Adult Basic Education

Science

Chemistry 3102C

Acid/Base Reactions and Electrochemistry

Study Guide

Prerequisite: Chemistry 3102A

Credit Value: 1

Text: Chemistry. Mustoe et al.; McGraw-Hill Ryerson, 2004

Chemistry Concentration

Chemistry 1102

Chemistry 2102A

Chemistry 2102B

Chemistry 2102C

Chemistry 3102A

Chemistry 3102A Chemistry 3102B

Chemistry 3102C

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To the Student

I. Introduction to Chemistry 3102C

The purpose of the first part of this course is to further develop your understanding of acid-base chemistry. You will be introduced to the analytical technique of titration. The remainder of the course will involve the study of electrochemistry which looks at how the transfer of electrons in chemical reactions can be used as a source of electricity or electricity can be used to cause chemical reactions.

In addition to your study guide and text, you will need a scientific calculator. As you work through each page of your study guide, you should ensure that your answers to the problems are correct, before proceeding to the next page.

You will have labs for this course. Let your instructor know in advance that you are getting close to needing to do these labs. Each lab will require a written lab report, which will be evaluated as part of your course mark.

To the Student

II. <u>Use of Science Study Guides</u>

Before beginning this course, ensure you have the text and any other resources needed (see the information in the Introduction to this course for specifics).

As you work through the Study Guide, you will see that it is divided according to the Units listed in the Table of Contents. When you open a unit it will have the following components:

Reading for this Unit:

Here you will find the chapters, sections and pages of the text you will use to cover the material for this unit. Skim the sections of the textbook, look at the titles of the sections, scan the figures and read any material in the margins. Once you have this overview of the unit, you are ready to begin. Do not be intimidated by the content. You will work through the text, section by section, gaining knowledge and understanding of the material as you go.

References and Notes

This left-hand column guides you through the material to read from the text. Read any highlighted notes that follow the reading instructions. The symbols DD direct you to the questions that you should complete when finished a reading assignment.

Work to Submit

You come across three (3) headings in this right-hand column.

Writing: This section comprises your notes for the unit.

Here you will find either written questions or references to specific questions or problems from your text. You may want to write out each question followed by the answer. This material should be checked by your instructor

before moving onto the next unit.

Mathematical problems should have their

solutions checked as you go.

Laboratory: This section indicates if there is a Core Lab

that should be completed for the unit. Let the instructor know in advance that you will be ready for the lab. A lab report should be submitted for each Core Lab. Your instructor will provide guidelines as to how she or he

wants the report written.

Assignment: This section indicates if there is an assignment

that should be completed for the Unit. The information in the "References and Notes" column will indicate how you obtain the assignment. These assignments frequently relate the science content to technology,

society and the environment.

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To the Student

III. Recommended Evaluation

Written Notes	10%
Labs/Assignments	20%
Test(s)	20%
Final Exam (entire course)	<u>50%</u>
	100%

The overall pass mark for the course is 50%.

Unit 1 - Acid-Base Equilibria

To fulfill the objectives of this unit, students should complete the following:

Reading for this unit: Chemistry

Chapter 15:

Introduction: page 582 Section 15.1: pages 583-597

References and Notes

Referring to pages, 584, 587, 592, 595-597, answer questions 1.1-1.7

Note:

 K_a and K_b are expressions using the same format as K_c , the equilibrium constant. Only the subscript is changed.

Work to Submit

Writing:

- 1.1 Explain the difference between monoprotic and polyprotic acids.
- 1.2 Explain what is meant by acid dissociation constant (K_a) .
- 1.3 Write the equilibrium constant expression from the equation of reaction with water.
- 1.4 Explain what is meant by base dissociation constant (K_b) .
- 1.5 Write the equilibrium constant expression from the equation of reaction with water.
- 1.6 Explain what is meant by a buffer solution and what it does.
- 1.7 Explain the function and importance of buffers in blood.

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Unit 2 - Acid-Base Titration

To fulfill the objectives of this unit, students should complete the following:

Reading for this unit: Chemistry

Chapter 15: Section 15.2: pages 599-607

Assignment: Appendix A

References and Notes	Work to Submit		
	Writing:		
Referring to pages 599 - 600, answer questions 2.1-2.3	2.1	Define neutralization reaction and salt.	
	2.2	Define acid/base indicators operationally.	
Study carefully the Sample Problem, "Finding Concentration," and the Sample Problem "Finding Volume,"		Define acid/base indicators theoretically.	
page 600-601. Then complete question 2.4 PP	2.4	Complete Practice Problems 17 - 20 on page 602.	
Note: Check your answers from page 619 before moving on.			
Referring to pages 603-605, answer questions 2.5-2.7. ▶▶	2.5	Define titration.	
questions 2.3-2.7. Ele	2.6	Define primary standard and explain its importance in a titration procedure.	
	2.7	Explain the difference between indicator end point and equivalence (stoichiometric) point.	

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Unit 2 - Acid-Base Titration

References and Notes

Review carefully the steps of a titration on pages 604-605 and observe your instructor's demonstration of a titration before you complete the Lab.

Consult with your instructor to find out what is expected in your Lab report.

Note:

Your instructor may replace Investigation 15-A with another similar Lab.

Read"Acids Around Us." from Appendix A. Refer to it as you complete 2.9 DE

See your instructor to discuss any additional work that you should do for this unit.

Work to Submit

Laboratory:

2.8 Complete Investigation 15-A, "The Concentration of Acetic Acid in Vinegar", on pages 606-607 of your text.

Assignment:

2.9 Complete the questions 1 to 3 and 7(a) from the **Understanding Concepts** section.

Unit 3 - Oxidation - Reduction

To fulfill the objectives of this unit, students should complete the following:

Reading for this unit: Chemistry

Introduction: pages 710-712

Chapter 18: Section 18.1: pages 713-720

Section 18.2: pages 721; 724-729 Section 18.3: pages 731-732; 734-738

References and Notes

Referring to pages 713-714 of Section 18.1, answer questions 3.1-3.4 ▶▶

Note:

Use the following to help you remember what is oxidized and reduced:

OIL - Oxidation Involves Loss.
RIG - Reduction Involves Gain.

Note:

Check your answers on page 754 before moving on.

Work to Submit

Writing:

- 3.1 What is the modern definition of
 - a) oxidation
 - b) reduction?
- 3.2 Define
 - a) oxidizing agent
 - b) reducing agent.
- 3.3 For the reaction:

$$Mg(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Mg^{2+}(aq)$$

identify the following:

- a) element oxidized
- b) element reduced
- c) the oxidizing agent
- d) the reducing agent
- 3.4 Complete Practice Problems 1-4 on page 715.

Unit 3 - Oxidation - Reduction

References and Notes

Referring to page 715-716, answer questions 3.5 - 3.6 ▶▶

Note:

Check your answers on page 754 before moving on.

Let your instructor know you are ready to complete Investigation 18-A on pages 718-719

Referring to page 721, answer question 3.8 ▶▶

Refer to page 724-725, and study the Sample Problem, "Assigning Oxidation Numbers". Then answer question 3.9

Note:

Check your answers to each set of Practice Problems before moving on.

Refer to pages 726-727, and study the Sample Problem, "Identifying Redox Reactions". Then answer questions 3.10 and 3.11

Work to Submit

Writing:

- 3.5 What is a half-reaction?
- 3.6 Complete Practice Problems 5-8 on page 716.

Laboratory:

3.7 Work through Investigation 18-A, "Single Displacement Reactions". Complete and submit your report to your instructor

Writing:

- 3.8 Define oxidation number.
- 3.9 Complete Practice Problems 9-12 on page 726.
- 3.10 Complete Practice Problems 13-16 on page 728.
- 3.11 Complete Problem 8 on page 729.

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Unit 3 - Oxidation - Reduction

References and Notes

Refer to pages 731-732, and study the Sample Problem, "Balancing a Half-Reaction in Acidic Solution". Then answer question 3.12

Refer to pages 734-738, and study the Sample Problem, "Balancing a Half-Reaction in a Basic Solution". Then answer questions 3.13-3.14

See your instructor to discuss any additional work that should be done for this unit.

Work to Submit

Writing:

- 3.12 Complete Practice Problems 17-20 on page 732.
- 3.13 Complete Practice Problems 25-27 on pages 738-739.
- 3.14 Complete Section Review Problems:

1(a)-(c); 2(a)-(b), 3,

5.

To fulfill the objectives of this unit, students should complete the following:

Reading for this unit: Chemistry

Chapter 19: Section 19.1: pages 757-764

Section 19.2: pages 768-775

Section 19.3: pages 776-777; 786-787

Section 19.4: pages 790-797 Investigation 19-A pages 762-763 Investigation 19-C: pages 794-795

Assignment: Appendix B

References and Notes

Referring to pages 757-761 of Section 19.1, answer questions 4.1 - 4.12

Work to Submit

Writing:

- 4.1 What is electric current?
- 4.2 What is a spontaneous reaction?
- 4.3 What is a galvanic cell?
- 4.4 What is an external circuit?
- 4.5 What is an electrode?
- 4.6 What is an electrolyte?
- 4.7 What is an (a) anode and (b) cathode?
- 4.8 What is the path for electron flow in a galvanic cell?

Note:

See page 809 to check the answers to the Practice Problems before moving on.

References and Notes	Work to Submit		
	Writing:		
	4.9 What is the purpose of the porous barrier galvanic cell?		
	4.10 What is a salt bridge and how does it wo		
	4.11 For the short hand notation for a galvanic cell, what do and represent?		
	4.12	Complete Practice Problems 1- 4 on page 761.	
Read "Introducing Cell Potentials" on page 761. Then answer questions 4.13-4.14	4.13	What is electric potential (E) of a cell? What unit is used to measured electric potential?	
	4.14	What does a cell potential of 0 V mean?	
Let your instructor know you are	Labo	ratory:	
ready to complete Investigation 19-A on pages 762-763. D	4.15	Complete Investigation 19-A and submit a report to your instructor.	
	Writi	ng:	
Referring to page 764, answer	4.16	What is a dry cell?	
<i>questions 4.16-4.19.</i> ▶▶	4.17	What is a battery?	
	4.18	What is (a) primary battery and (b) secondary battery?	
	4.19	Describe the construction of the dry cell battery.	

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References and Notes	Work to Submit			
	Writing:			
Answer question 4.20 for review	4.20	Complete Section Review Problems 1-2; 4-5; 7 on page 767.		
Read pages 768-773 and study the Sample Problems on pages 771-773. Then answer questions 4.21-4.22	4.21	Complete Practice Problems 5-8 on page 773. Complete Section Review problems 1-2 on page 775.		
Note: See page 809 to check your answers to the Practice Problems and the Section Review questions for this unit.				
Referring to pages 776-777, answer	4.23	What is an electrolytic cell?		
<i>questions 4.23-4.26</i> ▶▶	4.24	What is electrolysis?		
	4.25	What does the term "molten" mean?		
	4.26	Complete Practice Problems 9-12 on pages 777-778.		

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References and Notes	Work to Submit				
Read page 786 "Spontaneity of Reactions", and study the Sample Problem, "Predicting Spontaneity". Then answer question 4.27		Writing:			
		Complete Practice Problems 17-20 on page 786-787.			
Read pages 790-792, and study the sample problem, "Calculating the	4.20				
Mass of an Electrolysis Product". Then answer questions 4.28-4.29 ▶▶	4.28	How is charge related to current and time?			
	4.29	Complete Practice Problems 21-24 on page 793.			
Referring to pages 793-797, answer					
questions 4.30-4.32 PP	4.30	State Faraday's Law.			
	4.31	What is extraction?			
	4.32	What is refining?			
Answer question 4.33 for review ▶▶	4.33	Complete Section Review problems 1-4 on page 797.			
	Laboratory:				
Let your instructor know you are ready for the Investigation	4.34	Complete Investigation 19-C and submit a report to your instructor.			
Read Appendix B: "From Mineral to		Assignment:			
Metal: Metallurgy and Electrolytic Refining"	4.35	Complete Questions 1-2, 5 and 9.			
See your instructor to discuss any additional work that should be done for this unit.					

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Acid Around Us

Introduction

What do the following have in common: a bee sting, burning coal to fuel factories, the winner of the Tour de France, diabetes, the colour of a hydrangea in full bloom, the taste of cola soft drinks, healthy blood, a soothing bath and sauerkraut? At first, we would all be hard pressed to find something in common between these phenonmena. Yet one exists: acid-base chemistry. This module will go beyond Arrhenius, Bronsted and Lowry and investigate some aspects of acid-base chemistry that may be relevant to you.

1. Acids and Bases: Would you believe that...

... a bee's sting is acidic, whereas a wasp's sting is basic.

While both stings are painful, the chemical makeup of each sting and how we treat them are very different. Consider what you know of household acids and bases and neutralization: which



Figure 1. A honeybee about to leave its stinger

household acids and bases would soothe each type of sting? Could you use the same substance to sooth both a bee's sting and a wasp's sting?

... if you don't like to exercise, blame it on an acid! If you've ever exercised to the point where your legs have that "burning" sensation, lactic acid is to blame. Lactic acid is produced by our bodies as we burn glycogen (stored carbohydrates), and it only takes as much as a teaspoon of lactic acid in your legs to cause them to scream "stop!" during intense physical activity. It has been said that the best cyclists or marathon runners are not necessarily in the best physical condition, but can withstand the burning pain of lactic acid buildup and continue to perform. A major part of a professional sports therapist's job is to find methods to reduce the effects of lactic acid for their athlete clients. Many sports therapists currently believe that long, relatively easy workouts that build an aerobic base is the key to both minimizing and tolerating the lactic acid produced during exercise.

... many flowers have colours that are dependent upon soil pH. A commonly grown garden plant in Atlantic Canada is the

hydrangea, as shown in Figure 2. In acidic soil, the flowers are blue in colour whereas in basic soil the same plant has pink flowers! This variation in colour is not unique to hydrangea. Some fruits and vegetables also have pH



Figure 2. Hydrangea

dependent colour, including blackberries, blueberries, strawberries and red cabbage. If any of the above are crushed and boiled in a small amount of water, the resulting solution can be used as a natural acid-base indicator. Blackberry extract, for example, is pinkred in acid and is deep purple in base.

... some of your favourite foods owe their taste to acids.

The operational definition of acids states that acids generally taste sour while bases are bitter. A check of some of your favourite foods ingredients, you will reveal some surprising results. For example, there is both phosphoric acid and carbonic acid in Pepsi® and Coke®! Even if you drink "no-name" colas, you will find that phosphoric acid is used to give the cola its characteristic tangy cola taste. Table 1 gives a small sample of foods which contain acids.

Food	Acid Present
vinegar	5% acetic acid v/v
tomato, spinach, rhubarb	oxalic acid
sour cream, sauerkraut, 'sour' cheeses	lactic acid
oranges, lemons, limes (citrus fruit)	citric acid

Table 1. Common Foods Containing Significant Amounts of Acid.

By the way, all of the above are digested by gastric juice - an enzyme of hydrochloric acid in your stomach. If you are a sufferer of 'heartburn', this affliction has nothing to do with your heart, but instead excess acid in your digestive system. One remedy: milk of magnesia - a base!

... if all of this chemistry is giving you a headache, take some acetylsalicylic acid!

Sound scary? Well, we're only talking about ASA, the common pain reliever in Aspirin®. If you would rather not run for the medicine cabinet but instead could just do with a nice soothing bath, why not

soothing bath, why not increase your comfort by using a bath fizzer? If you've never seen a bath fizzer (also

known as a "bath bomb"), the name pretty much says it all. When added to a hot bath, a bath fizzer produces a huge volume of soothing bubbles and some bath oil. The bubble effect is caused by the neutralization of sodium hydrogen carbonate (base) with citric acid, and the recipe for making the fizzers is given in the *Activity* section of this module.

2. Acid Deposition

From Environment Canada's website: "Acid deposition - commonly called acid rain - is caused by emissions of sulphur dioxide and nitrogen oxides. Although natural sources of sulphur oxides and nitrogen oxides do exist, more than 90% of the sulphur and 95% of the nitrogen emissions occurring in eastern North America are of human origin. These primary air pollutants arise from the use of coal in the production of electricity, from base-metal smelting, and from fuel combustion in vehicles. Once released into the atmosphere, they can be converted chemically into such secondary pollutants as nitric acid and sulfuric acid, both of which dissolve easily in water. The resulting acidic water droplets can be carried long distances by prevailing winds, returning to Earth as acid rain, snow, or fog. "7

According to Environment Canada, over 80% of Canadians live in areas with high acid rain levels, and the problem is not unique to the large cities of Canada and the US. In a long-term study conducted from 1980 to 1998 by Environment Canada, five sites in the Atlantic Provinces downwind from major North American polluters were equipped with Acid Precipitation Collectors (Figure 3). The results of the

study indicate that acid deposition exceeds critical levels across most of New Brunswick and Nova Scotia. Lowering the pH of Atlantic Canada's waterways has a devastating impact on its biodiversity of aquatic ecosystems. The environment will remain at risk and more damage to forest health and



Figure 3. An Acid Precipitation Collector.⁹

productivity will occur unless further drastic cuts to sulfur dioxide and nitrogen dioxide emissions are implemented. ^{7, 8, 9}

Since junior high, you may have encountered the issue of acid rain many times. Where do you stand in the acid rain debate? Are industries doing enough? Are governments doing enough? Are you doing enough?

3. Maintaining Blood pH - the Carbon Dioxide - Bicarbonate Buffer

A buffer is a solution, containing a weak acid and its conjugate or a weak base and its conjugate, which has the ability to maintain a relatively constant pH when limited amounts of strong acid or base are added to it. Consider: addition of 0.01 mol of HCl $_{(aq)}$ to 1 L of pure water causes the pH to drop from 7.0 to 2.0 - a drop of 5 pH units. That is an increase in [H 3O+] of 100000. When the same amount of acid is added to 1 L of naturally buffered blood, the pH drops from 7.35 to approximately 7.25. - a drop of only 0.1 in pH. That is an increase in [H₃O⁺] of 1.3. The ability for our blood to withstand large pH changes is a necessity. The pH of normal blood is 7.35; a difference of 0.2 pH units will greatly decrease the ability of blood to uptake oxygen, while a difference of 0.4 pH units is usually fatal.

A buffer is commonly made up of *a weak acid and its conjugate base*, allowing the buffer solution to withstand addition of either acid or base. One buffer is the ammonium - ammonia buffer:

$$NH_{4(aq)}^+ + H_2O_{(l)} \quad \Box \quad H_3O_{(aq)}^+ + NH_{3(aq)} \quad K_a = 5.6 \times 10^{-8}$$

Remember both NH₄ (aq) and NH_{3(aq)} are initially present in this buffer system. This means that if strong base is added, the ammonium (weak acid) component of the buffer will react with the added base and neutralize it; meanwhile, if strong acid is added to the buffer, the ammonia (conjugate base) component will react and neutralize the added acid. This is just an application of Le Châtelier's Principle. The pH of the buffered solution therefore does not change drastically with the stress of strong acid or base added to the system.

One of the major buffers which regulates blood pH is the equilibrium between carbonic acid and the bicarbonate ion. This buffer is created when dissolved carbon dioxide (from cellular respiration) in the blood plasma reacts with water to produce carbonic acid: $CO_{2(e)} + H_2O_{(1)} \square H_2CO_{3(aq)}$.

Carbonic acid then reacts with water to produce the buffer system:

$$H_2CO_{3(aq)} + H_2O_{(l)} \square HCO_{3(aq)} + H_3O_{(aq)}^+$$

When a base is added, it reacts with the carbonic acid in the buffer:

$$OH_{(aq)}^{-}$$
 + $H_2CO_{3(aq)}$ \Box $HCO_{3(aq)}^{-}$ + $H_2O_{(l)}$

When an acid is added, it reacts with the bicarbonate ion:

$$H_{3}O^{+}_{\;\;(aq)} \;\; + \;\; HCO_{3}^{\;\;-}_{\;\;(aq)} \quad \Box \quad H_{2}CO_{3(aq)} \quad + \;\; 2\; H_{2}O_{(I)}$$

Note that since we remove CO_{2(g)} from our bodies as we breathe, the rate at which we breathe will affect the amount of HCO_{3 (ao)} in our blood, and therefore will affect blood's natural buffer. This is particularly important in activities held at high altitude, such as mountain climbing. Since there is a lessened amount of oxygen in air at high elevation compared to sea level, a mountain climber (without supplemental oxygen) would breathe in more frequently to intake more oxygen. At the same time, breathing out more frequently would remove more dissolved CO2 (and thus HCO₃) than usual from the climber's blood buffer system. The climber would be at risk for alkalosis - the condition of blood pH increasing to dangerously high levels. Can you use Le Châtelier's Principle and the equation for the carbon dioxide bicarbonate buffer to explain alkalosis?

Another blood condition related to the blood's natural buffer is *acidosis* - the condition of blood pH decreasing to dangerously low levels. Acidosis may occur when blood's buffer is challenged with a sudden influx of acid. This may occur in diabetics or athletes undergoing prolonged, extensive exertion. Treating or preventing alkalosis and acidosis is an important part of a physical trainer's job. Accordingly, the careers of traditional medicine and sports medicine require a working knowledge of buffer systems.

So - What are your plans after graduation?

With the end of your high school career around the corner, hopefully you are starting to think about a potential profession. Note that several interesting careers have been introduced by this module, where a knowledge base of chemistry would be an asset. A horticulturist must have a working knowledge of pH and chemicals which could safely control water and soil pH; a nutritionist would need a knowledge of the chemical components within various foods; environmental chemists tackle the problem of acid deposition on a daily basis; sports physicians need to have a working knowledge of lactic acid formation and buffers. Is there a career in this module for you?

Understanding Concepts

- (a) List three substances or products that are found around the house that are acidic.
 - (b) List three substances or products that are found around the house that are *basic*.
 - (c) Decide which substance from your lists above that you would use to treat (i) a bee's sting versus (ii) a wasp's sting.
 - (d) A liquid pipe clog remover (such as Drano®) is basic. Why would this household item be inappropriate for treating either type of sting?
 - (e) What do you think would be the effect of placing vinegar on a bee's sting?
- What colour would be expected for blackberry extract in:
 - (a) soapy water?
 - (b) lemon juice?
- 3. Calculate the pH of a solution of vinegar, given that it is a 5% v/v solution of acetic (ethanoic) acid and that glacial (pure) acetic acid has a stock concentration of 17.4mol/L. (Hint: think about what "% v/v" means in terms of how the solution is prepared from pure acetic acid.)
- 4. Another acid that may cause bodily discomfort is uric acid. Gout, a form of arthritis, is caused by uric acid buildup in ankle and foot joints. An internet source¹⁰ states that taking 1/2 tsp. of baking soda will help reduce gout. Do you think this is a reasonable home remedy to treat gout? Why?

- 5. In the recipe for bath fizzers given in the Activity, it states that "any non-water containing oil suitable for skin contact" will work in sticking the bath fizzer together. Use collision theory (from the previous unit) to explain why water cannot be present when the bath fizzer ingredients are mixed.
- 6. Environment Canada states that sulfuric acid and nitric acid are the resulting products when sulfur dioxide and nitrogen dioxide react with moist air to form acid deposition. Write complete chemical equations for the production of (a) sulfuric acid and (b) nitric acid under these conditions.
- (a) State your position on acid rain, and whether you believe: (i) industry (ii) government and (iii) individuals within society are doing their part in reducing acid rain.
 - (b) Fully describe one suggestion for each of:

 (i) industry (ii) government and (iii)
 individual citizens to help out in acid rain reduction.
- 8. For blood's buffer, the Ka for the buffer equation is 4.4 x 10⁻⁷ @ 37°C. In most studies, an equilibrium temperature of 25°C is quoted. Explain why 37°C is used here.
- 9. What property of the bicarbonate ion is illustrated by the action of the buffer in the presence of excess acid or base?
- 10. Use Le Châtelier's Principle and the equation for the carbon dioxide bicarbonate buffer to explain alkalosis.
- 11. After taking an overdose in a narcotic, a person begins to breathe in a slow and shallow manner. Is this person potentially at risk for alkalosis or acidosis? Explain.
- 12. Which specific acid compound likely adds to the condition of acidosis in athletes? (Hint: think back to an earlier section in the module.)

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Making Extensions

- (a) Research the different colours of blueberry, strawberry and red cabbage extract in acids versus bases.
 - (b) Obtain samples of the berries and / or red cabbage, and use them to test various household substances that are expected to be acidic or basic.
- 2. Cola drinks have a phosphoric acid content that is described as "from 0.057 to 0.0684% of 75% phosphoric acid, by mass." Estimate the pH range of cola drinks corresponding to this range of H₃PO₄ (aq) content.
- 3. (a) Research and write the chemical structures for the acids found in food given in Table 1.
 - (b) What do each of these acids have in common?
- 4. In the bath fizzer activity, aqueous sodium citrate is given as the third product in the chemical equation and is quite safe for you to bathe in. In fact, citric acid and sodium citrate are the most widely used buffer systems in the food industry to control pH of foods and drugs. Using the internet or your local drug store, research some products that use the citric acid-sodium citrate buffer.
- 5. In teams, research and debate the issues surrounding acid deposition, given that industry and society seem to be having problems in reducing the emissions that cause acid rain.
- 6. Research the symptoms and effects of: (a) acidosis and (b) alkalosis.
- 7. During a climb up Alpe d'Huez during a recent Tour de France, one of the cyclists had such a buildup of acid in his muscles that the ratio of bicarbonate to carbonate in his system was decreased to 10. Is this athlete in physical danger? Explain. (Hint: Start with the Ka constant expression for the buffer, and substitute known quantities.)

References

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Acids and Bases - "Kitchen and Bathtub" Activity

Making Bath Fizzers

What you need:

2 tablespoons citric acid (available at a home-brewing store)

2 tablespoons cornstarch

1/4 cup baking soda

1/4 tsp essential oil or fragrance oil (optional; available at some cosmetics stores)

3-6 drops food colour (various colours)

3 tablespoons baby oil, vegetable oil or other non-water containing oil suitable for skin contact

2 bowls

waxed paper

Preparation:

- 1. Mix all dry ingredients: citric acid, baking soda and cornstarch in a bowl.
- 2. Mix the baby oil, fragrance or essential oils and colouring together in a separate bowl (or cup)
- 3. Slowly mix the liquid mixture into the dry ingredients.
- 4. Make small (2cm) balls of the mixture and place them on waxed paper to dry.
- 5. Allow 24 to 48 hours for the bath fizzer to dry completely. They should be completely dry before storage. Store bath balls in a tightly sealed container, away from moisture.

(For larger amounts of bath fizzers, expand the mixture, using the proportions above.)

Use:

- 1. Pour bath to desired warmth.
- 2. Toss in: 1) a bath fizzer and 2) yourself!
- 3. Enjoy!

Chemistry:

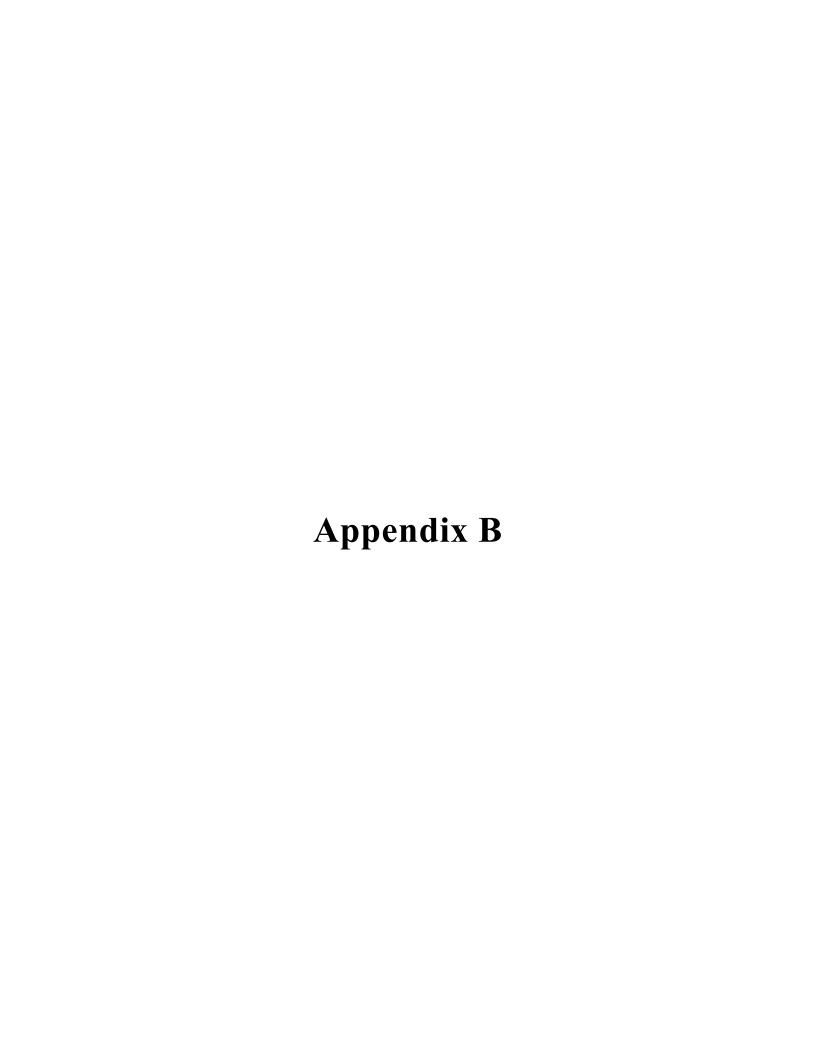
The chemical reaction employed by the bath fizzer is: $3 \text{ NaHCO}_3(s) + C_3H_5O(COOM_3)_3(s) \square CO_2(g) + H_2O(l) + C_3H_5O(COOM_3)_3(aq)$

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From Mineral to Metal: Metallurgy and Electrolytic Refining

Introduction

The use of metals has provided a means for historians to mark the evolution of world civilizations. Metalworking and copper smelters in Egypt date back to 4500BC; by 2500 BC, metalworking had spread through Europe and Asia. These early civilizations used copper, silver and gold because these are found in native form, uncombined with other elements. The ancient Roman civilization added tin, iron, lead and mercury to the list of known metals, and being able to use these metals helped the Roman civilization to spread throughout Europe. By 700 AD, alchemists had the dream of finding the philosopher's stone: a magical substance which was believed to turn base metals (such as lead) into precious metals (such as gold). While this dream has never been fulfilled, the development of *metallurgy*, the science of extracting and refining metals from their ores and compounding alloys, continued to evolve through the ages.

We depend upon metals for so much in our daily lives that producing a complete list of their uses would be impossible. Remember: we use more than pure metals; we also use metals in the form of alloys (mixtures of metals) and ionic compounds. The need for metals and alloys makes metal production a multi-billion dollar industry annually in Canada. Mineral shipments from Newfoundland and Labrador alone exceeded \$850 million in 2002, with 95% of the value of these shipments being the iron ore produced by the IOCC (Iron Ore Company of Canada) in Labrador City. Mining and metallurgy is considered a major growth industry in the province as the Voisey's Bay nickel-copper-cobalt project is added to an already vibrant mining and metallurgy sector. The purpose of this module is to introduce and explore the chemistry behind metallurgy - from mineral to metal.

Processing Ore: Pyrometallurgy vs. Hydrometallurgy

Most metals are not found in a native state. A *mineral* is a naturally occurring substance with a characteristic range of chemical composition. Table 1 lists the known native metals along with several examples of mineral types. The term *ore* is used to describe material with a sufficient amount of mineral deposit to allow for commercial recovery of the desired metal.

Native Metal / Mineral Type	Metal / Mineral Formula (and Name)
Native metals	Ag, Au, Bi, Cu, Ir, Os, Pd, Pt
Carbonate minerals	CaCO ₃ (calcite), CaCO ₃ · MgCO ₃ (dolomite), FeCO ₃ (siderite), BaCO ₃ (witherite)
Halide Minerals	CaF ₂ (fluorite), NaCl (halite)
Oxide Minerals	Al_2O_3 2 H_2O (bauxite), Cu_2O (cuprite), Fe ₂ O ₃ (haematite), Fe ₃ O ₄ (magnetite)
Sulfide Minerals	Cu ₂ S (chalcocite), CuFeS ₂ (chalcopyrite), NiS (millerite), Fe ₉ Ni ₉ S ₁₆ (pentlandite), FeS ₂ (pyrite)

Table 1. Native Metals and Minerals

In general, the three main steps in obtaining a pure metal from its ore are:

- 1. primary treatment,
- 2. extracting the metal,
- 3. refining the metal.

How these three are accomplished depends upon whether pyrometallurgy or hydrometallurgy is used. Pyrometallurgy (or "pyromet" for short) uses extreme heat (in blast furnaces at temperatures of 1500°C and above) to roast the ore into a form where the metal can be more easily isolated. Hydrometallurgy (or "hydromet", for short) uses chemicals to react and dissolve the metal from its ore, allowing the metal to be isolated at much more moderate temperatures.

One of the main debates around the Voisey's Bay project was whether a pyromet (i.e., classic smelter) or a hydromet facility should be used to process the ore. This module will compare pyrometallurgy versus hydrometallurgy for obtaining pure copper and nickel. Each process offers a wide range of impacts on our society, economy and the environment. Perhaps, after reading the module, you will decide which process you feel is best for the Voisey's Bay project.

Copper Pyromet Versus Hydromet

Pyrometallurgy of Copper

A common mineral of copper metal is chalcopyrite, CuFeS₂. The overall pyromet process is complex since the ore: 1) contains a equal amounts of iron to the desired copper, and 2) is usually very impure with clay and sand.

The primary treatment of chalcopyrite is concentration of the ore by *floatation*. This involves grinding the ore into a fine powder which is then added to a mixture of water, oil and detergent. Upon beating or blowing the ore mixture into a foam, the oil preferentially sticks to the mineral particles and carries the mineral to the top; the water-insoluble gangue (non-mineral impurities of clay and sand in the ore) then settles to the bottom. The foam, containing the mineral, is skimmed off the surface.

The second step is to heat the mineral in a blast furnace with the oxygen pressure and temperature carefully controlled. The copper and iron become separated from the chalcopyrite:

2 CuFeS
$$_{2(s)}$$
 + 4 O $_{2(g)}$ \Box
Cu $_2S_{(l)}$ + 2 FeO $_{(l)}$ + 3 SO $_{2(g)}$...
Equation 1

Sand (SiO₂) is then added to the blast furnace so that the iron(II) oxide produced is immediately converted into a dense liquid layer of iron(II) silicate, termed slag: $FeO_{(1)} + SiO_{2(s)} \square FeSiO_{3(1)}$

$$FeO_{(l)} + SiO_{2(s)} \square FeSiO_{3(l)}$$
 Equation 2

The slag is removed, and the copper(I) sulfide from Equation 1 is reduced to copper metal upon reaction with oxygen in air:

$$Cu_2S_{(1)} + O_{2(g)} \square 2 Cu_{(1)} + SO_{2(g)}$$
 Equation 3

Zinc and iron (from other trace minerals in the ore) are common impurities in the molten copper that forms by Equation 3. The final step in obtaining highly pure copper metal involves using an electrolytic cell to refine the copper. In the electrochemical cell, *impure* copper acts as the anode and *pure* copper acts as the cathode in a sulfuric acid solution containing Cu²⁺ ions. The cell is shown in Figure 1.

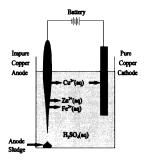


Figure 1. Electrolytic purification of copper.

The voltage applied to the electrodes is just high enough to oxidize the copper atoms at the anode to copper(II) ions. The copper(II) ions enter the solution and travel to the cathode (as indicated by the arrows) where they are reduced to *pure* copper metal.

The impurities which are more electrolytically active than copper dissolve from the anode, but are not reduced at the cathode (as shown by the single arrow from the anode). These ions remain in solution.

The anode sludge which forms as the impure anode disintegrates is definitely not garbage; it yields significant quantities of less active metals such as, gold, silver, platinum and palladium.

The copper which is purified by this process is usually at least 99.9% pure, as required for electrical wiring standards.

Hydrometallurgy of Copper

Once flotation is completed, the major difference with hydromet processes is *leaching* instead of roasting. Leaching refers to the dissolving of the

desired metal ions from the mineral into an aqueous solution. In the case of obtaining the copper from chalcopyrite, sulfuric acid is added to the ore in the presence of oxygen at room temperature:

Next, the iron (III) oxide and sulfur are filtered off. The solution is placed in an electrolytic cell to obtain pure metallic copper in a single step. The reactions at the anode and cathode are as follows:

anode:
$$2 H_2 O_{(1)} \square O_{2(g)} + 4 H^*_{(aq)} + 4 e^-$$
 ... Equation 5 cathode: $Cu^{2^+}_{(aq)} + 2 e^- \square Cu_{(s)}$ Equation 6

The hydromet process for obtaining pure copper is now complete. Looking back at the pyromet process for copper, do you see any advantages and/or disadvantages to using either method?

Pyrometallurgy Versus Hydrometallurgy for Nickel

Pyrometallurgy of Nickel

The two major nickel smelting methods currently used have been developed by the International Nickel Company of Canada (Inco) and Outokumpu Oy of Finland. The chemical reactions of the two processes are similar: after flotation, iron and sulfur are oxidized to produce impure liquid nickel.

The nickel deposit at Voisey's Bay is in the form of pentlandite (Fe₃Ni₉S₁₆). After the flotation of pentlandite, the mineral is smelted in two steps. First, the pentlandite is roasted at extremely high temperatures in air to yield iron(II) oxide and nickel(II) subsulfide, Ni₃S_{2(I)}. (Note that the nickel(II) subsulfide contains a rather unusual oxidation state for sulfur.)

2 Fe₉Ni₉S_{16(s)} + 29 O_{2(g)}
$$\Box$$

18 FeO_(l) + 6 Ni₃S_{2(l)} + 20 SO_{2(g)} ...Equation 7

The FeO gets converted to FeSiO₃ slag (as in Equation 2 for copper pyromet). Upon pouring off

the FeSiO₃, impure liquid nickel(II) subsulfide remains. The process may now take one of two routes: 1) conversion of the Ni_3S_2 to NiO, which is refined into pure nickel by a distillation known as the Mond process, or 2) placing the Ni_3S_2 in an electrolytic cell. We will only look at the electrolytic method here in detail.

Obtaining pure nickel from the impure Ni_3S_2 is also known as *electrowinning*. At the anode of the electrolytic cell, the Ni_3S_2 reacts to produce Ni^{2*} ions and S_8 ; the Ni^{2*} is then reduced at the cathode to produce nickel metal:

anode:
$$Ni_3S_{2(s)} \Box 3 Ni^{2+}_{(aq)} + 2/8 S_{8(s)} + 6 e^{-}$$
Equation 8 cathode: $Ni^{2+}_{(aq)} + 2 e^{-} \Box Ni_{(s)}$ Equation 9

Again, the electrolytic process provides an excellent method for refining a metal, as the nickel produced by electrowinning is over 99.9% pure.

Hydrometallurgy of Nickel

Hydromet is currently not the common method used by companies worldwide for nickel production. However, in 1954, Sherritt Gordon Mines Ltd. dissolved Ni²⁺ ions from sulfide ores using air, ammonia and water under high pressure and 85°C. While this was a successful process, Inco intends to dissolve Ni²⁺ ions from pentlandite using pure oxygen and water. The oxygen oxidizes most of the sulfide ions in the ore to solid sulfur; any excess sulfide is oxidized to sulfate ions (in the form of sulfuric acid), which helps to dissolve the metals. At the resulting pH of 3, solid Fe₂O₃ is produced. The reaction for this initial leaching process is:

2 Fe₉Ni₉S_{16 (s)} + 51 O_{2 (g)} + H₂O₍₁₎
$$\Box$$

18 NiSO_{4(aq)} + 13/8 S_{8(s)} + H₂SO_{4(aq)} + 9 Fe₂O_{3(s)}
... Fourtion 10

The byproduct $H_2SO_{4(aq)}$ which forms is later neutralized by adding limestone (Ca(OH)₂) to form gypsum, which separates from solution:

$$\begin{array}{cccc} \text{Ca}(\text{OH})_{2(s)} \ + \ \text{H}_2\text{SO}_{4(\text{aq})} \ \square & \text{CaSO}_42 \ \text{H}_2\text{O}_{(s)} \\ \text{limestone} & \text{gypsum} \\ & \dots \text{Equation } 11 \end{array}$$

Since all of the solid sulfur, gypsum and iron(III) oxide can be filtered off, the remaining solution contains only nickel(II) ions which may be reduced to pure nickel metal directly, without interference from all other ions and compounds originally in the ore.

Where do You Stand: Pyromet or Hydromet?

There are many considerations when choosing the type of processing plant for a mining project such as Voisey's Bay. There are environmental issues, factory cost, efficiency, employment and factory lifetime issues to consider. From the basic principles behind hydromet and pyromet technologies, which process would you endorse?

Understanding Concepts

- Use your knowledge of chemistry to give a brief explanation of why the philosopher's stone does not nor can not exist.
- Consider Equations 1 to 3 in the pyrometallurgy of chalcopyrite to yield copper. State two reasons why an environmentalist would be unimpressed with this means of copper extraction.
- (a) For the purification of copper (Figure 1), write complete half-reactions for the reaction at: (i) anode, and (ii) cathode.
 - (b) Attempt to write the "overall reaction" for the process, by showing the result of combining the anode half-reaction and the cathode half reaction from part (a) above.
 - (c) Use the result from part (b) above to explain while simple purification of the copper metal occurs during the electrolytic purification of copper, no other chemical processes occur for the copper.
- 4. Using Equations 5 and 6 under the hydromet process for isolating copper, determine:
 - (a) the overall cell reaction for the electrolysis.
 - (b) using a table of standard electrode potentials, the minimum potential required to electrolyze the solution and obtain copper metal.

- 5. The nickel(II) subsulfide, Ni₃S₂, obtained in the pyromet process for nickel has an unusual oxidation state for sulfur.
 - (a) What is the oxidation state of the sulfur?
 - (b) Why is this state considered "unusual"?
- 6. Given that the electrowinning process for refining nickel is an electrolytic process, what can be said about the sign and magnitude of the standard reduction potential of Ni₃S₂ in Equation 8?
- 7. For the hydromet process in isolating pure nickel electrolytically, propose the two reactions which occur at the anode and the cathode, the overall cell reaction, and the minimum voltage that would be necessary to carry out this process.
- 8. (a) Given the information provided in the module and any research you may care to follow up with, compare and contrast a pyromet processing plant versus a hydromet processing plant according to the following issues:
 - (i) environmental concerns
 - (ii) cost / efficiency of production
 - (iii) employment
 - (iv) factory lifetime / adaptability of the plant to be used with other ores / minerals.
 - (b) Based upon your response to (a), decide whether you believe pyromet or hydromet is a better process, assuming each process is viable for the ore which must be processed.

Making Extensions

- There was once a major iron ore mine on Bell Island. Research the mine, including type of iron mineral which was mined and mining methods.
- 2. In iron ore production (such as in the IOCC mines in Labrador City), the mineral magnetite (Fe₃O₄) can be separated from the gangue using other physical properties instead of the property of solubility used in the floatation process. Brainstorm or research the physical property that may be used to separate Fe₃O₄ from its

- gangue, and how this may be carried out on an industrial scale.
- 3. Research today's stock market closing values for copper, gold, silver and platinum. Use these results to explain why a small amount of anode sludge from electrolytic purification of copper can be as valuable as the pure copper produced by the process.
- Research the Mond process used to obtain and refine pure nickel from nickel (II) oxide. Make special note of any novel reactions, procedures or safety precautions employed. (Note: the process is also known as the "nickel carbonyl process".)

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