APPENDIX A

STSE

Science-Technology-Society and the Environment
Important Note

These STSE modules are intended for teacher reference. Each is designed to target specific outcomes within Chemistry 3202. It should be noted that the activities associated with each module are NOT mandatory. They are suggested activities to be used at the discretion of the teacher.
Smog, Catalytic Converters and You

**Outcomes:**
1. Describe a reaction mechanism and a catalyst’s role in a chemical reaction. (ACC-3)
2. Describe collision theory and its connection to factors involved in altering reaction rates. (ACC-1)
3. Identify and discuss properties (such as surface area) and situations which affect reaction rate. (ACC-2)
4. Analyze and describe examples where technologies were developed based upon scientific understanding. (116-4)
5. Analyze and describe examples where scientific understanding was enhanced or revised as a result of the invention of a technology. (116-2)
6. Identify and describe science and technology based careers. (117-7)

**Introduction**

A major event in any person’s life is getting his/her driver’s license, but with this great freedom comes great responsibility. A driver must obey the rules of the road, keep his insurance up-to-date and maintain the car in road worthy condition - not to mention keeping the gas hand off of "Empty"!

While these responsibilities are shared by all drivers, many car owners today are realizing an added responsibility to the environment when they buy cars with smaller motors and high gas mileage ratings. Even though many car owners still prefer larger sized vehicles for their needs, all car manufacturers are using chemistry and technology to minimize the amount of pollutants emitted through exhaust. Every automobile in Canada, regardless of whether it is a compact car or the largest truck on the lot, has a catalytic converter installed on its factory exhaust system. The catalytic converter reduces the amount of toxic chemicals that are released into the atmosphere, thus cutting down on the amount of smog produced.

You are just beginning your life as a driver and you are also the next generation of car buyers. This module will use your knowledge and understanding of catalysts, reaction mechanisms and kinetics to explain the chemical reactions which produce smog from exhaust.

**Smog Composition**

The word "smog" was originally derived from the phrase "smoke and fog", but today, unfortunately, the composition of smog is not that simple. Engine exhaust contains the primary pollutants that cause smog: the nitrogen oxides NO and NO₂ (known together as NOₓ), unburned hydrocarbons and carbon monoxide. The nitrogen oxides are formed when the O₂ and N₂, contained in air, react together with the hot exhaust gases. Incomplete combustion of gasoline in the engine produces the hydrocarbons and CO.

If you’ve ever been in a large city during a smog advisory, you have experienced the disgusting look and smell of smog. Smog can dominate a city’s skyline with haze (Figure 1). It is known for its brown colour and noxious smell (thanks mostly to the high NO₂ content), making breathing uncomfortable. The high CO content of smog is also a

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*Figure 1. Smog engulfs tourists overlooking Hong Kong harbour, January 2003.*
health problem. While carbon monoxide gas naturally has a trace concentration in air (~0.065 ppm), it can be poisonous. When in high concentrations CO combines with haemoglobin in our red blood cells better than oxygen, thereby disabling a red blood cell’s ability to uptake oxygen.

Compounding the CO problem, the NO and NO\textsubscript{2} components of smog can combine with O\textsubscript{2} in the air to create ground level ozone, O\textsubscript{3}. From what you have heard of “ozone layer depletion” in the upper atmosphere, you may have the impression that ozone is a beneficial compound. Yet, at ground level, ozone can pose a serious problem. Ground level ozone has a minuscule natural concentration in air (~0.01 ppm); at higher concentrations ground level O\textsubscript{3} irritates our respiratory tract and eyes, increases our chances of heart or lung disease, causes plant leaves to become brittle, bleaches colour from fabrics and hardens rubber. What do you think of ozone now?

**Ozone Formation: Reaction Mechanism**

The reaction mechanism for the formation of ozone from smog has been under constant study since the identification of smog by Arie J. Haagen-Smit in 1972. The currently accepted mechanism follows:

\[
\begin{align*}
\text{Step 1: } & \quad 2 \text{NO}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)} \quad \text{fast} \\
& \quad \text{hv} \\
\text{Step 2: } & \quad 2 \text{NO}_2\text{(g)} \rightarrow 2 \text{NO}_\text{(g)} + 2 \text{O}_\text{(g)} \quad \text{slow} \\
\text{Step 3: } & \quad 2 \text{O}_\text{(g)} + 2 \text{O}_2\text{(g)} \rightarrow 2 \text{O}_3\text{(g)} \quad \text{fast}
\end{align*}
\]

The overall equation for this mechanism indicates that ground level ozone is in fact a final product. Current law in Canada states that the maximum allowable ozone concentration is 82 ppb averaged over a one-hour period, yet this level is quite often exceeded in many Canadian cities thanks to our love of the automobile and our need for speed. Los Angeles, with one of the world’s worst smog problems, has even hit ground level ozone levels of 680 ppb. Current reports state that smog levels in Los Angeles have been reduced to a daily average of around 300 ppb, in large part due to the development of catalytic converters.

**The Catalytic Converter**

Think back to the chemicals in the exhaust that cause smog: NO, NO\textsubscript{2}, CO and ground level O\textsubscript{3}. To reduce smog, an efficient catalytic converter must serve two purposes. First, NO must be converted to harmless N\textsubscript{2} and O\textsubscript{2}. Second, CO must be converted to less harmful CO\textsubscript{2}. A catalytic converter is shown in Figure 2. Notice that it has either hundreds of beads or a convoluted surface (such as a honeycomb design) providing a large surface area to hold the catalyst. Common catalysts include palladium, platinum and rhodium and the metal oxides CuO and Cr\textsubscript{2}O\textsubscript{3}.

In a catalytic converter, the reactant molecules (NO or CO in the exhaust) pass along the surface where they become adsorbed. Weak chemical bonds form between the catalyst surface atoms and the adsorbed molecules, at the same time weakening the chemical bonds which hold the adsorbed molecules together. This process is often referred to as chemisorption. In the case of the CO, it is simply adsorbed; the NO not only adsorbs, its N-O bond is weakened to the point that it breaks (Steps 1 and 2 below in Figure 3). With the adsorbed NO broken into atoms, another NO molecule passing by reacts to produce nitrogen gas (Step 3, Figure 3). Since all of this happens very close to the CO on the catalyst surface, an O atom remaining from the NO decomposition combines with an adsorbed CO to give CO\textsubscript{2} (Step 4, Figure 3). Note that Steps 1 and 4 must occur twice for each time Steps 2 and 3 occur, in order to “mop up” all of the O atoms and convert all CO in the exhaust to CO\textsubscript{2}. 
Figure 3. The elementary processes in the operation of a catalytic converter.
The elementary steps which coincide with Figure 3 are given below; note that the symbolism "(ad)" refers to a substance which is "adsorbed" onto the catalyst surface.

**Step 1:** \(2\ CO(g) \rightarrow 2\ CO_{(ad)}\)

**Step 2:** \(NO(g) \rightarrow N_{(ad)} + O_{(ad)}\)

**Step 3:** \(N_{(ad)} + NO(g) \rightarrow N_2(g) + O_{(ad)}\)

**Step 4:** \(2\ CO_{(ad)} + 2\ O_{(ad)} \rightarrow 2\ CO_2(g)\)

This is one accepted mechanism for the operation of a catalytic converter. With literally hundreds of catalytic converters being used around the world today, other converters and mechanisms also exist, yet the same basic principle is followed: remove the NO and CO from the exhaust, cut down on the amount of smog produced.

One potential problem with the operation of a catalytic converter is that it may lose its effectiveness when impurities bind strongly to the catalyst surface and accumulate. When this occurs, the ineffective catalytic converter is said to be poisoned, and must be repaired or replaced. Up until the end of the 1980s, it was possible to buy "leaded gasoline" which contained the compound tetraethyl lead, \(\text{Pb(C}_2\text{H}_5)_4\). "Engine knock" seriously affects the efficiency and reliability of an automobile engine; the addition of tetraethyl lead allowed a car’s engine to run more smoothly with less engine knock. Unfortunately, this compound poisons catalytic converter surfaces, and in 1990 the sale of leaded gasoline was banned in Canada.

With the banning of tetraethyl lead, the search was on to find another compound which reduced engine knock but did not poison the catalytic converter. After significant research, methyl tertiary butyl ether (MTBE) was selected as a fuel additive in North America. Here’s an interesting twist in the story – more recent research has implicated MTBE as a carcinogen (cancer-causing agent). MTBE has been found in the groundwater wells in several cities and towns of North America, from gasoline spills that have run into the water table. As of 2003, Canada has not banned MTBE in gasoline. What should chemical engineers do? The search is still on for a gasoline enhancer that does not poison catalytic converters - or humans.

**Chemistry, the Future and You**

As stated at the outset, the purpose of this module is to inform you, the next generation of car buyers, about smog and the workings of catalytic converters, given that you have studied chemical kinetics. Now, after reading this module, perhaps as many questions have been raised as we have answered. What different designs are being used for current catalytic converters, and how can they be improved? How can a catalytic converter be made more efficient, cheaper, or longer lasting? Is there any way the poisoning of a catalytic converter can be avoided? Evidently, chemical engineers have a lot of work ahead of them.

Environmental chemists will also be busy. As carbon monoxide is removed from exhaust by a catalytic converter, an equivalent amount of carbon dioxide is produced. What is the environmental impact of this \(CO_2\)? Are catalytic converters really eliminating pollution, or should we be looking for alternate solutions? What damage will prolonged MTBE use do to Canada’s environment?

The answers to these questions require chemistry professionals. Chemical engineers and environmental chemists (both of whom are currently in demand) must continue to search for answers. Does one of these careers suit you?

**Understanding Concepts**

1. (a) List all of the chemical components of smog which are stated in this module.

   **(b) Write chemical reactions for:**
   (i) the production of NO from \(N_2\) and \(O_2\);
   (ii) the production of \(NO_2\) from \(N_2\) and \(O_2\);
   (iii) the production of carbon monoxide from the incomplete combustion of octane.

2. (a) Write the overall equation for the production of ground level \(O_3\) from smog using the three-step mechanism given in the article.
(b) Which step in the mechanism is the rate determining step? Why?
(c) State any intermediates in the mechanism.

3. Draw a reaction profile which is consistent with the reaction mechanism for the production of smog.

4. Use the complete reaction mechanism for ozone formation to show that by removing NO from exhaust by a catalytic converter, the problems of increasing both NO\(_2\) and ground level O\(_3\) concentrations from exhaust are also solved.

5. Why are catalytic converters designed with honeycomb surfaces to maximize the surface area inside the converter?

6. Write the overall balanced equation for the operation of the catalytic converter described in Figure 3 from the four elementary processes associated with the mechanism. Assume that the catalyst is palladium.

7. Use collision theory to explain how tetraethyl lead poisons a catalytic converter.

**Making Extensions**

1. Another currently accepted mechanism of smog formation simply adds a fourth step to the reaction mechanism given in the module, involving the reaction of ozone with nitrogen monoxide to produce nitrogen dioxide and oxygen.
   (a) Write a balanced chemical equation for the fourth elementary step from the description given above.
   (b) Include the fourth elementary step in the mechanism given in the module, and determine the overall equation for this mechanism with four elementary steps.
   (c) Does the overall reaction of this four-step mechanism solve the problem of ground level ozone production? Briefly explain your response.

2. When a catalytic converter destroys the carbon monoxide produced by a car’s motor, less harmful carbon dioxide is produced.
   (a) Explain why the module states that “less harmful” carbon dioxide is produced.
   (b) If you think that the current method of removing CO from exhaust is not perfect, suggest other chemical reactions that may be used in a catalytic converter to remove CO while producing harmless products. (You may wish to consult MSDS sheets to check on the toxicity of certain compounds.)

3. Use the learning resource centre at school or the internet to research catalytic converters to determine:
   (a) the actual chemical used as the catalyst and the reason(s) why that chemical was chosen;
   (b) the chemical equation(s) for chemical reaction(s) performed by the catalyst.

4. What is the difference between absorption and adsorption?

5. On the internet, an animation for a simple catalytic converter was found at the link: [http://www.wellesley.edu/Chemistry/chem120/catconv.swf](http://www.wellesley.edu/Chemistry/chem120/catconv.swf)
   Use the five elementary steps involving the adsorption of NO and CO onto a catalytic converter (as shown in Figure 3) as the basis for creating a computer animation for the NO - CO catalytic converter.

6. As of publication of this unit, Canada has not banned MTBE as a gasoline enhancer. Research the internet to find out the current status of MTBE in Canada’s gasoline industry.

**Teacher Demonstration - Model Smog**

Go to the link: [http://www.ecy.wa.gov/programs/air/aawaste/smog.html](http://www.ecy.wa.gov/programs/air/aawaste/smog.html) to find a class demonstration where model smog is formed.
Activities

1. Catalytic Converter Design
You have been hired by Ford of Canada to design a new catalytic converter for its largest personal use truck. Design the catalytic converter, keeping the following variables in mind:
   - materials to be used
   - design (both interior and exterior)
   - size
   - placement on the vehicle
   - cost
   - efficiency
   - expected lifetime of converter
You may wish to make a scale model of your converter and present your developed product.

2. Environmental Consultant
You have been hired by Health Canada to determine the toxicity of MTBE in gasoline. You may wish to study the following for your report:
   - previous chemical studies on MTBE (physical properties, chemical reactions)
   - previous health studies on MTBE (verify carcinogen claim, lab testing and results)
   - the amounts of MTBE currently added to gasoline, and the amount of gasoline currently used by Canadians per year
   - the current levels of MTBE found in various areas of Canada, in the atmosphere, soil and / or water supplies
   - public perception and knowledge of the issue
   - the gasoline industry’s stand on the issue
   - suggested action for future government policy
You may wish to present your report once a final draft has been completed.
Acid Around Us

Outcomes:
1. State general examples of how our lives are affected by acid-base chemistry. (ACC-5)
2. Analyze society’s influence on scientific and technological endeavours using examples from acid-base chemistry. (117-2)
3. Construct arguments to support a decision, recognizing various perspectives, concerning acid deposition (118-6)
4. Define a buffer according to both its components and its function. (ACC-6)
5. Recognize that blood is a buffer and that without this natural buffering, homeostasis would not be maintained (ACC-7)
6. Identify and describe science and technology based careers related to acid-base chemistry. (117-7)

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 phenomena. 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 household acids and bases would soothe each type of sting? Could you use the same substance to soothe 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...
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 pink-red 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.

<table>
<thead>
<tr>
<th>Food</th>
<th>Acid Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>vinegar</td>
<td>5% acetic acid v/v</td>
</tr>
<tr>
<td>tomato, spinach, rhubarb</td>
<td>oxalic acid</td>
</tr>
<tr>
<td>sour cream, sauerkraut,</td>
<td>lactic acid</td>
</tr>
<tr>
<td>'sour' cheeses</td>
<td></td>
</tr>
<tr>
<td>oranges, lemons, limes</td>
<td>citric acid</td>
</tr>
<tr>
<td>(citrus fruit)</td>
<td></td>
</tr>
</tbody>
</table>

*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 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.”

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 productivity will occur unless further drastic cuts to sulfur dioxide and nitrogen dioxide emissions are implemented.
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 $[\text{H}_3\text{O}^+]$ of $10^5$. 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 $[\text{H}_3\text{O}^+]$ 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:

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(_l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq) \quad K_a = 5.6 \times 10^{-4}$$

Remember both $\text{NH}_4^+(aq)$ and $\text{NH}_3(aq)$ 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:

$$\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq).$$

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

$$\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq)$$

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

$$\text{OH}^-(aq) + \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l)$$

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

$$\text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + 2 \text{H}_2\text{O}(l)$$

Note that since we remove $\text{CO}_2(g)$ from our bodies as we breathe, the rate at which we breathe will affect the amount of $\text{HCO}_3^-$ 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 $\text{CO}_2$ (and thus $\text{HCO}_3^-$) 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

1. (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?

2. 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 17.4 mol/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 source 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.

7. (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 $4.4 \times 10^{-7}$ @ 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.)
Making Extensions

1. (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 $H_3PO_4(aq)$ 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 $K_a$ constant expression for the buffer, and substitute known quantities.)

References


6. www.holistic-online.com/remedies/arthritis/arth_gout_folk-remedies.htm


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:

\[ 3 \text{NaHCO}_3(\text{s}) + \text{C}_3\text{H}_5\text{O}\text{(COOH)}_3(\text{s}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)} + \text{C}_3\text{H}_5\text{O}(\text{COONa})_3(\text{aq}) \]

**Internet References**

[www.essentialoil.com/bathbomb.html](http://www.essentialoil.com/bathbomb.html)
[www.pvsoap.com/recipe_bath_bomb.htm](http://www.pvsoap.com/recipe_bath_bomb.htm)
[www.nexus.chemistry.duq.edu/snes/chemistry/faculty/isenhour/chem121f/Chap04.htm](http://www.nexus.chemistry.duq.edu/snes/chemistry/faculty/isenhour/chem121f/Chap04.htm)
What Fuels You?

Outcomes:
1. Define, calculate and compare fuel values (ACC-8)
2. Propose alternative solutions to solving energy problems and identify the potential strengths and weaknesses of each, using the concepts of fuel value and molar enthalpy of combustion (214-15)
3. Analyze examples where technologies were developed based on thermochemistry, using the idea of the choice of fuel in a device (116-4)
4. Identify perspectives that influence a decision involving fuels used in devices, and, the choices made in the Calorie content and serving size of the foods we eat (215-4)
5. Analyze why scientific and technological activities take place when making choices for maintaining a healthy lifestyle (117-6)
6. Analyze the risks and benefits to society and the environment in relation to fossil fuel use and healthy lifestyle choices (118-2)
7. Analyze the knowledge acquired in their study of thermochemistry to identify areas of further study, specifically chemical engineering and nutrition (117-9)

Introduction

Fuel. What does that word mean? Consider: For a home, “fuel” is what provides the energy for our heating system. For a car, “fuel” is the gasoline that keeps the motor running. For our bodies, “fuel” consists of the foods we eat to keep our bodies running. Does this imply that fueling a car is no different from fueling our bodies? This module will ask you to apply your knowledge and understanding of thermochemistry in examining our daily use of fossil fuel, and compare it to our daily use of food to meet our energy (or calorie) requirements.

Fossil Fuel Use

Fossil fuels are produced from organic matter which, buried millions of years ago in the evolution of Earth, transferred to coal, crude oil, and natural gas. One of the most important fossil fuels for our society is crude oil. After the crude oil is extracted and refined, consumers purchase various fuel products for their use. Propane is purchased for barbecues, fireplaces, kitchen appliances and general home heating. Butane is used in lighters. A mixture of mostly hydrocarbons ranging from six to twelve carbons are blended into gasoline.

Why isn’t gasoline used in jet plane engines? Have you ever wondered why butane is used in a lighter, but not in fueling cars? The answer to these questions are based on two characteristics of all fuels: practical convenience and fuel value.

Fuel value is defined as the heat evolved per gram of fuel burned. Mathematically, we can express fuel value (FV) as:

\[ FV = \frac{q}{m} \]

Equation 1

where 'q' is the heat given off by a given mass (m) of fuel. If the heat evolved is measured in "kJ" and the mass is in "g", then the unit for fuel value is "kJ/g".
Note that the equation for fuel value is quite close to that of molar enthalpy, ΔH:

\[ \Delta H = \frac{q_{sys}}{n} \]  

Equation 2

where the enthalpy of the system (q_{sys}) is quoted per mole (n).

Chemists, working on a daily basis with the quantity of the mole, find molar enthalpy useful in comparing heat changes of different systems. The use of fuel value allows the same comparison, except that a more familiar unit - mass - is the basis of the comparison. Using the idea of fuel value is also more convenient in expressing to the public the amount of heat a fuel may produce per amount burned, since "mass" is a much more common term than the "mole".

The fuel values and molar enthalpies of combustion for various hydrocarbons are listed in Table 1. Hydrogen, while not a hydrocarbon, is used as a fuel in the space industry and is also included in the table.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Chemical Formula</th>
<th>Fuel Value (kJ/g)</th>
<th>Molar Enthalpy of Combustion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>H₂</td>
<td>141.5</td>
<td>-285.8</td>
</tr>
<tr>
<td>ethanol</td>
<td>C₂H₅OH</td>
<td>29.66</td>
<td>-1366.8</td>
</tr>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>55.48</td>
<td>-890.4</td>
</tr>
<tr>
<td>propane</td>
<td>C₃H₈</td>
<td>50.33</td>
<td>-2219.9</td>
</tr>
<tr>
<td>butane</td>
<td>C₄H₁₀</td>
<td>45.73</td>
<td>-2658.3</td>
</tr>
<tr>
<td>octane</td>
<td>C₈H₁₈</td>
<td>47.7</td>
<td>-5450.5</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane</td>
<td>C₈H₁₈</td>
<td>47.75</td>
<td>-5455.6</td>
</tr>
</tbody>
</table>

Table 1. Fuel Values and Molar Enthalpy of Combustion Data for Various Fuels.

Hydrogen, with such a low molar mass, has a huge fuel value even though its molar enthalpy of combustion is lower than the others. The large fuel value for hydrogen translates into a huge amount of energy produced for a relatively small mass burned. This, of course, is why the space industry uses this lightweight, efficient fuel in its rockets.

Table 1 also shows that the fuel values for common hydrocarbons are of the same magnitude, meaning that the choice of a specific hydrocarbon in a device is not simply choosing the highest fuel value. For example, propane and butane are easily liquefied when compressed, so these are the chosen fuels when a large volume of gas must be easily contained and transported in a relatively small container (such as a propane tank or lighter).

Octane and 2,2,4-trimethylpentane are major components in gasoline. The fuel values of these two hydrocarbons are almost equal. However, "premium" gasoline contains a greater percentage of 2,2,4-trimethylpentane. 2,2,4-trimethylpentane does not significantly increase the energy output, however, it burns much more smoothly with less engine knock.

Fuel values for the compounds in Table 1 are determined by bomb calorimetry, using the same thermodynamic concepts as you have already studied for molar enthalpy of combustion determination. Using this method to determine fuel values is a simpler process than determining molar enthalpies since calculating a fuel value (Equation 1) requires the heat of the system to be divided simply by the mass of the fuel - a conversion from mass to moles is not required.
Fueling our Bodies - Caloric Intake

When you first heard someone refer to "burning off some calories", did you think there was an actual fire burning inside the person’s body? This may actually be close to the truth. Metabolism of our food "fuel" consists of a series of complex reactions in which the final products are carbon dioxide and water - the same products as a hydrocarbon combustion. We may consider metabolism of the calories as a "slow burn". So, we can apply our understanding of combustion reactions, fuel values and bomb calorimetry to our caloric intake.

Before going further we must clarify a potentially confusing unit related to the Calories quoted on food labels. A calorie (cal) is the amount of energy required to increase the temperature of one gram of water by degree Celsius:

\[
1 \text{ cal} = 4.184 \text{ J}
\]

yet this is not the same "calorie" as the food Calorie (Cal). One food Calorie is equal to one kilocalorie (note the uppercase "C" in the unit for food Calorie):

\[
1 \text{ food Calorie} = 1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal} = 4.184 \text{ kJ}
\]

In Canada, federal law states that the number of Calories per serving of a purchased food must be made available to the consumer, and usually this means the information is directly on a Nutrition Food Label (Figure 1). One serving of the drink described in the label in Figure 1 has 80 food Calories, or 335kJ. As of January 1, 2003, federal law requires this type of label to be on all foods sold in Canada except raw meat, fresh fruit and vegetables, herbs and spices, beverages with more than 0.5-per-cent alcohol and food prepared in-store, such as fast food and bakery products.

There is a lot more information on the label than calories. The serving size is given just below the heading in grams. The measured food Calories for that serving size is listed just below that. This means we can modify the fuel value Equation 1 for our foods used as “fuel”:

\[
\text{FV} = \frac{\text{Food kJ}}{m} \quad \text{Equation 3}
\]

Since "Food kJ" is the food energy and "m" is the mass in grams, Equation 3 gives a food’s fuel value in a unit of "kJ/g". Using this formula, what is the fuel value using the product’s food label in Figure 1?

Just as fuel values for hydrocarbons are measured by bomb calorimetry, the same method is used to determine the fuel values of foods. Bomb calorimetry is a very useful method of determining energy changes from chemical reactions. In determining the food energy (or Calories) in a food product, the mass of a sample of the food (not necessarily a full serving size) is measured in grams. If the food contains a considerable amount of water, it is first dehydrated and then placed in a bomb calorimeter’s inner chamber. Once the experiment is run, the heat evolved is calculated in kilojoules (as well as converted to Calories). Equation 3 is then used to calculate the food’s fuel value. Multiplication of the food fuel value by the serving size then gives the energy content in one serving. The Sample Problem below performs the above steps for determining the energy (or Calorie) content in a 23g granola bar by bomb calorimetry.

**Sample Problem**

A 2.50g sample of granola bar is placed in a bomb calorimeter with a heat capacity of 13.17 kJ/°C. The temperature of the calorimeter contents increases by 3.86°C upon complete combustion of the sample.
Determine:  
(a) the food value, and  
(b) number of Calories in a 23.0g serving (one granola bar).

**Solution**

(a) First, determine the heat of the calorimeter surroundings:

\[ q_{\text{surr}} = C \Delta T = (13.17 \text{ kJ/°C}) (3.86 \text{ °C}) = 50.8 \text{ kJ} \]

Second, we could state the heat evolved by the system (the granola bar) as:

\[ q_{\text{sys}} = - q_{\text{surr}} = -50.8 \text{ kJ} \]

We can use just the positive value for the energy since food energy (and Calories) are quoted as positive values.

Next, using Equation 3:

\[ \text{FV} = \frac{\text{Food kJ}}{m} = \frac{50.8 \text{ kJ}}{2.50 \text{ g}} = 20.3 \text{ kJ/g} \]

The food value of the granola bar is found to be 20.3 kJ/g using bomb calorimetry measurements.

(b) Rearranging Equation 3 gives us a formula to calculate the total Calories in a 23.0g serving:

\[ \text{Food kJ} = \text{FV} \times m = (20.3 \text{ kJ/g}) \times (23.0 \text{ g}) = 467 \text{ kJ} \]

In case you are "counting calories", since 1 Cal = 4.184 kJ, the same food energy in the old unit of Calories is:

\[ \text{Cal} = (467 \text{ kJ}) \times (1 \text{ Cal} / 4.184 \text{ kJ}) = 112 \text{ Cal} \]

The 23g granola bar contains 467 kJ, or 112 Calories. Yum!

Given that the serving size of the foods we eat varies, it is useful to know that fats have an average fuel value of 44 kJ/g (9.1 Cal/g) while carbohydrates and proteins have fuel values averaging 17.5 kJ/g (4.2 Cal/g). This information is often used by professional athletes on strict training regimens, who weigh the foods they consume to determine the amount of Calories (i.e. energy) their bodies take in. Lance Armstrong, multiple winner of the Tour de France, attributes his success in the month long endurance race by measuring his energy (or Calorie) intake in this way, ensuring that he is at his optimum body mass when the race reaches the Alps each year.

**What Fuels You? Healthy Choices and a Healthy Lifestyle**

According to Canada’s Food Guide, the amount of food you need every day depends on your age, body size, activity level, and whether you are male or female. The Food Guide covers a range of energy needs from 7530 to 13 400 kJ (1800 to 3200 Cal) per day, according to where you fit on the range of servings given for each food group (Figure 2). This allows Canadians to make the correct individual choices. Based upon body size, developmental stage and activity level, young children would require the smaller range of servings, while teenage boys would require the larger range of servings; most other people may make their serving choices somewhere in between. For more details to help you make your own right choice of number of servings, consult the Canada Food Guide... it’s even available on the Web!
Nutrition recommendations advise Canadians to get 30% or less of their day’s energy from fat. This translates into a range of fat, in grams, that can be used as a benchmark against which individual foods and meals can be evaluated. A fat intake of 30% or less of a day’s Calories means a fat intake between 60 g and 105 g of fat (Table 2).

<table>
<thead>
<tr>
<th>Total Energy Intake, kJ (Cal)</th>
<th>Total Grams of Fat (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7530 (1800)</td>
<td>60</td>
</tr>
<tr>
<td>11 300 (2700)</td>
<td>90</td>
</tr>
<tr>
<td>13 400 (3200)</td>
<td>105</td>
</tr>
</tbody>
</table>

*Table 2. Benchmarks for Fat Intakes per Day*

The Food Guide states that fat is not evil; it is actually necessary. We just need to make healthy choices. The guide suggests, for example, choosing lower-fat dairy products, leaner meats and food prepared with little or no fat. Some choices are not difficult to make when at the grocery store: instead of ice cream, choose frozen yogurt; instead of homogenized milk, choose 2% or skim.

For a healthy lifestyle, the Food Guide recommends that Canadians should achieve and maintain a healthy body weight by enjoying regular physical activity with healthy eating. Table 3 shows some common activities, with their approximate energy expenditures based upon a 68 kg (150lb) person. Do you see anything in the table that you enjoy?
### Table 3. Energy Expenditures for Various Activities

<table>
<thead>
<tr>
<th>Activity</th>
<th>Energy Expenditure, kJ/h (Cal/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobics (heavy)</td>
<td>2760 (660)</td>
</tr>
<tr>
<td>Basketball</td>
<td>1500 - 2760 (360-660)</td>
</tr>
<tr>
<td>Cycling (25 km/h)</td>
<td>2300 (550)</td>
</tr>
<tr>
<td>Rowing / Rowing Machine</td>
<td>3500 (835)</td>
</tr>
<tr>
<td>Running (10 km/h)</td>
<td>3140 (750)</td>
</tr>
<tr>
<td>Running (20 km/h)</td>
<td>4730 (1130)</td>
</tr>
<tr>
<td>Walking (level road, 6 km/h)</td>
<td>1675 (400)</td>
</tr>
<tr>
<td>Gardening, with much lifting / stooping</td>
<td>2100 (500)</td>
</tr>
</tbody>
</table>

(Note: There is a 10% increase in caloric expenditure for each 6.8 kg (15 pounds) over this weight and a 10% decrease for every 6.8 kg (15 pounds) under.)

### Thermochemistry Comes Alive...

If you thought that thermochemistry is all about abstract terms like "average kinetic energy" or "specific heat capacity", hopefully this look at What Fuels You has challenged these thoughts. Chemical engineers (studying fossil fuel combustion) and health care workers (studying healthy diets and lifestyles) use thermochemistry to improve our quality of living. Would one of these careers interest you?

### Understanding Concepts

1. (a) Calculate the fuel value of hexane if 4.00g of C₆H₁₄ produces 214.4kJ of heat.
   (b) What mass of hexane must be burned to produce 250kJ of heat?

2. What are THREE advantages of quoting fuel values as opposed to quoting enthalpy of combustion values to communicate the amount of heat produced when a fuel is burned?

3. Why is it more important to have a high fuel value compound providing the fuel for a rocket than for a car?

4. If hydrogen has such a high fuel value, why is it not currently used instead of gasoline to fuel our cars?

5. Use the fuel values in Table 1 and practical considerations to hypothesize why manufacturers produce gasoline-fueled cars instead of butane-fueled cars.

6. Henry Ford was a major advocate of using ethanol instead of gasoline as the fuel for the first cars that he designed. What would have been one disadvantage and one advantage of an ethanol fueled car over a gasoline fueled car? (Remember that two major components of gasoline are octane and 2,2,4-trimethylpentane.)

7. (a) When a 4.75g sample of airplane fuel is exploded in a bomb calorimeter with a heat capacity of 30.58kJ/°C, the calorimeter contents increases in temperature from 22.35°C to 34.90°C. What is the fuel value of the airplane fuel? (Hint: Use the same procedure as you would for calculating the molar enthalpy of combustion, except use Equation 1 (for FV) in the final step of your calculation.)
   (b) State TWO reasons why calculating the fuel value of the airplane fuel is easier and more practical than attempting to calculate the molar enthalpy of combustion for the same mixture.

8. Using the formula for food fuel value, what is the fuel value using the product’s food label in Figure 1?

9. Why would a food with a high water content be dehydrated before being placed in a bomb calorimeter for determination of its Calorie content?

10. Several companies hire Bocknek Laboratories, Inc., to determine the food energy (and Calorie) values for servings of their food products. A cheese manufacturer supplies Bocknek Labs with samples of their new cheddar for testing. The results of the bomb calorimetry experiment
are provided below, directly from Bocknek’s lab books:

**Determination of Cheese Sample Size**

mass of cheese + weighing boat: 6.84g
mass of weighing boat (after transfer): 1.32g
mass of cheese: ____________________

**Calorimetry Data and Results**

Heat Capacity of Bomb Calorimeter: 10.27 kJ/°C
final temperature of calorimeter: 24.95 °C
(initial temperature of calorimeter: 20.82 °C
(before combustion)

temperature change for calorimeter: ____________________

Determine: (a) the fuel value of the cheese, and
(b) the food energy (in kJ) and the Calories (in Cal) contained in a 50 g serving of the cheddar.

11. Why are the food values quoted for fats, carbohydrates and proteins stated as "average" food values?

12. A pro cyclist has two 30g servings of dry cereal for breakfast and then trains on her bike for one hour. Assuming the cereal has the average food value of carbohydrates and she expends energy at a rate of 2750 kJ/h, should the cyclist experience weight loss after her training?

13. A college student on a steady diet of hamburgers, French fries and other fast foods receives 170g of fat in his diet per day.
(a) Using the average fuel value for fat, determine the number of Calories the student obtains from fat daily on such a diet.
(b) If the student’s total daily food intake is 16735 Calories, determine the percentage of the student’s daily Calorie intake from fat.
(c) Use the percentage obtained above and the Canada Food Guide statistic for recommended daily fat intake to comment on the student’s diet.

14. The Nutrition Label on a 270g bag of Krusty® potato chips states that a serving is 28g (approximately 20 chips). The Calorie content in one serving is 644 kJ (154 Cal).
(a) How many servings are in a single bag of Krusty® potato chips?
(b) How much energy is consumed if the full bag is eaten?
(c) How many calories are consumed if the full bag is eaten?
(c) For the following activities, calculate the number of hours it would take doing the activity to "burn off" the full bag of Krusty® chips:
(i) running at 10km/h
(ii) rowing
(iii) gardening

15. The Nutrition Label states that one serving of Krusty® chips is approximately 20 chips. If you can resist eating the whole bag:
(a) determine from the number of Krusty® chips you would regularly eat, and calculate the corresponding number of servings.
(b) determine the number of Calories you would eat from the above number of chips.
(c) choose your favourite activity from Table 3, and determine how long it would take you to use the energy in the amount of Krusty® chips you have eaten.
(d) after performing the above calculations, are you reconsidering your potato chip diet?

16. Zeke is trying to lose a few pounds, so he goes for a half hour walk each night at 6km/h. As a little reward afterwards, he hangs out in front of the TV and has a "small" 70g bag of Krusty® chips mentioned in question 14. Is Zeke’s physical activity going to provide him with the weight loss he is looking for?

17. According to a local milk producer’s website, a serving of milk is 250 mL. For homogenized milk and skim milk, the food energy (Calorie) intakes are 657 kJ (157 Cal) and 372 kJ (89 Cal), respectively. Obviously, there is more energy in one serving of homogenized milk. Use the data in Table 3 to compare how much more time it would take to "walk off" a...
serving of homogenized milk compared to skim milk.

Making Extensions

1. (a) Use the data in Table 1 along with Equations 1 and 2 to determine a method of converting a quoted value of molar enthalpy of combustion into a fuel value for the same compound.
(b) The molar enthalpy of combustion for methanol is -726.5 kJ/mol. Determine the fuel value for methanol.
(c) Use (i) the molar enthalpy of combustion, and (ii) the fuel value for methanol to separately calculate the amount of heat, in kilojoules, which is produced when 3.25g of methanol is burned.
(d) What are the advantages of using one means of calculation in (c) over the other?

2. While fuel value is used to compare the efficiency of burning a hydrocarbon in terms of amount of mass burned, octane rating is another method of stating fuel efficiency. Research the definition of octane rating and the ratings for various hydrocarbons. What advantage(s) would there be for quoting an automobile gasoline quality using octane rating?

3. Research the careers of chemical engineering, dietician and / or nutritionist, and report your findings. In your research you may want to also research post-secondary institutions which offer programs in these fields.

Activity 8

The Food Energy and Calorie Content of Mini Marshmallows and Cheese Sticks

Objective: In this activity, you will construct a simple calorimeter and then utilize it to measure the amount of heat energy present in a serving of: (a) miniature marshmallows and (b) cheese sticks, and compare your results to the Nutritional Food Label on the packaging.

Materials:
- water
- matches
- one package of mini marshmallows
- one package of cheese sticks
- balance
- straight pins
- aluminum foil
- ring stand and clamp
- aluminum soft drink can
- 100 mL graduated cylinder

Procedure:
1. Set up the aluminum can and ring stand as shown in the figure below.

2. Use the graduated cylinder to measure an accurate amount (roughly 100 mL) of water. Record the accurate mass of water used and pour it into the aluminum can. (Remember that 1 mL of water has a mass of 1 gram).

3. Use the Celsius thermometer to take the temperature of the water (to one decimal place) and record it on your data sheet.

4. Obtain the mass of a mini marshmallow which is to be soon sacrificed in the name of science.

5. Place the head of a straight pin into a piece of cork or a chunk of clay. The cork is best to use since it will not melt. Insert the head of the pin into a miniature marshmallow.
6. Light the marshmallow with a match and quickly place it under the can of your calorimeter, and allow it to burn completely. If the marshmallow flame goes out, reignite it.

7. After the marshmallow has burned completely, take the temperature of the water again and record the final temperature on your data sheet.

8. Perform the **Analysis** questions to calculate the Calories of the food sample, using simple calorimetry formulas and the fact that 1 Cal = 4.184 kJ = 4.184 x 10\(^3\) J.

**Data Sheet:**

<table>
<thead>
<tr>
<th>Mini Marshmallow</th>
<th>Cheese Stick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of Food Sample (g)</td>
<td></td>
</tr>
<tr>
<td>Mass of Water in Calorimeter (g)</td>
<td></td>
</tr>
<tr>
<td>Final Water Temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>Initial Water Temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>Change in Water Temperature (°C)</td>
<td></td>
</tr>
</tbody>
</table>

**Analysis:**

1. Use simple calorimetry concepts to calculate the heat given off by burning:
   (a) the marshmallow
   (b) the cheese stick

2. Use the energy released and the mass of each food to determine the food value of:
   (a) the marshmallow
   (b) the cheese stick

3. Check the package for each food to find the mass of one serving of:
   (a) the marshmallows
   (b) the cheese sticks

4. Calculate the experimentally determined food energy (in kJ) in one serving of:
   (a) the marshmallow
   (b) the cheese stick using the results of questions 2 and 3 above.

5. Calculate the experimentally determined Calories (in Cal) in one serving of:
   (a) the marshmallow
   (b) the cheese stick using the results of questions 2 and 3 above.

6. Compare your results for the food energy (or Calorie) content per serving of each food with the Nutritional Label on the packages for each food.

7. Did all the heat from the marshmallow and cheese stick go directly into the water? Explain.

8. State TWO ways in which the determination of the food energy content of the foods could be improved.

**References**


# From Mineral to Metal: Metallurgy and Electrolytic Refining

**Outcomes:**

1. Define metallurgy, pyrometallurgy and hydrometallurgy (116-5)
2. Define and describe the process of *flotation*, as it applies to the mining industry (ACC-9)
3. Define the terms slag and leaching, as they apply to pyrometallurgy and hydrometallurgy, respectively (ACC-10)
4. Recognize the environmental hazards of roasting sulfide ores with processes using pyrometallurgy, given that sulfur dioxide is a byproduct (118-1)
5. Describe the process of electrowinning pure nickel from a nickel(II) subsulfide matte, used in the industrial production of pure nickel (ACC-11)
6. Evaluate the processes of pyrometallurgy versus hydrometallurgy for the production of copper and nickel from two representative minerals and determine which industrial process would be best (116-5)

## 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.
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, CuFeS$_2$. 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:

$$2 \text{CuFeS}_2(s) + 4 \text{O}_2(g) \rightarrow \text{Cu}_2\text{S}_3(l) + 2 \text{FeO}(l) + 3 \text{SO}_2(g)$$

...Equation 1

Sand (SiO$_2$) 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**:

$$\text{FeO}(l) + \text{SiO}_2(s) \rightarrow \text{FeSiO}_3(l)$$

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:

$$\text{Cu}_2\text{S}_3(l) + \text{O}_2(g) \rightarrow 2 \text{Cu}(l) + 3 \text{SO}_2(g)$$

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 Cu$^{2+}$ ions. The cell is shown in Figure 1.

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:

$$2 \text{CuFeS}_2(s) + \text{H}_2\text{SO}_4(aq) + 4 \text{O}_2(g) \rightarrow 2 \text{CuSO}_4(aq) + \text{Fe}_2\text{O}_3(s) + 3/8 \text{S}_8(s) + \text{H}_2\text{O}(l)$$  ... Equation 4

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:  $2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^-$

...Equation 5

cathode: $\text{Cu}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cu}(s)$  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 ($\text{Fe}_9\text{Ni}_9\text{S}_{16}$). 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, $\text{Ni}_3\text{S}_2(l)$. (Note that the nickel(II) subsulfide contains a rather unusual oxidation state for sulfur.)

$$2 \text{Fe}_9\text{Ni}_9\text{S}_{16}(s) + 29 \text{O}_2(g) \rightarrow 18 \text{FeO}(l) + 6 \text{Ni}_3\text{S}_2(l) + 20 \text{SO}_2(g)$$  ...Equation 7

The FeO gets converted to FeSiO$_3$ slag (as in Equation 2 for copper pyromet). Upon pouring off
the FeSiO$_3$, impure liquid nickel(II) subsulfide remains. The process may now take one of two routes: 1) conversion of the Ni$_3$S$_2$ to NiO, which is refined into pure nickel by a distillation known as the Mond process, or 2) placing the Ni$_3$S$_2$ in an electrolytic cell. We will only look at the electrolytic method here in detail.

Obtaining pure nickel from the impure Ni$_3$S$_2$ is also known as electrowinning. At the anode of the electrolytic cell, the Ni$_3$S$_2$ reacts to produce Ni$^{2+}$ ions and S$_8$; the Ni$^{2+}$ is then reduced at the cathode to produce nickel metal:

\[
\text{anode: } \text{Ni}_3\text{S}_2(s) \rightarrow 3 \text{Ni}^{2+}(aq) + 2/8 \text{S}_8(s) + 6 e^- \quad \text{...Equation 8}
\]

\[
\text{cathode: } \text{Ni}^{2+}(aq) + 2 e^- \rightarrow \text{Ni}(s) \quad \text{Equation 9}
\]

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 Ni$^{2+}$ 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 Ni$^{2+}$ 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 Fe$_2$O$_3$ is produced. The reaction for this initial leaching process is:

\[
2 \text{Fe}_2\text{Ni}_3\text{S}_{16}(s) + 51 \text{O}_2(g) + \text{H}_2\text{O}(l) \rightarrow 18 \text{NiSO}_4(aq) + 13/8 \text{S}_8(s) + \text{H}_2\text{SO}_4(aq) + 9 \text{Fe}_2\text{O}_3(s) \quad \text{... Equation 10}
\]

The byproduct H$_2$SO$_4(aq)$ which forms is later neutralized by adding limestone (Ca(OH)$_2$) to form gypsum, which separates from solution:

\[
\text{Ca(OH)}_2(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4.2\text{H}_2\text{O}(s) \quad \text{limestone \rightarrow \text{gypsum} \quad \text{... Equation 11}}
\]

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**

1. Use your knowledge of chemistry to give a brief explanation of why the philosopher’s stone does not nor can not exist.

2. 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.

3. (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, $\text{Ni}_3\text{S}_2$, 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 $\text{Ni}_3\text{S}_2$ 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.

References
