents, identify the limiting and excess reagents, and find the mass of excess reagent that will remain unreacted:
   (a) 10.0 g of carbon and 10.0 g of oxygen
   (b) 4.00 g of aluminium and 4.50 g of chlorine
   (c) 12 mg of barium nitrate in solution and 44 mg of potassium sulfate in solution
   (d) 1.31 kg of lithium hydroxide in solution and 7.50 kg of acetic acid

5. Read the entire question before attempting this mind exercise. You are to make cheese sandwiches, each of which consists of two bread slices and one cheese slice. The equation symbols might be shown as $2\ \mathrm{B} + \mathrm{C} \rightarrow \mathrm{S}$. You have a 500 g loaf of sliced bread and a 300 g package of cheese slices. All slices are uniform, and there are no crusts, condiments, or complications. How many sandwiches can you make? Which constituent will be in excess, and by how many slices? As with your chemistry studies, a lot of the tricky details and exceptions are left out of this question, so you can concentrate on the concept.
   (a) What precise information *must* be added (learned) in order for you to be able to answer this question?
   (b) What factor of a gravimetric stoichiometry calculation is analogous to the information you require for this question?
   (c) Bread and cheese slices are sold by measured mass but "assembled" by counted numbers. Explain how this is parallel to chemical reaction systems. (Except, of course, that with real bread and cheese slices you could "cheat" because you *could* actually count them.)
   (d) Now apply the concept. Make up your own values for the required information, and solve the problem with those numbers. Alternatively, research your local food store, and use real (empirical) evidence.
   (e) Suggest a possible practical application for this example in society.

DID YOU KNOW ?

Mind Exercises

Thought experiments are often used by scientists, especially when trying to understand aspects of the natural world that do not allow direct observation, such as changes in (or even the existence of) chemical entities. The human mind is the original "useful tool," and thinking can be considered the original technology applied to problem solving. Aboriginal peoples historically did a great deal of their learning by observation and creative thinking. The Cree word for "mind" is *mamtunahunichican*, which translates literally as "the thinking tool."

INVESTIGATION 8.2 *Introduction*

Percent Yield of Barium Sulfate

Barium sulfate is a white, odourless, tasteless powder that has a variety of different uses: as a weighting mud in oil drilling; in the manufacture of paper, paints, and inks; and it can be taken internally for gastrointestinal X-ray analysis. It is so insoluble that it is nontoxic, and is therefore very safe to handle.

To determine the predicted (theoretical) yield in the Prediction, you will need to identify the limiting and excess reagents before using the stoichiometric method to predict the expected mass of product.

Purpose

The purpose of this investigation is to use the stoichiometric method to evaluate a commercial procedure for producing barium sulfate.

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
● Prediction
○ Design
● Materials
● Procedure
● Evidence
● Analysis
● Evaluation (1, 2, 3)

Problem

What is the percent yield of barium sulfate in the reaction of aqueous solutions of barium chloride and sodium sulfate?

Design

A 40.0 mL sample of 0.15 mol/L sodium sulfate solution is mixed with 50.0 mL of 0.100 mol/L barium chloride solution. A diagnostic test is performed to check for completeness of precipitation of the limiting reagent. The mass of the filtered, dried precipitate is measured. The experimental mass of the precipitate is compared to the predicted mass.

To perform this investigation, turn to page 341.

Case Study

The Haber Process

In the late 19th century, rapid population growth in Europe and North America began to outstrip the supply of fresh food. Scientists knew that if they added nitrogen-based fertilizers (such as sodium nitrate, $NaNO_3(s)$, or ammonium nitrate, $NH_4NO_3(s)$) to the soil, crop yields would increase and a worldwide food shortage could be prevented. The world supply of fertilizers could not keep up with the growing demand for food, however, because large amounts of sodium nitrate were also being used to produce explosives such as gunpowder and nitroglycerine. Additional sources of ammonia or nitrate had to be found to avoid a global catastrophe.

In 1909, a leading German chemical company, Badische Anilin und Soda Fabrik (BASF), started to investigate the possibility of producing ammonia, $NH_3(g)$, from atmospheric nitrogen, $N_2(g)$. Little did they know that one year earlier, Fritz Haber, a professor at a technical college in Karlsruhe, Germany, had discovered a method for doing just that (**Figure 3**).

Haber realized, after much experimentation, that nitrogen gas and hydrogen gas react to form ammonia as the only product. Optimum conditions for the reaction included a closed container, a suitable catalyst (such as iron oxide, $Fe_2O_3(s)$), a temperature of 500 °C, and a pressure of 40 MPa.

$$N_2(g) + 3\,H_2(g) \xrightarrow{Fe_2O_3(s)} 2\,NH_3(g)$$

Haber's method for producing ammonia is now called the *Haber process*. BASF bought the rights to the Haber process. With the help of Carl Bosch, BASF's chief chemical engineer, BASF built a giant industrial plant that was capable of producing 10 000 t of ammonia per year. Today, ammonia is in sixth position in a ranking of chemicals produced worldwide, with over 80 billion kilograms produced each year.

The Temperature–Pressure Puzzle

The reaction of nitrogen and hydrogen at low temperatures is so slow that the process becomes uneconomical. Adding heat increases the rate of the reaction, which is important in any industrial process. In this reaction, however, the higher the temperature, the lower the percent yield of ammonia. The relationship between percent yield and temperature is shown in **Figure 4**.

Haber had to balance the rate of the reaction (increased by higher temperatures) against the decrease in percent yield of ammonia at higher temperatures. He discovered that using an iron oxide catalyst eliminates the need for excessively high temperatures. Without the catalyst, the production of significant amounts of ammonia is too slow to be economical. Haber also discovered that the pressure at which the reaction is allowed to occur affects the percent yield of ammonia. In general, higher pressures increase the percent yield (**Figure 5**).

Haber and his students carried out the reaction under various conditions of temperature and pressure. They found that a satisfactory percent yield of ammonia could be obtained at a temperature of 500 °C and a pressure of 40 MPa. After a suitable length of time under these conditions, the yield of ammonia is about 40%.

Figure 3
Fritz Haber discovered a method for converting atmospheric nitrogen into ammonia at a technical college in Karlsruhe, Germany. He was awarded the Nobel Prize in chemistry in 1918 for discovering the process that now bears his name.

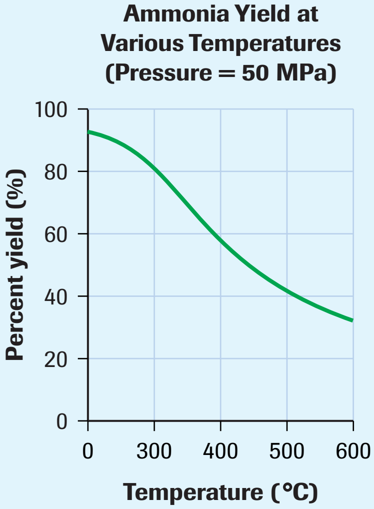

Figure 4
The percent yield of ammonia decreases with increasing temperature.

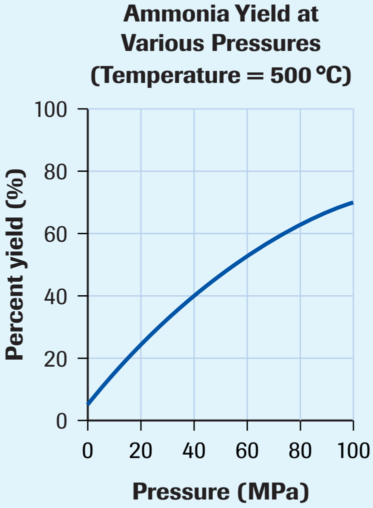

Figure 5
The percent yield of ammonia increases with increasing pressure.

Figure 6
This huge production facility, located 50 km southeast of Calgary at Carseland, can synthesize 535 000 t of ammonia per year. Agrium Corporation, which operates this plant, has three other plants like it in Alberta, with a total ammonia production capacity of nearly 2.5 Mt per year. Most of this ammonia is not used directly as fertilizer; it is further processed (reacted) to make, among other chemicals, fertilizers such as urea, ammonium nitrate, and ammonium phosphate.

Figure 7
Ammonia fertilizer can be added directly to the soil.

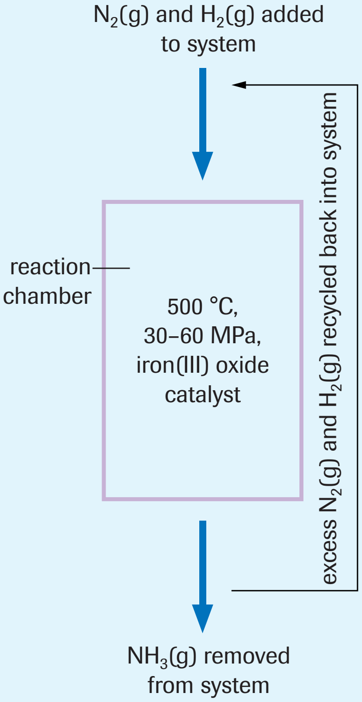

Figure 8
Outline of the Haber process

Today, the Haber process is used to produce ammonia from its elements in over 335 active synthetic ammonia plants worldwide (**Figure 6**). Much of the ammonia that is produced is used in agriculture (**Figure 7**). As a fertilizer, the ammonia dissolves in moisture that is present in the soil. If the soil is slightly acidic, the ammonia is converted to nitrate ions by soil bacteria. Nitrate ions are absorbed by the roots of plants and used in the synthesis of proteins, chlorophyll, and nucleic acids. Without a source of nitrogen, plants do not grow; they produce yellow leaves and die prematurely.

Case Study Questions

1. Recall that reactions for which stoichiometric calculations can be used for analysis are usually required to be spontaneous, fast, quantitative, and stoichiometric. Consider the information provided in this Case Study about the conditions under which the Haber process reaction is done industrially.
   (a) The Haber process reaction is not spontaneous. At SATP, nitrogen and hydrogen do not react at all. How is this problem overcome in the production of ammonia? Use the collision–reaction theory in your explanation.
   (b) When the reaction is set up under conditions in which it is spontaneous, it is not fast. This problem can be helped by adding finely powdered Fe_2O_3(s) to act as a *catalyst*. Explain what effect this has on the reaction, and what role the iron(III) oxide plays.
   (c) Once the reaction rate is increased, the reaction is not quantitative. Even at the usual industrial conditions, ammonia seems to stop forming when less than 40% of the reactants have reacted. If increasing pressure increases percent yield, why is the process not just done at extremely high pressures? *Hint:* Think about the warnings on aerosol spray can labels.
   (d) Percent yield is improved by lowering the temperature. Why do industrial chemists not use low temperatures?
   (e) The reaction is stoichiometric. The amounts of nitrogen and hydrogen that react do so in an exact 1:3 proportion. Considering the composition of Earth's atmosphere, which of these reagents do you think would concern the company accounting department?

2. The process to remove the ammonia from the nitrogen and hydrogen remaining in the reaction pressure vessel is quite simple. When the three mixed gases are cooled at fairly high pressure, the ammonia condenses and can be drained out of the bottom of the vessel, leaving the hydrogen and nitrogen behind. More of each reagent is then added, and the temperature is raised to make the gases react again. This process is repeated continuously (**Figure 8**).
   (a) Explain why, in a chemical plant that runs continuously, the rate of reaction is much more important to industrial chemists than the percent reaction.
   (b) Ammonia is actually a smaller molecule (by mass, or electron count) than nitrogen. Explain why ammonia's condensation temperature should be so much higher than nitrogen's.

Extension

3. Working in a small group, research the Internet and other sources to find out where and how Alberta ammonia producers get the hydrogen they use for this reaction. Prepare a brief report or presentation, including graphics. Include a discussion of the likelihood of long-term (centuries) sustainability of Haber process technology as applied in Alberta, and its value from economic and environmental perspectives.

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SUMMARY Limiting/Excess Reagent Calculations

- Identify the limiting reagent by choosing either reagent amount, and use the reaction mole ratio to compare the required amount of the other reagent with the amount actually present.
- The quantity in excess is the difference between the amount of excess reagent present and the amount required for complete reaction.
- A reasonable reagent excess to use to ensure complete reaction is 10%.

EXTENSION

Limiting Reagents

Try this exercise to help consolidate your understanding of limiting and excess reagents.

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Section 8.3 Questions

1. List the necessary assumptions about a reaction done for chemical analysis.

2. When testing gravimetric stoichiometry using an experiment, should you combine the two reactants in the same ratio as they appear in the balanced chemical equation? Justify your answer.

3. When calculating a percent yield, where does the value of the actual yield come from? Where does the predicted yield come from?

4. A quick, inexpensive source of hydrogen gas is the reaction of zinc with hydrochloric acid (**Figure 9**). If 0.35 mol of zinc is placed in 0.60 mol of hydrochloric acid,
   (a) which reactant will be completely consumed?
   (b) what mass of the other reactant will remain after the reaction is complete?

Figure 9
Zinc reacting with hydrochloric acid

5. A chemical technician is planning to react 3.50 g of lead(II) nitrate with excess potassium bromide in solution.
   (a) What would be a reasonable mass of potassium bromide to use in this reaction?
   (b) Predict the mass of precipitate expected.

6. In a chemical analysis, 3.40 g of silver nitrate in solution reacted with excess sodium chloride to produce 2.81 g of precipitate. What is the percent yield?

7. A solution containing 9.8 g of barium chloride is mixed with a solution containing 5.1 g of sodium sulfate.
   (a) Which reactant is in excess?
   (b) Determine the excess mass.
   (c) Predict the mass of precipitate.

8. A solution containing 18.6 g of chromium(III) chloride reacts with a 15.0 g piece of zinc to produce chromium metal (**Figure 10**).
   (a) Which reactant is in excess?
   (b) Determine the excess mass.
   (c) If 5.1 g of chromium metal is formed, what is the percent yield?

Figure 10
Electroplating produces a thin metal coating on objects such as the car door handles shown in the photograph. Chromium plating is used for esthetic as well as technical reasons because it creates a shiny surface and also prevents corrosion. Chromium ions are toxic, however, and environmental damage may result if the chromium solutions are dumped as waste. Treating toxic wastes to transform them into safe materials is sometimes prohibitively expensive.

9. A technical college instructor wishes a first-year chemistry group to perform an investigation to practise precipitation and filtration techniques and to calculate a percent yield. The class will react 50.00 mL pipetted samples of 0.200 mol/L potassium phosphate solution with an excess of 0.120 mol/L lead(II) nitrate solution.
   (a) Which reagent is intended to be the limiting reagent?
   (b) What is the minimum volume of lead(II) nitrate solution required?
   (c) What volume of lead(II) nitrate solution should the instructor tell the students to use?
   (d) Describe how the students can test for completeness of reaction of the limiting reagent.

8.4 Titration Analysis

Titration is a common experimental design used to determine the amount concentration of substances in solution (see Appendix C.4). **Titration** is the process of carefully measuring and controlling the addition of a solution, called the **titrant**, from a burette into a measured fixed volume of another solution, called the **sample**, usually in an Erlenmeyer flask (**Figure 1**) until the reaction is judged to be complete. A *burette* is a precisely marked glass cylinder with a stopcock at one end. It allows precise, accurate measurement and control of the volume of reacting solution. This technique is a good example of a chemical technology that is reliable, efficient, economical, and simple to use.

When doing a titration, there will be a point at which the reaction is complete. In other words, chemically equivalent amounts of reactants, as determined by the mole ratio, have been combined. The point at which the exact theoretical amount of titrant has been added to completely react with the sample is called the **equivalence point**. To measure this point experimentally, we look for a sudden change in some observable property of the solution, such as colour, pH, or conductivity. The point during a titration when this sudden change is observed is called the **endpoint**. At the endpoint, the titration is stopped and the volume of titrant is determined. Ideally, the volume at the empirical endpoint and the volume corresponding to theoretical equivalence point should coincide.

A titration analysis should involve several trials, to improve the reliability of the answer. A typical requirement is to repeat titrations until three trials result in volumes within a range of 0.2 mL. These three results are then averaged before carrying out the solution stoichiometry calculation, disregarding any trial volumes that do not fall within this range.

Learning Tip

A titration analysis of an unknown amount concentration requires that the chemical reaction be spontaneous, fast, quantitative, and stoichiometric. The amount concentration of one reactant used must be accurately known. The solution of known amount concentration may be used as either the titrant or the sample; it makes no difference to the analysis.

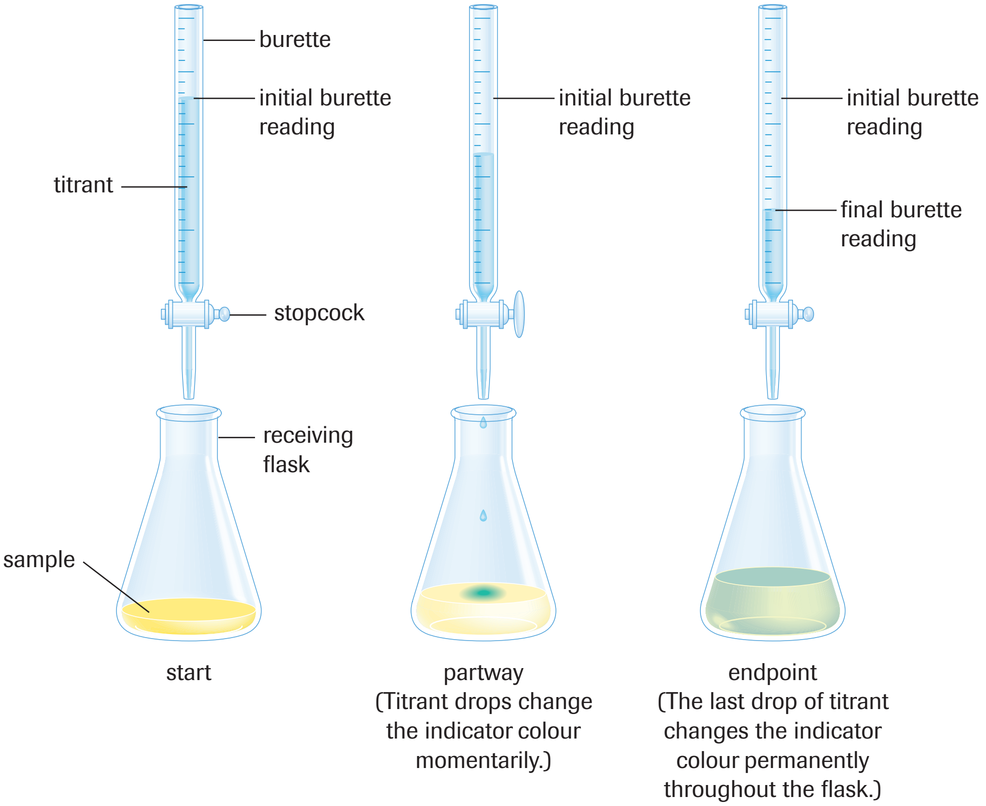

Figure 1
An initial reading of volume is made on the burette before any titrant is added to the sample solution. Then titrant is added until the reaction is complete; that is, when a final drop of titrant permanently changes the colour of the sample. The final burette reading is then taken. The difference in burette readings is the volume of titrant added. Appendix C.4 describes the titration process in detail.

SAMPLE problem 8.4

Determine the concentration of hydrochloric acid in a commercial solution that is used to treat concrete prior to painting.

A 1.59 g mass of sodium carbonate, $Na_2CO_3(s)$, was dissolved to make 100.0 mL of solution. Samples (10.00 mL) of this standard solution were then taken and titrated with solution, which was prepared by diluting the original commercial solution, HCl(aq), by a factor of 10. The titration evidence collected is shown in **Table 1**. Methyl orange indicator was used.

Table 1 Titration of 10.00 mL of $Na_2CO_3(aq)$ with Diluted HCl(aq)

Trial	**1**	**2**	**3**	**4**
final burette reading (mL)	13.3	26.0	38.8	13.4
initial burette reading (mL)	0.2	13.3	26.0	0.6
volume of HCl(aq) added (mL)	13.1	12.7	12.8	12.8
indicator colour	red	orange	orange	orange

First, calculate the amount concentration of the sodium carbonate solution:

$$
\begin{aligned}
n_{Na_2CO_3} &= 1.59\ \cancel{g} \times \frac{1\ \text{mol}}{105.99\ \cancel{g}}\\
&= 0.0150\ \text{mol}
\end{aligned}
$$

$$
\begin{aligned}
[Na_2CO_3(aq)] &= \frac{0.0150\ \text{mol}}{0.1000\ \text{L}}\\
&= 0.150\ \text{mol/L}
\end{aligned}
$$

Now write the balanced chemical equation:

$$
\begin{array}{lll}
2\,HCl(aq) & + \; Na_2CO_3(aq) \rightarrow H_2CO_3(aq) + 2\,NaCl(aq) \\
12.8\ \text{mL}^{*} & 10.00\ \text{mL} \\
c & 0.150\ \text{mol/L}
\end{array}
$$

* The volume of HCl(aq) used is an average of trials 2, 3, and 4.

$$
\begin{aligned}
n_{Na_2CO_3} &= 10.00\ \text{m}\cancel{\text{L}} \times \frac{0.150\ \text{mol}}{1\ \cancel{\text{L}}}\\
&= 1.50\ \text{mmol}
\end{aligned}
$$

$$
\begin{aligned}
n_{HCl} &= 1.50\ \text{mmol} \times \frac{2}{1}\\
&= 3.00\ \text{mmol}
\end{aligned}
$$

$$
\begin{aligned}
[HCl(aq)] &= \frac{3.00\ \cancel{\text{m}}\text{mol}}{12.8\ \cancel{\text{m}}\text{L}}\\
&= 0.235\ \text{mol/L}
\end{aligned}
$$

or

$$
\begin{aligned}
[HCl(aq)] &= 10.00\ \cancel{\text{m}}\ \cancel{\text{L}\ Na_2CO_3} \times \frac{0.150\ \cancel{\text{mol}\ Na_2CO_3}}{1\ \cancel{\text{L}\ Na_2CO_3}} \times \frac{2\ \text{mol HCl}}{2\ \cancel{\text{mol}\ Na_2CO_3}} \times \frac{1}{10.00\ \cancel{\text{m}}\ \text{L HCl}}\\
&= 0.235\ \text{mol/L HCl (the diluted analysis solution)}
\end{aligned}
$$

Since the sample of concrete cleaner had been diluted by a factor of 10, the original concentration of the commercial hydrochloric acid must be 10 times greater, or 2.35 mol/L.

Learning Tip

Notice in **Table 1** that four trials were done, and the volume added in the first trial is significantly higher than in the others. This value is thus disregarded when calculating an average volume of HCl(aq) that reacts. In titration analysis, the first trial is typically done very quickly. It is just for practice, to learn what the endpoint looks like and also to learn the approximate volume of titrant required to get to the endpoint. Then greater care is taken with subsequent trials.

Learning Tip

Any property of a solution, such as colour, conductivity, or pH, that changes abruptly can be used as an endpoint. However, some changes may not be very sharp or may be difficult to measure accurately. This may introduce error into the experiment. Any difference between the titrant volumes at the empirical (observed) endpoint and the theoretical equivalence point is known as the titration error.

SUMMARY Titration Analysis

- Titration is the technique of carefully controlling the addition of a volume of solution (the titrant) from a burette into a measured fixed volume of a sample solution until the reaction is complete.
- The concentration of one reactant must be accurately known.
- The equivalence point is the point at which the exact theoretical (stoichiometric) reacting amount of titrant has been added to the sample.
- The endpoint is the point during the titration at which the sudden change of an observable property indicates that the reaction is complete.
- Several trials must be completed. When at least three trials result in values that are all within a range of 0.2 mL, those values are averaged. The average value is used for the stoichiometry calculation.

Standardizing Titrant Solutions

Before any titration is performed to analyze a solution, it is absolutely necessary that you know the amount concentration of one of the solutions to a high degree of certainty, because that value will be used to calculate your answer. Chemists call a solution of highly certain concentration a **standard solution**. In Chapter 5, you learned techniques for preparing standard solutions of accurately known amount concentration by carefully measuring both the mass of the solute and the volume of the solution. Sometimes, however, that process does not work because the solute you need is not what chemists call a primary standard.

A **primary standard** is a chemical that can be obtained at high purity, with mass that can be measured to high accuracy and precision. Some chemicals cannot be obtained at high purity, and measuring the mass of a chemical that is not pure is pointless—you have no way of knowing how much of that mass is made up of the impurities. Some chemicals, although pure, cannot be measured accurately with a balance because their mass will not remain constant. For example, sodium hydroxide in solution is a very common and useful strong base, but you cannot prepare a standard solution from solid sodium hydroxide. The pure solid compound attracts water so strongly that it will absorb water vapour rapidly from the air. If you take some NaOH(s) out of a closed container and place it on a balance, it will absorb water and increase in mass while you are trying to measure it. Once dissolved in pure water, however, the concentration of a dilute solution of sodium hydroxide will remain constant. Therefore, what is required is a way to analyze the concentration after the solution is prepared.

CAREER CONNECTION

Hydrologist

Water is one of the most necessary substances for life. Hydrologists study water and how it flows around the atmosphere and the planet, looking at water's movement through rivers, glaciers, and geologic formations. These specialists examine data to make sure that water supply and quality meet public and industrial demands. They also make recommendations for environmental impact assessments.

Research this career and associated specialties online.

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If a solute is a gas, it cannot be a primary standard. In anything other than a very dilute solution, some gas will escape any time the container is opened, decreasing the amount concentration. Ammonia and hydrochloric acid are common examples.

Standardizing a solution means finding the concentration of a solution *after* it is prepared, by reacting it with another solution that has been prepared from a primary standard. A stoichiometric calculation is then used to find the unknown concentration. This procedure is really just a titration analysis like any other. A primary standard often used to make a solution for standardizing basic solutions is potassium hydrogen phthalate, $KC_7H_4O_2COOH(s)$. Investigation 8.3 illustrates the total process of first making a standard solution, and then using it to analyze (and thus standardize) another solution. In this case, the sodium hydroxide solution to be standardized is also the titrant solution that will be used for Investigations 8.4 and 8.6.

INVESTIGATION 8.3 *Introduction*

Standardization Analysis of NaOH(aq) (Demonstration)

A large (stock) volume of sodium hydroxide solution is prepared for use in Investigations 8.4 and 8.6 by dissolving 6 g of solid for each litre of solution required. Because this solute is not a primary standard, this solution must be standardized to accurately determine its concentration. This will be accomplished by titration against a standard potassium hydrogen phthalate (KHP) solution.

Purpose

The purpose of this investigation is to use a titration design to standardize a solution for future chemical analysis.

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ● Evidence
- ● Analysis
- ○ Evaluation

Problem

What is the concentration of a stock NaOH(aq) solution?

Design

A standard solution of KHP is prepared, and it is then used to standardize a stock solution of sodium hydroxide. Samples of KHP are titrated with sodium hydroxide titrant, using phenolphthalein as an indicator.

To perform this investigation, turn to page 342.

Practice

1. When adding titrant to a burette, it is critical that the concentration of the solution remain constant. Ideally, the burette should be cleaned and dried just before use to make sure that no impurities change the titrant concentration. It is extremely difficult, however, to quickly dry a burette that has just been cleaned. What technique is used to solve this problem?
2. When a titration analysis is performed, multiple trials are normally run. This means that successive equal volumes (called aliquots) of the sample solution must be taken. What technology is used to ensure that the volumes of sample for each trial are as identical as possible?
3. One purpose of doing multiple trials for an analysis is to immediately identify any mistakes in procedure because these will cause discrepant results. What is the other reason for doing multiple trials?
4. Acid–base titrations, like Investigation 8.3, typically do not produce any visible product, which presents a problem. There is no direct way of knowing when such a reaction is complete. Explain how this problem is overcome by using another substance that is not part of the reaction, what characteristic of this substance is useful, and what characteristic of the reaction solution is detected by this substance. (*Hint:* Review Section 6.3.)

INVESTIGATION 8.4 *Introduction*

Titration Analysis of Vinegar

Some consumer food products are required by law to have the minimum quantity of the active ingredient listed on the product label. According to the label, a vinegar manufacturer states that the vinegar contains 5% acetic acid by volume, which translates to a minimum amount concentration of 0.83 mol/L.

Purpose

The purpose of this investigation is to test the manufacturer's claim of the concentration of acetic acid in a consumer sample of vinegar.

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ● Materials
- ● Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 2, 3)

Problem

What is the amount concentration of acetic acid in a sample of vinegar?

Design

A sample of commercial white vinegar is diluted by a factor of 5 to make a 100.0 mL final solution. Samples of this diluted solution are titrated with a standardized sodium hydroxide solution (from Investigation 8.3) using phenolphthalein as the indicator.

To perform this investigation, turn to page 343.

Section 8.4 Questions

1. Ammonia is a very useful chemical; our society consumes it in huge quantities. Farmers use the pure substance in liquid form as a fertilizer. Pure liquid ammonia is called anhydrous, which means "without water," to distinguish it from aqueous solutions. In solution, ammonia has an outstanding ability to loosen dirt, oil, and grease, so it is commonly used in premixed home cleaners such as window cleaning sprays, along with other ingredients. Aqueous ammonia is also sold in most stores for household use, to be diluted at home to make solutions for cleaning and wax stripping (**Figure 2**). Such solutions can legally be anywhere from 5% to 30% ammonia by weight.

   A student wishing to find the concentration of ammonia in a commercial solution decides to do an analysis, titrating 10.00 mL samples of NH_3(aq) with a standardized solution of 1.48 mol/L HCl(aq). Her first trials use more than 50 mL (a burette full) of the acid, so she throws out the results and prepares a new ammonia sample solution by diluting the original commercial solution 10:1, that is, increasing a volume tenfold to reduce the concentration to precisely one-tenth of the original value. Using **Table 2**, complete the Analysis of her investigation report.

   Purpose

   The purpose of this investigation is to use a titration design to analyze a solution of ammonia.

   Problem

   What is the amount concentration of the original ammonia solution?

   Design

   The original ammonia solution is diluted tenfold. Samples of diluted solution are titrated with a standard 1.48 mol/L solution of hydrochloric acid. The colour change of bromocresol green indicator from blue to yellow is used as the endpoint.

   Evidence

Table 2 Titration of 10.00 mL of NH_3(aq) with 1.48 mol/L HCl(aq)

Trial	1	2	3	4
final burette reading (mL)	15.0	29.1	43.0	14.4
initial burette reading (mL)	0.3	15.0	29.1	0.4
volume of HCl(aq) added (mL)				
colour at endpoint	yellow	green	green	green

2. Assume a hydrochloric acid solution is prepared by diluting commercial lab reagent solution (approximately 12 mol/L) by a factor of 20:1. For concentrated HCl(aq) solutions, complete the following:
   (a) Explain why the label concentration is necessarily uncertain for concentrated solutions of gases dissolved in water. *Hint:* Think about opening carbonated beverages.
   (b) Explain how the concentration changes each time the stock bottle is opened.

Figure 2
Household ammonia is sold as a fairly concentrated aqueous solution, making it very convenient to store, transport, dilute, and dispense.

3. Describe a design for precisely determining the concentration of (standardizing) a diluted hydrochloric acid solution, assuming you know that it will react quantitatively with the base sodium carbonate, which is a primary standard solid, and that methyl orange indicator's endpoint will accurately indicate the reaction equivalence point.

Extension

4. Sulfur impurities in fuels produce SO_2(g) when the fuel is burned. This is a pollutant that contributes to acid deposition and is a serious respiratory irritant (**Figure 3**). To analyze the sulfur content in a fuel, the sample may be burned, and the SO_2(g) may then be "dissolved" in water, which really means that it reacts with water to become sulfurous acid, H_2SO_3(aq). The sulfurous acid can then be analyzed by titration with a standardized solution of NaOH(aq). If, on average, 12.0 mL of 0.110 mol/L NaOH(aq) reacts with 100 mL samples of H_2SO_3(aq), what chemical amount of sulfur atoms was present in the 100 mL acid sample?

Figure 3
Acid rain is responsible for the damage to this sculpture. Sulfur dioxide is one of the two primary causes of acid rain. The other primary cause is nitrogen oxides.

Acid–Base Titration Curves and Indicators

8.5

Investigations 8.3 and 8.4 are titration analyses involving acid–base reactions. (You might find it helpful to review Sections 6.2 and 6.3.) While other types of reactions are sometimes useful for titration analysis, acid–base reactions predominate for several reasons. Perhaps most important, acidic and basic substances are very common, and a great number of reactions cause a change in the pH of a solution. Just as important is the fact that it is easy to find substances to act as indicators for acid–base titrations. Acid–base reactions are normally invisible in solution, so direct observation cannot tell you when a reaction is complete. Technological devices, such as pH meters, can be used to detect the equivalence point, but, as you have already experienced, there is an easier way. Because many organic substances (such as litmus) change colour depending on whether they are in an acidic or basic solution, such indicators (Chapter 6) make it easy to titrate acid–base reactions accurately to an observable endpoint. During titration, the indicator shows a momentary colour change where the titrant stream contacts the sample in the flask. Closer to the endpoint, the colour change lingers longer, allowing you to add titrant more slowly, drop by drop, until at the endpoint one final drop of titrant changes the colour of the flask contents permanently (**Figure 1**). The key to accurate titration analysis is making sure that the observed endpoint really occurs as close as possible to the reaction's equivalence point, as discussed in Section 8.4. To explore the connection of these two points for acid–base reactions, it is necessary to know exactly how the pH changes during a titration. This is demonstrated in Investigation 8.5.

Figure 1
Accurate titration analysis depends on applying a combination of specialized knowledge and specific skills. (See Appendix C.4.)

INVESTIGATION 8.5 *Introduction*

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
● Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
○ Evaluation

pH Curves (Demonstration)

When titrating a basic sample with an acidic titrant, you would expect the pH to be high initially, then to decrease as acid is progressively added, and finally to be low when a large excess of acid has been added. This expectation turns out to be correct. However, what is interesting and important is the *way* that the pH decreases. A titration pH curve is very useful evidence, providing valuable information about any acid–base reaction. Your Analysis involves plotting graphs of pH against volume of acid added. Alternatively, a computer program using a pH sensor probe may be used (if available) to plot the graph on screen as the titrations occur.

Purpose

The purpose of this demonstration is to create pH curves and observe the function of an indicator in an acid–base reaction.

Problem

What are the shapes of the pH curves for the continuous addition of hydrochloric acid to a sample of a sodium hydroxide solution and to a sample of a sodium carbonate solution?

Design

Small volumes of hydrochloric acid are added continuously to a measured volume of a base. After each addition, the pH of the mixture is measured. The volume of hydrochloric acid is the manipulated variable, and the pH of the mixture is the responding variable.

To perform this investigation, turn to page 344.

WWW ***WEB Activity***

Web Quest—Blood Alcohol Content

This Web Quest will lead you to research the chemistry of blood alcohol analysis. You will be responsible for the defense of someone charged with impaired driving. How accurate are roadside alcohol tests? Learn the issues, and make a case to present in criminal court.

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Learning Tip

As in many other areas, in chemistry the simplest system that "works" is usually preferred.

When chemists write net ionic acid–base equations for titration reactions, they often write the hydrogen ions as $H^+(aq)$ rather than $H_3O^+(aq)$, even though you learned in Chapter 6 that evidence indicates that the latter representation is more correct. The more complex notation is normally only used when the water *must* be considered as a reactant to understand the reaction.

Interpreting Titration pH Curves

When a titration is done to create a pH curve, the addition of titrant is not stopped at the endpoint, but is continued until a large excess has been added. This emphasizes the significance of such a curve: the very rapid change in pH passing the equivalence point. For the NaOH(aq)–HCl(aq) pH curve plotted in Investigation 8.5, the initial sample is a strong base, and the pH is high. As the titration proceeds and acid is added, some of the base is reacted with the added acid, but anywhere before the equivalence point some excess base will remain, so the pH stays relatively high. Very near the equivalence point, a small excess of base becomes a small excess of acid with the addition of just a few more drops of HCl(aq), and the pH abruptly changes from high to low. This rapid pH change is what makes an acid–base equivalence point easy to detect. The equivalence point is at the centre of the change, where the curve is most nearly vertical. Note that for strong monoprotic acid–strong monoprotic base reactions (Chapter 6), the net ionic equation will always be the same, because ions other than hydrogen and hydroxide ions are always spectator ions for these substances:

$$\mathrm{NaOH(aq)} + \mathrm{HCl(aq)} \rightarrow \mathrm{NaCl(aq)} + \mathrm{H_2O(l)}$$

$$\cancel{\mathrm{Na^+(aq)}} + \mathrm{OH^-(aq)} + \mathrm{H^+(aq)} + \cancel{\mathrm{Cl^-(aq)}} \rightarrow \cancel{\mathrm{Na^+(aq)}} + \cancel{\mathrm{Cl^-(aq)}} + \mathrm{H_2O(l)}$$

$$\mathrm{OH^-(aq)} + \mathrm{H^+(aq)} \rightarrow \mathrm{H_2O(l)} \text{ (net ionic equation)}$$

For convenience, aqueous hydrogen ions are written here in their simplest (Arrhenius) form. Now, consider this titration done in reverse, by titrating a strong acid sample with a large excess of strong base titrant so that the pH value will start low and end high. The net ionic equation is the same, and so is the equivalence point; the pH curve (**Figure 2**) is just a mirror image of the example in Investigation 8.5. When a strong monoprotic acid completely reacts with a strong monoprotic base, the products are always water and neutral spectator ions, so you can predict what the pH must be at the equivalence point. Recall from Chapter 6 that water has a (neutral) pH of 7, so a strong monoprotic acid–strong monoprotic base titration must have a pH of 7 at the equivalence point.

It is important to note that the equivalence point pH is 7 only *for this one specific type* of acid–base reaction. For every other acid–base reaction, the solution at the equivalence point will contain ions and/or molecules that are *not* spectators, and the pH will vary depending on which entities are present as well as on their concentration. This

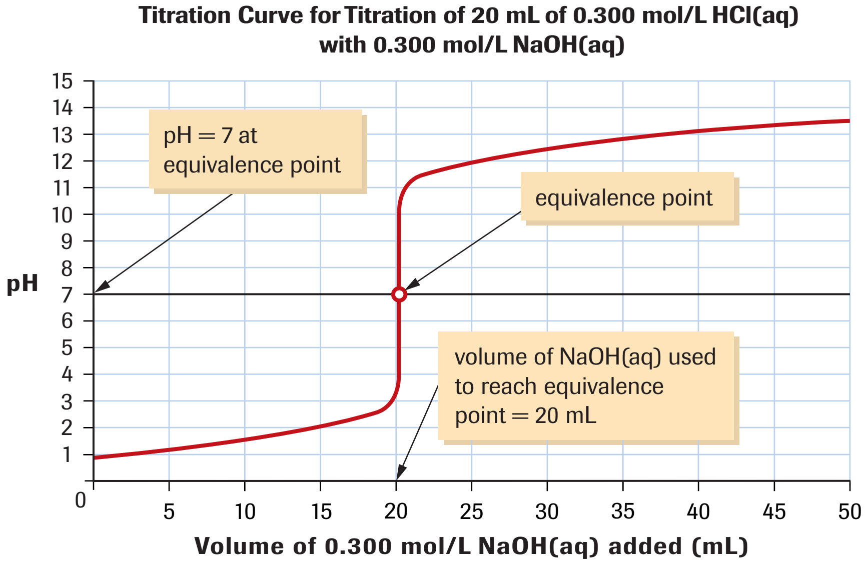

Figure 2
This curve is typical of curves depicting the titration of a strong acid with a strong base. Notice that the curve sweeps up and to the right as NaOH(aq) is added, beginning at a pH below 7 and ending at a pH above 7. After adding 20 mL of titrant, the pH is 7; the equivalence point has been reached.

means that a pH titration curve must always be done empirically, to determine the pH at the equivalence point before any acid–base reaction using an indicator can be used for titration analysis.

An equivalence point is read from a pH curve by estimating the inflection point position in the part of the curve where the slope steepens. An *inflection point* is the point where the direction of curvature changes, like the centre point of the letter S.

Recall the pH titration curve from Investigation 8.5 for a sodium carbonate solution sample titrated with hydrochloric acid. This titration produces a very different pH curve from the curve you just examined. A similar pH curve is shown in **Figure 3**. Observing this curve, you can see that the centre of the most rapid pH change (steepest slope) corresponds to a pH value of about 3.6. The balanced reaction equation follows:

$$\mathrm{Na_2CO_3(aq)} + 2\,\mathrm{HCl(aq)} \rightarrow 2\,\mathrm{NaCl(aq)} + \mathrm{H_2CO_3(aq)}$$

which can also be written as

$$\cancel{2\,\mathrm{Na^+(aq)}} + \mathrm{CO_3^{2-}(aq)} + 2\,\mathrm{H^+(aq)} + \cancel{2\,\mathrm{Cl^-(aq)}} \rightarrow$$

$$\cancel{2\,\mathrm{Na^+(aq)}} + \cancel{2\,\mathrm{Cl^-(aq)}} + \mathrm{H_2CO_3(aq)}\ \text{(total ionic equation)}$$

$$\mathrm{CO_3^{2-}(aq)} + 2\,\mathrm{H^+(aq)} \rightarrow \mathrm{H_2CO_3(aq)}\ \text{(net ionic equation)}$$

In this reaction, the base is diprotic, meaning that it will react with two hydrogen ions. If you observe the curve closely, you see that there are two places where the curve steepens as the titration proceeds. This happens because the two hydrogen ions attach to the carbonate ion one at a time. We use the second reaction equivalence point, because we want the pH value when the reaction is complete.

When this reaction is stoichiometrically complete (at the equivalence point), the only substances present are water, sodium ions, chloride ions, carbonic acid molecules, and a very small amount of methyl orange indicator. It seems logical to find experimentally that the solution pH is acidic at this reaction's equivalence point, since it contains water, spectator ions, and the weak acid $\mathrm{H_2CO_3(aq)}$. Experimentally plotting a pH titration curve is essential for selecting the right indicator for acid–base titration analysis reactions. It is also critical that the amount of indicator used be extremely small. In theory, some titrant volume must be used to react with the indicator to make it change colour, but if the indicator amount is kept very small (a drop or two of solution), then the volume of titrant used in this way will be too small to be measurable, and the accuracy of the titration will not be affected.

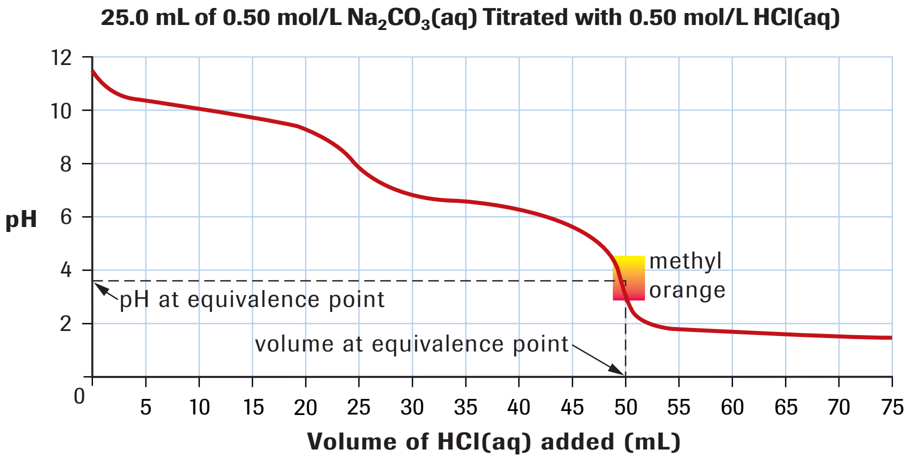

Figure 3
A pH curve for the addition of hydrochloric acid to a sample of sodium carbonate

Learning Tip

Acid–base reaction pH curves provide a wealth of information:
- initial pH levels
- volume of titrant at the equivalence point
- pH (for indicator selection) at the equivalence point
- number of reaction steps

Choosing Acid–Base Indicators for Titration

Experimentally plotting a pH titration curve is essential for selecting the right indicator for acid–base titration analysis reactions, so the endpoint observed for the indicator chosen will closely match the equivalence point of the reaction. For the equivalence point of the reaction in Figure 3, the pH was 3.6. To accurately show when this reaction is complete, an indicator must be chosen that changes colour across a pH range that has a central value close to 3.6. According to the Acid–Base Indicators table on the inside back cover, the indicator methyl orange is yellow above pH 4.4 and red below pH 3.1. This makes it a good choice for this reaction. The colour change pH range for methyl orange is superimposed on the pH curve in Figure 3 to show how an indicator is chosen to match observed endpoint to a reaction equivalence point. Showing three indicator choices for an HCl–NaOH titration is another way to illustrate this point (**Figure 4**).

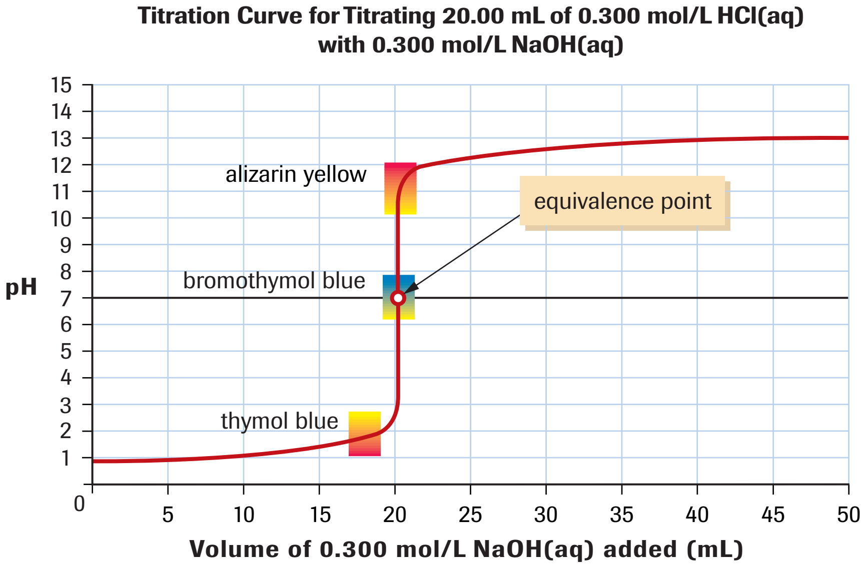

Figure 4
Thymol blue is an unsuitable indicator for this titration because it changes colour before the equivalence point (pH 7). Alizarin yellow is also unsuitable because it changes colour after the equivalence point. Bromothymol blue is suitable because its endpoint pH of 6.8 (assume the middle of its pH range) closely matches the reaction equivalence point pH of 7, and the colour change is completely on the vertical portion of the pH curve.

EXTENSION

Indicator Choice
So, you are planning an investigation involving an acid–base titration. How do you know which indicator to use? This audio clip will help you understand how to choose an appropriate indicator for an acid–base titration.

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Practice

1. What is the difference in meaning between endpoint and equivalence point?
2. (a) Sketch a pH curve for the titration of HNO_3(aq) with KOH(aq).
   (b) What will be the equivalence point pH? Why?
3. Which of the following indicators would show an “intermediate” endpoint colour of orange: bromocresol green, methyl red, phenolphthalein, or methyl violet?
4. According to the Acid–Base Indicators table on the inside back cover, what is an appropriate indicator for a titration with an equivalence point pH of 4.4?

WEB Activity

Simulation—Titration Curves

This computer simulation enables you to select from a variety of acids and bases, and to choose an indicator. The program automatically plots a pH curve as you add the titrant,

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SUMMARY Acid–Base Indicators, Endpoints, and Equivalence Points

- An indicator for an acid–base titration analysis must be chosen to have an endpoint (change of colour) at very nearly the same pH as the pH at the equivalence point of the reaction solution.
- The pH of the solution at the equivalence point for a strong monoprotic acid–strong monoprotic base reaction will be 7.
- The pH of the solution at the equivalence point for any other acid–base reaction must be determined experimentally, by plotting a titration pH curve.

Case Study

Analytic Measurement Technology

Developments in analytic measurement technology are giving scientists the ability to detect increasingly tiny amounts of substances. These technological developments are driven in part by the need to trace the path of toxic substances in ecosystems and in the human body. Contamination of the environment by heavy metals and semi-metals is a serious problem worldwide. Although the concentrations of most toxic substances in the environment are far below the lethal level, they may still cause serious damage to life processes when they are ultimately incorporated into drinking water and become concentrated by moving up the food chain. Top predators like swordfish and tuna have far more mercury in their tissue than the bait fish they eat, for example, so these fish should be consumed less frequently by humans. Since metals are biologically nondegradable, they tend to accumulate in vital organs, so that prolonged exposure to trace concentrations of metals and semi-metals can sometimes lead to long-term health effects.

Metals and semi-metals can be divided into three groups based on their toxicity:

- toxic at very low concentrations and with no known biological function, for example, lead, cadmium, and mercury
- toxic above trace amounts and with no known biological function, for example, arsenic, indium, antimony, and thallium
- toxic above certain concentrations and required for various biochemical processes, for example, copper, zinc, cobalt, selenium, potassium, and iron

One widely used technology for measuring very low concentrations of metals and semi-metals is *voltammetry*, which uses electrodes to apply a voltage to an aqueous sample and then measures the current produced (**Figure 5**). The magnitude of the current is proportional to the concentration of metal ions in the sample. Voltammetric methods have detection limits as low as a few picograms (10^{-12} g) and have been used to detect lead, cadmium, zinc, and copper in single raindrops. The main weakness of this technology is that its ability to distinguish between one element and another is poor at very low concentrations.

In the 1970s, a reliable method of counting individual atoms was developed to detect trace impurities in the materials used

Figure 5
Stationary voltammetry electrodes

to make computer chips (**Figure 6**). Some modern electronic components are so small that a few foreign atoms can cause them to malfunction. The technology for counting atoms uses photons from a laser to knock one electron out of the outer shell of each atom of a specific element; the electrons released are then counted. The energy of electrons in atoms is quantized into specific levels, rather like the rungs on a ladder that the electron has to climb to escape from the atom. The spacing of these energy rungs is different for every element, so by supplying the precisely correct amount of energy using the laser, electrons can be knocked off the atoms of a selected element while leaving the electrons in other atoms undisturbed. Counting these electrons provides an accurate measure of the number of atoms of a specific element in a sample.

In addition to being able to detect extremely small traces of various elements, atom counting technology dramatically reduces the size of samples required for laboratory tests. This technology is ideal for studying the effects of extremely small traces of various elements on the human body. For example, by using atom counting techniques, researchers have found that traces of metals like chromium, copper, and zinc, which are required for normal development, are transferred from the mother to the fetus late in pregnancy. Consequently, a very premature baby may lack these elements and suffer various ailments and birth defects unless supplied with the proper amounts of these elements.

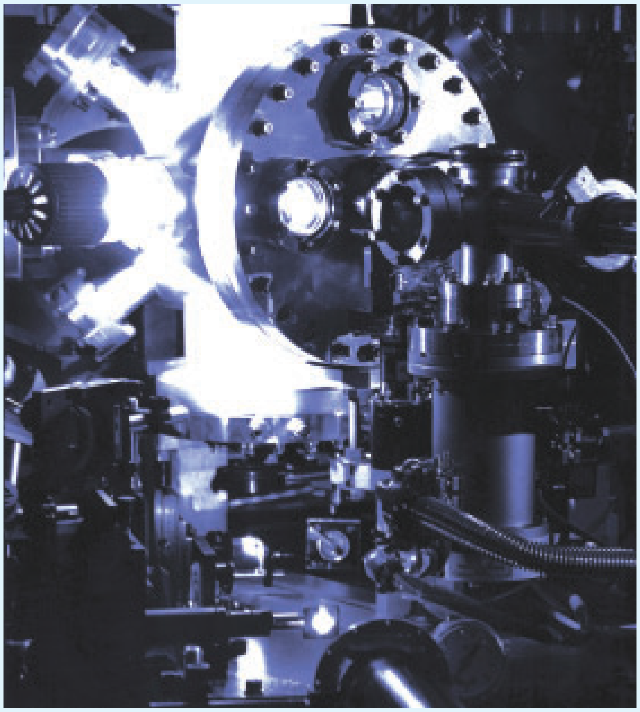

Figure 6
Technology has reduced the limit of detectability of an element to a single atom. There is no longer a concentration that is too small to be measured. The atom-counting instrument shown is able to count atoms of specific elements in tiny samples, such as water, air, blood, and microchips.

On a smaller scale, University of Alberta Professor Jed Harrison (**Figure 7**) is researching the application of microfabrication technology to create tiny analytical instruments. Employing micromachining techniques, he uses semiconductors to create sensors that can detect tiny amounts of chemicals. These sensors will be useful in a wide range of situations, including blood tests for hormones and drugs, and soil testing (**Figure 8**).

Figure 7
Jed Harrison (1954-)

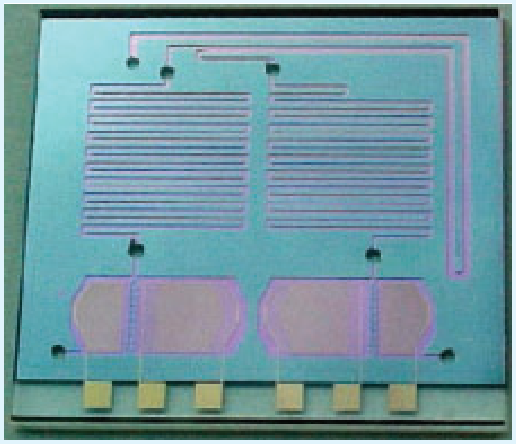

Figure 8
This 2 cm × 2 cm glass and silicon microchip uses electrolysis of water in the two lower chambers to create a gas pressure that pumps a blood sample and test mixture together, allowing the isolation of rare or diseased cells for clinical diagnostic assays.

Case Study Questions

1. What societal needs drive the development of increasingly sensitive measurement technology?
2. In the fictional television series, *Star Trek*, the crew of the space ship carried devices called "tricorders." These devices could perform a complete analysis of whatever organism was before them. State an argument for, and one against, the possibility of society ever developing analysis technology to the level imagined for the "tricorder."

INVESTIGATION 8.6 *Introduction*

Titration Analysis of ASA

Acetylsalicylic acid, known as ASA, is the most commonly used pharmaceutical drug, with over 10 000 t manufactured in North America every year. ASA, $C_8H_7O_2COOH(s)$, is an organic acid like acetic acid and reacts with strong bases such as sodium hydroxide in the same way that acetic acid does.

Purpose

The purpose of this investigation is to use titration analysis techniques to accurately determine the ASA content of a consumer product: a standard pain-relief tablet.

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 3)

Problem

What is the mass of ASA in a consumer tablet?

Design

An ASA tablet is dissolved in methanol and then titrated with standardized sodium hydroxide solution (from Investigation 8.3) using phenolphthalein as the indicator.

To perform this investigation, turn to page 345.

Section 8.5 Questions

For the following questions, use the Acid–Base Indicators table on the inside back cover where appropriate.

1. In the titration of dilute ammonia with dilute hydrochloric acid, a trial pH curve titration found the equivalence point pH of the solution to be 4.8. Explain why bromocresol green is a better indicator choice than alizarin yellow for this titration.
2. Why must only a very small amount of indicator be used in a titration analysis?
3. If congo red indicator is used in the titration of dilute nitric acid, $HNO_3(aq)$, with dilute sodium hydroxide, $NaOH(aq)$, will the indicator endpoint of the titration correspond to the equivalence point? Explain, using a sketch of the pH titration curve to illustrate your reasoning.
4. For a titration analysis to determine the concentration of an oxalic acid solution, complete the following:
   (a) What information must you have in order to select an indicator for this reaction?
   (b) What equipment and procedure would be required to get this information?
5. Why is it necessary to start a titration analysis with at least one standard solution?
6. Define the following terms:
   (a) titration
   (b) titrant
   (c) endpoint
   (d) equivalence point
7. In a titration analysis, state the function of
   (a) an Erlenmeyer flask
   (b) a volumetric pipette
   (c) a burette
   (d) a meniscus finder
8. A chemistry student is given the task of accurately and precisely determining the amount concentration of a hydrochloric acid solution so it can be used as a standard solution. She chooses sodium carbonate to prepare her initial primary standard solution.
   (a) What mass of pure dry sodium carbonate will she require to prepare 100.0 mL of 0.120 mol/L solution?
   (b) Write the steps for a complete procedure for her titration, including waste disposal.
   (c) What should she do to ensure her safety while performing this titration?
9. Copy and complete **Table 1** in Evidence, and complete the Analysis of the following investigation report.

Purpose

The purpose of this investigation is to use titration design to standardize a solution of hydrochloric acid.

Problem

What is the amount concentration of the hydrochloric acid solution?

Design

A standard sodium carbonate solution is prepared. Samples of this standard solution are titrated with the unknown solution of hydrochloric acid. The colour change of methyl orange is used to indicate the endpoint.

Evidence

Table 1 Titration of 10.00 mL of 0.120 mol/L $Na_2CO_3(aq)$ with $HCl(aq)$

Trial	1	2	3	4
final burette reading (mL)	17.9	35.0	22.9	40.1
initial burette reading (mL)	0.3	17.9	5.9	22.9
volume of HCl(aq) added (mL)				
colour at endpoint	red	orange	orange	orange

Chapter 8 INVESTIGATIONS

INVESTIGATION 8.1

Analysis of Sodium Carbonate

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
○ Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
● Evaluation (1, 3)

Sodium carbonate has been used for all of recorded history in a variety of applications, from glassmaking to detergent manufacture to water treatment. A common name for sodium carbonate is soda ash, an appropriate name because it can easily be extracted from wood ashes. Sodium carbonate is one of the ten highest-volume chemicals produced in North America.

In this investigation, you will use techniques and equipment common to gravimetric analysis to analyze a sodium carbonate solution. For a description of a method for filtering a precipitate, see Appendix C.4.

Purpose

The purpose of this investigation is to use the stoichiometric method as part of a gravimetric analysis.

Problem

What is the mass of solute in a 50.0 mL sample of sodium carbonate solution?

Design

The mass of sodium carbonate present in the sample solution is determined by having it react with an excess quantity of a calcium chloride solution. The mass of calcium carbonate precipitate formed is used in a stoichiometric calculation to determine the mass of sodium carbonate that reacted.

Sodium carbonate and calcium chloride solutions can irritate skin. As always, wash your hands before leaving the laboratory.

Materials

lab apron
eye protection
$Na_2CO_3(aq)$
$CaCl_2(aq)$
wash bottle of pure water
50 mL or 100 mL graduated cylinder
100 mL beaker
250 mL beaker
400 mL beaker
stirring rod
medicine dropper
filter paper
filter funnel, rack, and stand
centigram balance

Procedure

1. Measure 50.0 mL of $Na_2CO_3(aq)$ in the graduated cylinder, and transfer this sample into a clean 250 mL beaker. (See Appendix C.3.)
2. Measure 60 mL of $CaCl_2(aq)$ in a clean 100 mL beaker.
3. Slowly add about 50 mL of $CaCl_2(aq)$, with stirring, to the $Na_2CO_3(aq)$.
4. Allow the mixture to settle. When the top layer of the mixture becomes clear, use the dropper to add a few extra drops of $CaCl_2(aq)$.
5. If any new cloudiness is visible (**Figure 1(a)**), repeat steps 2 to 4, adding as much $CaCl_2(aq)$ as necessary, until this test indicates the reaction is complete (**Figure 1(b)**).
6. Measure the mass of a piece of filter paper.
7. Filter the mixture, and discard the filtrate in the sink. (See Appendix C.4.)
8. Dry the precipitate and filter paper overnight on a folded paper towel.
9. Measure the mass of the dried filter paper plus precipitate.
10. Dispose of the precipitate in the trash (solid waste).

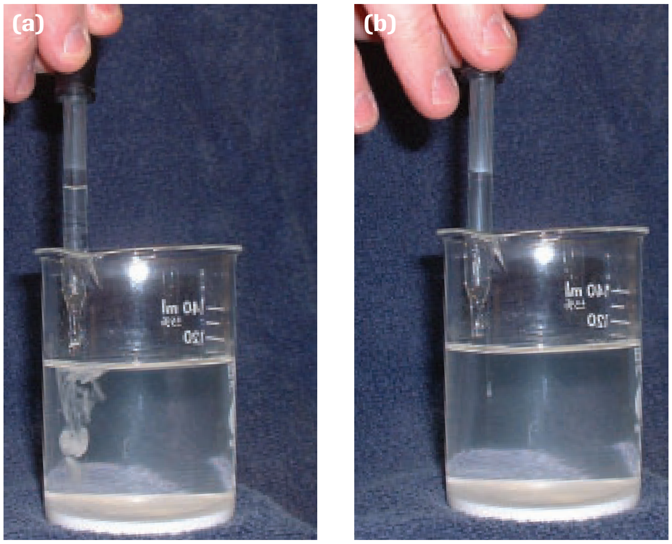

Figure 1
(a) Visible evidence of incomplete reaction
(b) Visible evidence of complete reaction

INVESTIGATION 8.2

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
● Prediction
○ Design
● Materials
● Procedure
● Evidence
● Analysis
● Evaluation (1, 2, 3)

Percent Yield of Barium Sulfate

Barium sulfate is a white, odourless, tasteless powder that has a variety of different uses: as a weighting mud in oil drilling; in the manufacture of paper, paints, and inks; and taken internally for gastrointestinal X-ray analysis. It is so insoluble that it is nontoxic, and is therefore safe to handle.

The reaction studied in this investigation is similar to the one used in the industrial manufacture of barium sulfate. To determine the predicted (theoretical) yield in the Prediction, you will need to identify the limiting and excess reagents before using the stoichiometric method to predict the expected mass of product.

Purpose

The purpose of this investigation is to use the stoichiometric method to evaluate a commercial procedure for producing barium sulfate.

Problem

What is the percent yield of barium sulfate in the reaction of aqueous solutions of barium chloride and sodium sulfate?

Design

A 40.0 mL sample of 0.15 mol/L sodium sulfate solution is mixed with 50.0 mL of 0.100 mol/L barium chloride solution. A diagnostic test is performed to check for completeness of precipitation of the limiting reagent (**Figure 2**). The mass of the filtered, dried precipitate is measured. The experimental mass of the precipitate is compared to the predicted mass.

Soluble barium compounds, such as barium chloride, are toxic and must not be swallowed. Wear gloves and wash hands thoroughly after handling the barium ion solution.

Wear eye protection and a laboratory apron.

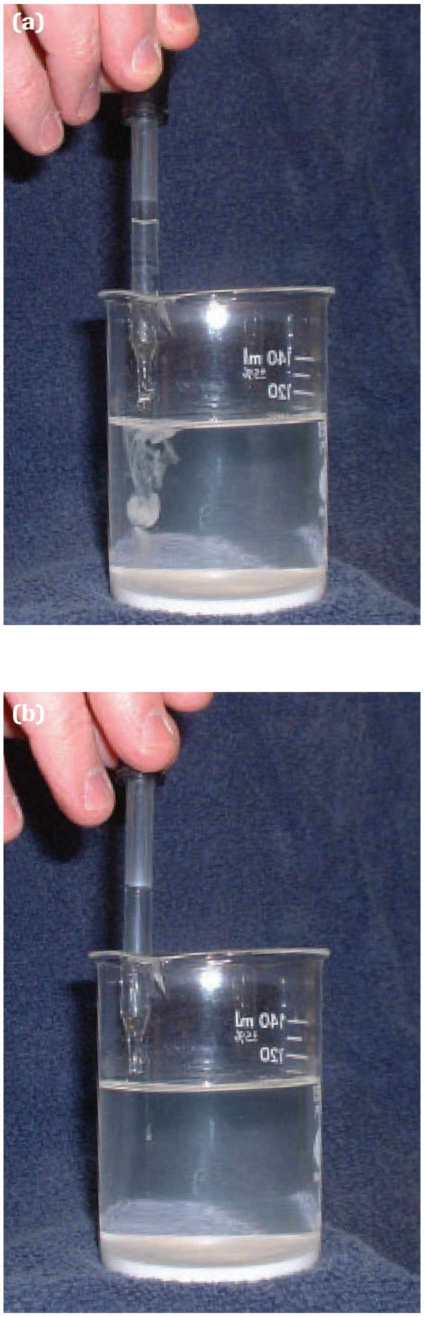

Figure 2
(a) Visible evidence of incomplete reaction
(b) Visible evidence of complete reaction

INVESTIGATION 8.3

Standardization Analysis of NaOH(aq) (Demonstration)

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
○ Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
○ Evaluation

A large (stock) volume of sodium hydroxide solution is prepared for use in Investigations 8.4 and 8.6 by dissolving 6 g of solid for each litre of solution required. Because this solute is not a primary standard, this solution must be standardized to accurately determine its concentration. This will be accomplished by titration against a standard potassium hydrogen phthalate (KHP) solution. The balanced reaction equation is

$$KC_7H_4O_2COOH(aq) + NaOH(aq) \rightarrow KNaC_7H_4O_2COO(aq) + H_2O(l)$$

Purpose

The purpose of this investigation is to use a titration design to standardize a solution for future chemical analysis.

Problem

What is the concentration of a stock NaOH(aq) solution?

Design

A standard solution of KHP is prepared, and is then used to standardize a stock solution of sodium hydroxide. Samples of KHP are titrated with sodium hydroxide titrant, using phenolphthalein as an indicator.

Materials

lab apron
eye protection
$KC_7H_4O_2COOH(s)$
NaOH(aq)
phenolphthalein
wash bottle of pure water
150 mL beaker
250 mL beaker
250 mL Erlenmeyer flask
100 mL volumetric flask with stopper
50 mL burette
10 mL volumetric pipette
pipette bulb
ring stand
centigram balance
laboratory scoop
stirring rod
small funnel
meniscus finder

Procedure

1. Prepare a 100.0 mL standard solution of 0.150 mol/L KHP. (See Appendix C.4.)
2. Place approximately 70 mL of NaOH(aq) in a clean, dry, labelled 150 mL beaker.
3. Set up the burette with NaOH(aq), following the accepted procedure for rinsing and for clearing the air bubble. (See Appendix C.4 and the Nelson Web site.)

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4. Pipette a 10.00 mL sample of KHP into a clean Erlenmeyer flask, and add 2 drops of phenolphthalein indicator.
5. Record the initial burette reading to the nearest 0.1 mL.
6. Titrate the KHP sample with NaOH(aq) until a single drop produces a permanent colour change, from colourless to pink.
7. Record the final burette reading to the nearest 0.1 mL.
8. Repeat steps 4 to 7 until three consistent results are obtained.
9. Dispose of all solutions in the sink, and flush with lots of water.

INVESTIGATION 8.4

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ● Materials
- ● Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 2, 3)

Titration Analysis of Vinegar

Some consumer food products are required by law to have the minimum quantity of the active ingredient listed on the product label. Companies that produce chemical products usually employ analytical chemists and technicians to monitor the final product in a process known as quality control. Nevertheless, government consumer affairs departments also use chemists and technicians to check products, particularly in response to consumer complaints. According to the label, a vinegar manufacturer states that the vinegar contains 5% acetic acid by volume, which translates to a minimum amount concentration of 0.83 mol/L (**Figure 3**).

In the Evaluation section of your report, collect and average analysis values from all groups performing this investigation. Explain what should be done with discrepant results. Include safety and disposal instructions with the procedure.

Figure 3
Is there really 5% acetic acid by volume, in this bottle of vinegar?

Purpose

The purpose of this investigation is to test the manufacturer's claim of the concentration of acetic acid in a consumer sample of vinegar.

Problem

What is the amount concentration of acetic acid in a sample of vinegar?

Chemicals used may be flammable or corrosive.

Design

A sample of commercial white vinegar is diluted by a factor of 5 to make a 100.0 mL final solution. Samples of this diluted solution are titrated with a standardized sodium hydroxide solution (from Investigation 8.3) using phenolphthalein as the indicator.

INVESTIGATION 8.5

pH Curves (Demonstration)

When titrating a basic sample with an acidic titrant, you would expect the pH to be high initially, then to decrease as acid is progressively added, and finally to be low when a large excess of acid has been added. This expectation turns out to be correct. However, what is interesting and important is the *way* that the pH decreases. A titration pH curve is very useful evidence, providing valuable information about any acid–base reaction. Your Analysis involves plotting graphs of pH against volume of acid added. Alternatively, a computer program using a pH sensor probe may be used (if available) to plot the graph on screen as the titrations occur.

Purpose

The purpose of this demonstration is to create pH curves and observe the function of an indicator in an acid–base reaction.

Problem

What are the shapes of the pH curves for the continuous addition of hydrochloric acid to a sample of a sodium hydroxide solution and to a sample of a sodium carbonate solution?

Design

Small volumes of hydrochloric acid are added continuously to a measured volume of a base. After each addition, the pH of the mixture is measured. The volume of hydrochloric acid is the manipulated variable, and the pH of the mixture is the responding variable. **Figure 4** shows a stirring system that can be used for this lab, if available.

Figure 4
A burette and magnetic stirrer provide for a very efficient procedure.

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
● Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
○ Evaluation

Materials

lab apron
0.10 mol/L HCl(aq)
0.10 mol/L Na_2CO_3(aq)
methyl orange indicator
magnetic stirrer (optional)
150 mL beaker
50 mL graduated cylinders (2)
pH 7 buffer solution for calibration of pH meter
pH meter or pH probe with computer interface
eye protection
0.10 mol/L NaOH(aq)
bromothymol blue indicator
distilled water
50 mL burette and funnel
250 mL beakers (2)

Acids and bases are corrosive and toxic. Avoid skin and eye contact. If you spill any of the chemical solutions on your skin, immediately rinse the area with lots of cool water. In the unlikely situation of getting some of the chemicals in your eye, immediately rinse your eye for at least 15 min and inform your teacher.

Procedure

1. Set the temperature on the pH meter and calibrate it by adjusting it to indicate the pH of the known pH 7 buffer solution.
2. Place 50 mL of 0.10 mol/L sodium hydroxide solution in a 150 mL beaker, and add a few drops of bromothymol blue indicator.
3. Measure and record the pH of the sodium hydroxide solution.
4. Successively add small quantities of HCl(aq), measuring the pH and noting any colour changes after each addition, until about 80 mL of acid has been added.
5. Repeat steps 1 to 4 for 50 mL of 0.10 mol/L sodium carbonate in a 250 mL beaker with the methyl orange indicator. Continue titrating until 130 mL of HCl(aq) has been added.
6. Dispose of all solutions in the sink, and flush with lots of water.

INVESTIGATION 8.6

Report Checklist

○ Purpose
○ Problem
○ Hypothesis
○ Prediction
○ Design
○ Materials
○ Procedure
● Evidence
● Analysis
● Evaluation (1, 3)

Titration Analysis of ASA

Acetylsalicylic acid, known as ASA, is the most commonly used pharmaceutical drug, with over 10 000 t manufactured in North America every year (**Figure 5**). ASA, $C_8H_7O_2COOH(s)$, is an organic acid like acetic acid and reacts with strong bases such as sodium hydroxide in the same way that acetic acid does.

As part of your evaluation, find the percent difference between your experimental averaged value for the mass of ASA in a sample tablet, and the value for the mass (in mg) that is listed on the product label.

Purpose

The purpose of this investigation is to use titration analysis techniques to accurately determine the ASA content of a consumer product: a standard pain-relief tablet.

Problem

What is the mass of ASA in a consumer tablet?

Design

An ASA tablet is dissolved in methanol and then titrated with standardized sodium hydroxide solution (from Investigation 8.3) using phenolphthalein as the indicator.

Materials

lab apron
eye protection
standardized NaOH(aq)
ASA tablets
phenolphthalein
30 mL methanol
wash bottle of pure water
50 mL beaker
250 mL beaker
50 mL burette
10 mL volumetric pipette
pipette bulb
ring stand
burette clamp
stirring rod
small funnel
meniscus finder
250 mL Erlenmeyer flask

Methanol is toxic by ingestion. It may cause permanent blindness if swallowed.

Methanol is volatile (it evaporates easily) and is very flammable. Do not use it near any ignition source or open flame.

Procedure

1. Add about 30 mL of methanol to one ASA tablet in a clean Erlenmeyer flask (**Figure 5**).

Figure 5
ASA, or acetylsalicylic acid

2. Stir and crush the tablet until the solid has mostly dissolved. (The final mixture will probably be slightly cloudy because of the presence of inert ingredients.)
3. Add 1 or 2 drops of phenolphthalein indicator.
4. Set up the burette with standardized NaOH(aq) titrant, using accepted techniques for rinsing and for eliminating the air bubbles (Appendix C.4).
5. Record the initial burette reading to the nearest 0.1 mL.
6. Titrate the ASA sample with NaOH(aq) until a single drop produces a permanent change from colourless to pink.
7. Record the final burette reading to the nearest 0.1 mL.
8. Repeat steps 1 to 7 until three consistent results are obtained.
9. Dispose of all solutions into the sink, and flush with lots of water.

Chapter 8 SUMMARY

Outcomes

Knowledge

- contrast quantitative and qualitative chemical analysis (8.1)
- use the stoichiometric method to calculate quantities of substances in chemical reactions (8.2, 8.3, 8.4)
- describe different designs for determining the concentration of a solution (8.2, 8.4)
- identify and calculate limiting and excess reagents in chemical reactions (8.3)
- identify the equivalence point on a strong acid–strong base titration curve, and differentiate between an indicator endpoint and a reaction equivalence point (8.4, 8.5)
- describe the function and choice of indicators in acid–base titrations (8.4, 8.5)

STS

- state examples of science leading technology and technology leading science (8.1, 8.3)
- state that a goal of technology is the solution of practical problems (8.2, 8.3, 8.4, 8.5)

Skills

- initiating and planning: design an experiment to identify an ion (8.1); design a method using crystallization, filtration, or titration to determine the concentration of a solution (8.4); describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (8.3, 8.4); predict the approximate equivalence point for a strong monoprotic acid–strong monoprotic base titration and select an appropriate indicator (8.5)
- performing and recording: perform a titration to determine the concentration of an acid or base restricted to monoprotic acid–monoprotic base combinations (strong acid–strong base, strong acid–weak base, and weak acid–strong base) (8.4)
- analyzing and interpreting: interpret stoichiometric ratios from chemical reaction equations (8.2, 8.3, 8.4); evaluate an experiment based on a precipitation reaction, to determine the concentration of a solution (8.2); create and interpret titration curve graphs for acid-base experiments restricted to strong monoprotic acid–strong monoprotic base combinations (8.5); calculate theoretical and actual yield and percent yield and error, and account for discrepancies (8.3); use appropriate SI notation, fundamental and derived units, and significant digits when performing stoichiometric calculations (8.1, 8.2, 8.3, 8.4, 8.5)
- communication and teamwork: standardize an acid or base solution and compare group results (8.4)

Key Terms

8.1

colorimetry

gravimetric analysis

titration analysis

8.4

titration

titrant

sample

equivalence point

endpoint

standard solution

primary standard

standardizing

MAKE a summary

1. Outline a concept map as a series (hierarchy) of levels. The first level will be Chemical Analysis, the second Qualitative and Quantitative Analysis, and the third will be the types of each of the concepts of the second level. Subsequent levels should gradually develop and include all concepts connected with and relevant to the process of analysis.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

Go To

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The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 8
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

EXTENSION

CBC radio ONE QUIRKS & QUARKS

Aspirin's Aspirations

ASA is famous for its painkilling properties. It is also used as an anti-inflammatory and a blood thinner and is prescribed to reduce the risk of heart attacks. Is it possible that this humble little pill could also ward off Alzheimer's disease and cancer?

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Chapter 8 REVIEW

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

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Part 1

1. The method of analysis that uses stoichiometric calculations from a measured mass of a reagent is
   A. titration analysis
   B. qualitative analysis
   C. gravimetric analysis
   D. calorimetric analysis

2. A 1.0 mol/L aqueous solution of an ionic compound is blue–green in colour. Which of the following solutions would *not* be this colour?
   A. $CuNO_3(aq)$
   B. $Ni(NO_3)_2(aq)$
   C. $Cr(NO_3)_3(aq)$
   D. $Co(NO_3)_2(aq)$

3. When flame-tested, an ionic solution produces a yellow–red flame. Of the following ions, the colour could only be caused by
   A. Ba^{2+}
   B. Ca^{2+}
   C. Cu^{2+}
   D. Sr^{2+}

4. In demonstrating a precipitation reaction, a chemistry teacher adds an excess of potassium iodide to a solution of lead(II) nitrate. After the precipitate has settled, the solution will contain
   A. $K^+(aq)$ only
   B. $K^+(aq)$ and $NO^-{}_3(aq)$ only
   C. $K^+(aq)$, $NO^-{}_3(aq)$, and $I^-(aq)$ only
   D. $K^+(aq)$, $NO^-{}_3(aq)$, $I^-(aq)$, and $Pb^{2+}(aq)$

5. NR Using stoichiometry, the mass of precipitate produced by the reaction of silver nitrate and potassium bromide was predicted to be 2.47 g. In the experiment, 2.16 g of precipitate was obtained. The percent yield of this reaction was ________%.

6. Which of the following reagents can be used to precipitate acetate ions from a solution of sodium acetate?
   A. $AgNO_3(aq)$
   B. $BaCl_2(aq)$
   C. $CaCl_2(aq)$
   D. $Pb(NO_3)_2(aq)$

7. Which of the following statements about titration analysis is *false*?
   A. Several trials should always be completed.
   B. The concentration of both reactants must be accurately known.
   C. The equivalence point is the point at which the exact theoretical (stoichiometric) amount has been added to the sample.
   D. The endpoint is the point during the titration at which the sudden change of an observable property indicates that the titration should be stopped.

8. NR Three 10.0 mL aliquots (samples of equal volume) of vinegar were each titrated with 0.125 mol/L NaOH(aq). An average volume of 14.5 mL of the base was required to reach the endpoint. The concentration of the acetic acid in the vinegar is calculated to be ________ mmol/L.

9. When planning a chemical reaction, stoichiometric calculations can be used to predict each of the following *except*
   A. the limiting reagent
   B. the rate of the reaction
   C. a reasonable mass of excess reagent to use
   D. how much excess reagent will remain unreacted

10. When a sample of a strong acid is titrated with a large excess of a strong base titrant, the pH of the sample will
   A. start low and end high
   B. start high and end low
   C. start low and end at pH = 7
   D. start high and end at pH = 7

11. Bromothymol blue indicator is added to a solution with pH = 6.8. In this solution the colour of the indicator is predicted to be
   A. colourless
   B. yellow
   C. green
   D. blue

12. In a procedure for standardizing hydrochloric acid, 25.0 mL of 0.50 mol/L $Na_2CO_3(aq)$ is titrated with HCl(aq) using bromothymol blue indicator. In this procedure the titrant is
   A. bromothymol blue
   B. $Na_2CO_3(aq)$
   C. $H_2O(l)$
   D. HCl(aq)

Part 2

13. For each of the following combinations of reagents, **identify** the limiting and excess reagents, and determine the chemical amount of excess reagent that will remain unreacted.
   (a) 0.250 mol of aqueous lead(II) nitrate and 0.350 mol of aqueous sodium chloride
   (b) 5.00 mol of propane and 20.00 mol of oxygen
   (c) 1.00 mol of zinc and 1.00 mol of acetic acid
   (d) 300 mmol of sulfuric acid and 500 mmol of sodium hydroxide

14. Strips of copper can be used to recover silver from waste solutions produced by a chemistry lab. An excess of copper was added to 4.54 L of waste solution containing 0.0756 mol/L of silver nitrate, and 29.5 g of solid silver was recovered. **Determine** the percent yield of this process.

15. A lab technician plans to use aqueous sodium carbonate to precipitate all the copper(II) ions from 750 mL of 0.0634 mol/L waste $CuSO_4$(aq). What would be a reasonable volume of 1.00 mol/L Na_2CO_3(aq) to use?

16. A student plans to use zinc to extract lead from a 375 mL sample of 0.100 mol/L $Pb(NO_3)_2$(aq). **Determine** what would be a reasonable mass of zinc to use.

17. For each titration curve in **Figure 1**,
    (a) **determine** the volume of titrant used to reach the equivalence point
    (b) **determine** the pH at the equivalence point (to the nearest whole number)
    (c) suggest a suitable indicator for a titration analysis to be done using these reagents

18. Consider the (double replacement) reaction between aqueous solutions of potassium iodide and lead(II) nitrate, done using an excess of potassium iodide. When the precipitate has settled enough so the top layer of solution is clear, it is possible to test for completeness of reaction. **Describe** how this is done, what the observations might be, and **how** any possible observations should be interpreted.

19. Complete the Analysis of the following lab report:

Problem

What is the molar concentration of a hydrochloric acid solution?

Design

100.0 mL of a standard solution of sodium carbonate was prepared using 1.74 g of the pure dry solid. Using methyl orange indicator to detect the second equivalence point, several 10.0 mL samples of this standard solution were titrated with hydrochloric acid.

Evidence

Table 1 Titration of 10.0 mL samples of Na_2CO_3(aq) with HCl(aq)

Trial	1	2	3	4
final burette reading (mL)	16.1	31.5	46.9	16.9
initial burette reading (mL)	0.2	16.1	31.5	1.5
volume used				
indicator colour	red	orange	orange	orange

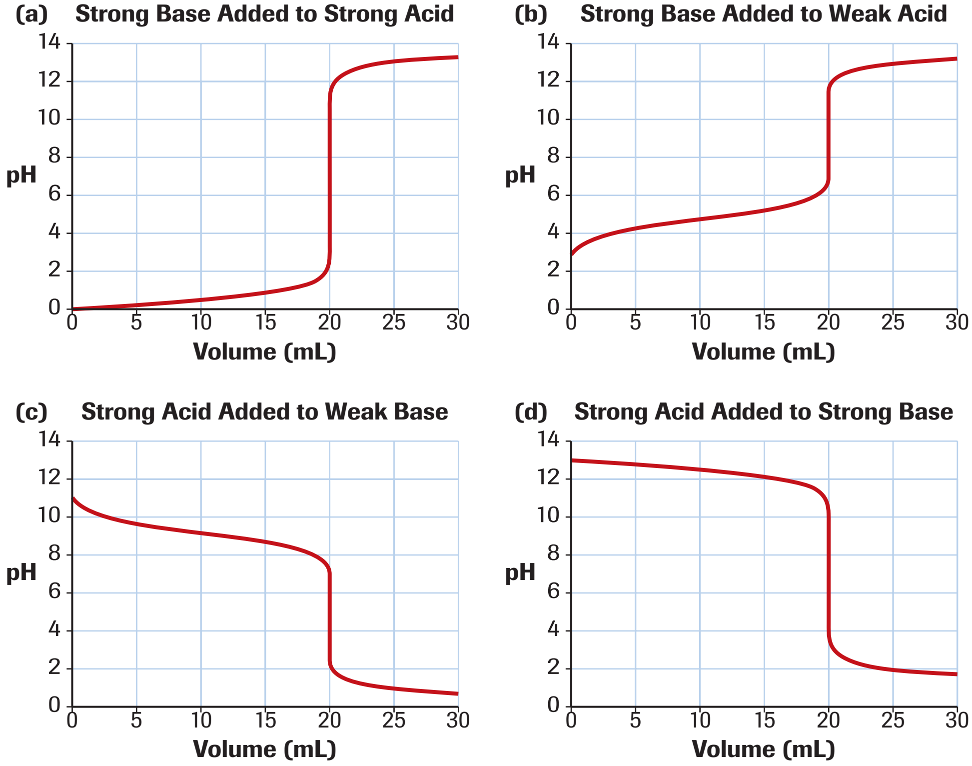

Figure 1
pH curves for titrations involving monoprotic acids and bases of equal concentration

Unit 4 REVIEW

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

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Part 1

1. The only condition that must be assumed in order to do a calculation of the theoretical yield for a reaction is that the reaction is
A. spontaneous
B. quantitative
C. rapid
D. stoichiometric

Use this information to answer questions 2 to 6.

Urea is the most concentrated dry source of nitrogen available and is used extensively as a fertilizer in the agricultural industry. Other large-scale uses of urea include the production of resins for making plywood, forestry fertilization, and airport runway de-icer.

Urea, $CO(NH_2)_2(s)$, is produced in large quantities from ammonia and carbon dioxide in plants in Redwater, Carseland, and Fort Saskatchewan (**Figure 1**) according to the following unbalanced chemical equation:

$NH_3(g) + CO_2(g) \rightarrow CO(NH_2)_2(s) + H_2O(l)$

Figure 1
The Agrium plant at Fort Saskatchewan

2. NR When this chemical equation is balanced with whole numbers, the coefficients, in order, are ___, ___, ___, and ___.

3. What information does the balanced chemical equation *not* communicate?
A. chemical formulas and states of the initial reactants
B. chemical formulas and states of the final products
C. relative chemical amounts of reactants and products
D. reaction conditions and time required for the reaction

4. NR If 240 mol of urea is produced in this reaction, the chemical amount of ammonia required is __________ mol.

5. The technology for production of urea was developed
A. to meet the needs of society for this product
B. as a scientific research project to study chemical reactions
C. first before any use for this product existed
D. to lead to new scientific discoveries

6. Technologies can be classified by the scale of the operation. Urea production would be classified as
A. small
B. consumer
C. industrial
D. commercial

---

7. A qualitative analysis of a sample would *never* involve use of a
A. titration
B. precipitation
C. spectrophotometer
D. diagnostic test

8. NR After the reaction of a mixture of 4.00 mol of $H_2(g)$ with 4.00 mol of $O_2(g)$ in a sealed container, the remaining amount of the reagent in excess will be __________ mol.

9. Which of the following is *not* likely to be a logical explanation for an observation that the actual yield for a reaction is less than the theoretical (calculated) yield?
A. The reaction equation used was not really stoichiometric.
B. Some product precipitate was lost through a filter paper tear while filtering.
C. The mass measurement of limiting reactant was too low due to balance error.
D. Some precipitate was dissolved by too much washing while in the filter paper.

10. Which one of the following steps is common to all types of stoichiometry?
A. converting a mass to chemical amount
B. using the mole ratio from a balanced chemical equation
C. converting a chemical amount to a volume of a gas
D. using the formula $c_iV_i = c_fV_f$ to convert chemical amounts

11. In a water treatment plant, small suspended particles are removed by the process of flocculation, forming a light, jelly-like precipitate that settles slowly and carries the suspended particles to the bottom of a tank. In a simple demonstration of this process, aqueous aluminium sulfate is added to a dilute solution of sodium hydroxide. The net ionic equation for this reaction is
A. $2\,Na^+(aq) + SO_4^{2-}(aq) \rightarrow Na_2SO_4(aq)$
B. $Al^{3+}(aq) + 3\,OH^-(aq) \rightarrow Al(OH)_3(s)$
C. $Al_2(SO_4)_3(aq) + 6\,NaOH(aq) \rightarrow 2\,Al(OH)_3(s) + 3\,Na_2SO_4(aq)$
D. $2\,Al^{3+}(aq) + 3\,SO_4^{2-}(aq) + 6\,Na^+(aq) \rightarrow 2\,Al(OH)_3(s) + 6\,Na^+(aq) + 3\,SO_4^{2-}(aq)$

12. Sources of experimental uncertainty are always present in an experiment. Which one of the following is not an acceptable example of an experimental uncertainty?
- A. all measurements
- B. empirical constants
- C. purity of chemicals
- D. human error

13. A primary standard for solution preparation must be
- A. stable when its container is opened
- B. an ionic compound
- C. an acidic substance
- D. colourless in solution

14. The main benefit of preparing a graph of relative proportions of substances in a chemical reaction, when that reaction is constantly used for repetitive analysis, is that the graph
- A. improves accuracy
- B. saves calculation time
- C. illustrates the proportionality visually
- D. allows percent yields to be found

15. NR A student analyzes the concentration of some propanoic acid, $C_2H_5COOH(aq)$, by titrating 10.00 mL samples with a standardized solution of 0.186 mol/L sodium hydroxide, $NaOH(aq)$, using phenolphthalein as the indicator. If the average volume of sodium hydroxide used to reach endpoint is 14.0 mL, the amount concentration of the propanoic acid solution is __________ mmol/L.

16. NR Pure chromium metal can be obtained in a laboratory by heating chromium(III) oxide mixed with powdered aluminium. This reaction releases a great deal of heat. Assume that a 20% excess of $Al(s)$ must be mixed with a 20.0 g sample of $Cr_2O_3(s)$ to ensure complete reaction. The mass of aluminium required will be __________ g.

17. Which indicator from **Table 1** would be most suitable to use for a titration of $HCl(aq)$ with $NaOH(aq)$?

Table 1 For question 17

	Indicator	pH change range
A.	p-naphtholbenzene	8.2–10.0
B.	brilliant yellow	6.6–7.8
C.	propyl red	4.8–6.6
D.	2,4-dinitrophenol	2.8–4.0

Part 2

18. Briefly **describe** each of the four main assumptions usually made about chemical reactions done in school classrooms and laboratories.

19. In both scientific studies and technological applications of chemical reactions, one reactant is usually a limiting reagent, and the other reactant is an excess reagent. **Distinguish** between these two terms, and suggest a general reason for using one reactant in excess.

20. In a gravimetric analysis, **explain** how you know that the reaction is complete.

21. (a) In a titration analysis, explain how you know that the reaction is complete.
- (b) **Sketch** a pH curve of a titration reaction in which a strong monoprotic acid is titrated with a strong monoprotic base. On the curve, indicate the pH at the equivalence point.
- (c) Name three specific chemicals that would be appropriate materials for this titration.

Use this information to answer questions 22 to 24.

The common mineral apatite (**Figure 2**) has a characteristic hexagonal crystal structure. Apatite is an impure form of calcium phosphate, which is widely used as a supplement for all types of animal feed. Calcium phosphate supplies phosphorus and calcium, two essential nutrients for the growth of all animals. In addition, this compound is the chief component of the hard parts of teeth and the chief cementing material in the solid parts of bones. In a laboratory, pure calcium phosphate can be produced from the reaction of aqueous solutions of calcium chloride and sodium phosphate, because the product compound has extremely low solubility.

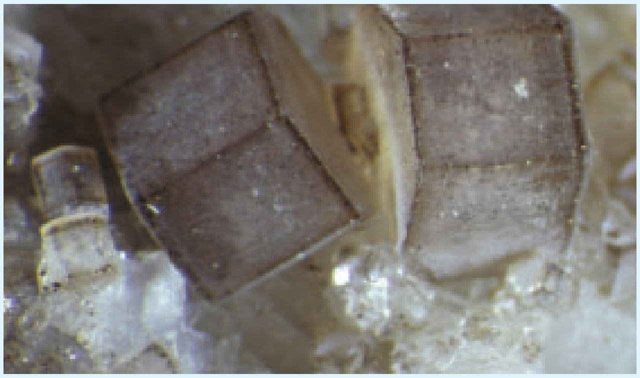

Figure 2
Apatite

22. Write the net ionic equation for this reaction.

23. **Identify** the spectator ions, and **explain** why only some of the ions present are described as spectator ions.

24. In a quantitative study of the laboratory reaction, a student predicted that 2.34 g of calcium phosphate product should form. In the experiment, 2.47 g of product was obtained.
- (a) **Determine** the percent yield.
- (b) What is unusual about your answer? Suggest several sources of experimental uncertainty that might account for this result.

25. In the Canadian steel industry, iron(III) oxide, from a previous roasting step, is reduced by reacting with carbon to produce iron metal and carbon dioxide. **Predict** what mass of iron metal could be produced from 1.00 t of iron(III) oxide.

26. **Identify** the limiting and excess reagents for each of the following pairs of reactants, and **determine** the chemical amount in excess in each case.

(a) $Zn(s) + CuSO_4(aq) \rightarrow$
0.42 mol   0.22 mol
(b) $Cl_2(aq) + NaI(aq) \rightarrow$
10 mmol   10 mmol
(c) $AlCl_3(aq) + NaOH(aq) \rightarrow$
20 g   20 g

Use this information to answer questions 27 to 30.

Air bag technology has saved many lives (**Figure 3**). The reaction that causes the air bag to inflate (in less than 30 ms) is the simple decomposition of sodium azide, $NaN_3(s)$. This reaction is initiated by an electrical signal from a sensor.

Figure 3
Crash test dummies testing air bags

27. If 70 L of gas at 20 °C and 98.5 kPa is required to completely fill a typical air bag, **determine** what mass of sodium azide must be stored in the inner reaction container.

28. This reaction is very fast and spontaneous when the electrical signal is sent. What other assumptions did you make when answering question 27?

29. If this were the only reaction to occur, what safety concerns would you have? Use your chemical knowledge and WHMIS to describe the possible dangers.

30. Research answers to the following questions.
(a) What other substances are included along with the primary reactant, sodium azide?
(b) What is the purpose of each of these substances?
(c) The use of air bags is somewhat controversial. Comment on the pros and cons of air bags from four perspectives.

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31. In a study of rust-removing solutions, 27.8 mL of 0.115 mol/L phosphoric acid reacts completely with 0.245 mol/L sodium hydroxide. **Predict** the minimum volume of sodium hydroxide required for this reaction.

Use this information to answer questions 32 to 35.

Aqueous solutions of ammonia and hydrochloric acid produce strong, irritating fumes as the dissolved gas escapes from solution. When beakers of concentrated solutions of aqueous ammonia and hydrochloric acid are placed side by side, a white "smoke" forms in the air between them, and a solid powder deposits on the beakers (**Figure 4**). This white solid is ammonium chloride. Suppose that 2.00 g of hydrogen chloride gas were to be mixed with 2.00 g of ammonia gas, in a closed container.

Figure 4
Aqueous solutions of ammonia and hydrochloric acid

32. Which gas would be a limiting reagent?

33. What mass of solid product would form?

34. (a) Which reactant would remain when the reaction is complete?
(b) **Predict** the mass that would remain.

35. **Explain** how your answers to questions 33 and 34 support the law of conservation of mass.

36. Scientific concepts need to be tested in many different situations. In the following investigation report, complete the Prediction, Analysis, and Evaluation.

Purpose

The purpose of this experiment is to test the concept of stoichiometry.

Problem

What mass of magnesium metal will react completely with 100.0 mL of 1.00 mol/L HCl(aq)?

Evidence

volume of 1.00 mol/L HCl(aq) = 100.0 mL
initial mass of Mg(s) = 3.72 g
final mass of Mg(s) = 2.45 g

37. Review the focusing questions on page 270. Using the knowledge you have gained from this unit, briefly **outline** a response to each of these questions.