Educational Study Guide for AP Chemistry

Title: Fuel Cell Application Problems for Advanced High School General Chemistry

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Grade Level / Subject:
10th-12th grade/ Accelerated or Advanced Placement High School General Chemistry

Curriculum Standards (from *National Science Education Standards)* for Science Grades 9-12:

Standard B: Physical Science

Structure of Atoms

• Matter is made of minute particles called atoms, and atoms are composed of even smaller components. These components have measurable properties such as mass and electrical charge. Each atom has a positively charged nucleus surrounded by negatively charged electrons. The electric force between the nucleus and electrons holds the atom together.

Structure and Properties of Matter

• Atoms interact with one another by transferring or sharing electrons that are furthest from the nucleus. These outer electrons govern the chemical properties of the element.
• An element is composed of a single type of atom. When elements are listed in order according to the number of protons (called the atomic number), repeating patterns of physical and chemical properties identify families of elements with similar properties. This "Periodic Table" is a consequence of the repeating pattern of outermost electrons and their permitted energies.
•Bonds between atoms are created when electrons are paired up by being transferred or shared. A substance composed of a single kind of atom is called an element. The atoms may be bonded together into molecules or crystalline solids. A compound is formed when two or more kinds of atoms bind together chemically.
•The physical properties of compounds reflect the nature of the interactions among its molecules. These interactions are determined by the structure of the molecule, including constituent atoms and the distances and angles between them.
• Solids, liquids and gases differ in the distances and angles between molecules or atoms and therefore the energy that binds them together. In solids the structure is nearly rigid; in liquids molecules or atoms move around each other but do not move apart; and in gases molecules or atoms move almost independently of each other and are mostly far apart.
• Carbon atoms can bond to each other in chains, rings and branching networks including synthetic polymers, oils and the large molecules essential to life.

Chemical Reactions

• Chemical reactions occur all around us, for example in health care, cooking, cosmetics and automobiles. Complex reactions involving chemical reactions involving carbon-based molecules take place constantly in every cell in our bodies.

• Chemical reactions may release or consume energy. Some reactions such as the burning of fossil fuels release large amounts of energy by losing heat and emitting light. Light can initiate many chemical reactions such as photosynthesis and urban smog.

• A large number of important reaction involve the transfer of either electrons(oxidation-reduction reactions) or hydrogen ions (acid/base reactions) between reacting ions, molecules, or atoms. In other reactions, chemical bonds are broken by heat or light to form very reactive radicals with electrons ready to form new bonds. Radical reactions control many processes such as the presence of ozone and greenhouse gases in the atmosphere, burning and processing of fossil fuels, the formation of polymers, and explosions.

• Chemical reactions can take place in time periods ranging from a few femto seconds (10-15 seconds) required for an atom to move a fraction of a chemical bond distance to geologic time scales of billions of years. Reaction rates depend on how often the reacting atoms and molecules encounter one another, on the temperature, and on the properties—including shape—of the reacting species.

• Catalysts, such as metal surfaces, accelerate chemical reactions. Chemical reactions in living systems are catalyzed by protein molecules called enzymes.

Conservation Of Energy and The Increase in Disorder

• The total energy of the universe is constant. Energy can be transferred by collisions in chemical and nuclear reactions, by light waves and other radiation, and in many other ways. However, it can never by destroyed. As these transfers occur, the matter involved becomes steadily less ordered.

• All energy can be considered to be either kinetic energy, which is the energy of motion; potential energy, which depends on relative position; or energy contained by a field, such as electromagnetic waves.

• Heat consists of random motion and the vibrations of atoms, molecules, and ions. The higher the temperature, the greater the atomic or molecular motion.

• Everything tends to become less organized and less orderly over time. Thus, in all energy transfers, the overall effect is that energy is spread out uniformly. Examples are the transfer of energy from hotter to cooler objects by conduction, radiation, or convection and the warming of our surroundings when we burn fuels.

Content Standard E: Science and Technology

Abilities of Technological Design

• IDENTIFY A PROBLEM OR DESIGN AN OPPORTUNITY. Students should be able to identify new problems and improve current technological designs.

•PROPOSE DESIGNS AND CHOSE BETWEEN ALTERNATIVE SOLUTIONS.
Students should demonstrate thoughtful planning for a piece of technology or technique.
Students should be introduced to the roles of models and simulations in these processes.

•IMPLEMENT A PROPOSED SOLUTION. A variety of skills can be needed in
proposing a solution depending on the type of technology that is involved. The
construction of artifacts can require the skills of cutting, shaping, treating and joining
common materials—such as wood, metal, plastics and textiles. Solutions can also be
implemented using computer software.

•EVALUATE THE SOLUTION AND ITS CONSEQUENCES. Students should test any
solution against the needs and the criteria it was designed to meet. At this stage, new
criteria not originally considered may be reviewed.

•COMMUNICATE THE PROBLEM, PROCESS, AND SOLUTION. Students should
present their results to students, teachers, and others in a variety of ways, such as orally,
in writing, and in other forms—including models, diagrams, and demonstrations.

Understandings about Science and Technology

•Scientists in different disciplines ask different questions, use different methods of
investigation, and accept different types of evidence to support their explanations. Many
scientific investigations require the contributions of individuals from different disciplines,
including engineering. New disciplines of science, such as geophysics and biochemistry
often emerge at the interface of the two older disciplines.
•Science often advances with introduction of new technologies. Solving technological
problems often results in new scientific knowledge. New technologies often extend the
current levels of scientific understanding and introduce new areas of research.
•Creativity, imagination, and a good knowledge base are all required in the work of
science and engineering.
•Science and technology are pursued for different purposes. Scientific inquiry is driven
by the desire to understand the natural world, and technological design is driven by the
need to meet human needs and solve human problems. Technology, by its nature, has a
more direct effect on society than science because its purpose is to solve human
problems, help humans adapt, and fulfill human aspirations. Technological solutions may
create new problems. Science by its nature, answers questions that may or may not
directly influence humans. Sometimes scientific advances challenge people's beliefs and
practical explanations concerning various aspects of the world.

Content Standard F: Science In Personal And Social Perspectives

Natural Resources

• Human populations use resources in the environment in order to maintain and improve their existence. Natural resources have been and will continue to be used to maintain human populations.

• The earth does not have infinite resources; increasing human consumption places severe stress on the natural processes that renew some resources, and it depletes those resources that cannot be renewed.

• Humans use many natural systems as resources. Natural systems have the capacity to reuse waste, but that capacity is limited. Natural systems can change to an extent that exceeds the limits of organisms to adapt to naturally or humans to adapt technologically.

Environmental Quality

•Natural ecosystems provide an array of basic processes that affect humans. Those processes include maintenance of the quality of the atmosphere, generation of soils, control of the hydrologic cycle, disposal of wastes, and recycling of nutrients. Humans are changing many of these basic processes, and the changes may be detrimental to humans.

•Materials from human societies affect both physical and chemical cycles of the earth.

• Many factors influence environmental quality. Factors that students might investigate include population growth, resource use, population distribution, overconsumption, the capacity of technology to solve problems, poverty, the role of economic, political, and religious views, and different ways humans view the earth.

Natural and Human-Induced Hazards

• Human activities can enhance potential for hazards. Acquisition of resources, urban growth, and waste disposal can accelerate rates of natural change.

• Natural and human-induced hazards present the need for humans to assess potential danger and risk. Many changes in the environment designed by humans bring benefits to society as well as cause risks. Students should understand the costs and trade-offs of various hazards—ranging from those with minor risk to a few people to major catastrophes with major risk to many people. The scale of events and accuracy with which scientists and engines can (and cannot) predict events are important considerations.

Overview:
This module contains a series of application, inquiry-based, problems for advanced high school general chemistry students on fuel cell research for cars of the future. The problems cover various topics including stoichiometry, kinetic molecular theory, bonding/intermolecular forces, kinetics, equilibrium, thermodynamics and electrochemistry. The problems are designed to provide students with an opportunity to see how simple concepts from general chemistry can be applied to the development of important real world applications involving energy and environmental problems, specifically possible fuels for cars of the future. The module problems are organized into three sections. Concise introductions are used to put the problems into their proper context. Section 1 examines some of the energy efficiency and environmental impact

issues associated with using hydrogen, one possible fuel of the future, instead of gasoline to power cars. Section 2 examines the difficulties of having a gas phase fuel, such as hydrogen, instead of a liquid phase fuel. Section 3 addresses some of the basic electrochemistry of hydrogen and direct methanol fuel cells.

Purpose:

Developing problem solving abilities is universally recognized as important skill for chemistry students. Ultimately we would like students to be able to make the connections not only between the different concepts learned within a course, but also between the theoretical information they have learned in the classroom and its practical applications. The problems in this module are designed to help students improve their problem solving skills and help them make connections between previously learned concepts. By taking an inquiry approach to investigating a topic of interest to most teenagers (cars), it is hoped that students will be able to see how concepts learned in the course can be applied to address important societal issues. The problems in this module could be used as extra practice within a traditional unit or at the end of the course for review and reinforcement or as cumulative test questions. In addition, individual questions or small blocks could be used within a traditional unit.

Learning Objectives:

After completing this lesson, students will be able to:

- Apply concepts from stoichiometry, kinetic molecular theory, bonding/intermolecular forces, kinetics, equilibrium, thermodynamics and electrochemistry to solving "real world" problems.

- Understand while it is possible to convert energy from one form to another it is not possible to do so with 100% work efficiency.

- Understand that fuel cells have the potential to be more efficient than combustion reactions because less energy is lost as heat.

- Use resources such as the CRC handbook, textbook tables or internet sources to acquired information needed to solve a problem.

- Understand that combining knowledge from many different areas of chemistry is usually required to solve real research questions.

- Understand that there are no simple, single perfect solutions to complex technology problems. Each possible solution generally has tradeoffs that must be evaluated.

EDUCATION MODULE ACTIVITIES

General Introduction for Possible Fuels for Cars of the Future

At the present time, almost all of our cars are powered by the combustion of gasoline. Gasoline is a mixture of hydrocarbon chains derived from petroleum. Petroleum is an example of a non-renewable resource in that once it is used up it cannot be easily regenerated. As our petroleum supplies dwindle during the twenty-first century, we will need to explore different methods of producing energy. Scientists in government laboratories such as the National Renewable Energy Laboratory (NREL) and universities and in the automobile industry are researching different options for powering of cars of the future. At the present time, one branch of research is focused on replacing combustion gasoline engines with fuel cells. Fuel cells convert the most of the energy from oxidation of fuel directly into an electric current instead releasing all of the energy as heat and light as in a combustion reaction. Fuel cells differ from a battery in that the reactants (fuel) are continually resupplied. While the power output from a conventional battery will eventually drop and go to zero, a fuel cell will theoretically continue to produce electricity at a constant level as long as fuel is resupplied. Two potential fuels that are currently the subject of intensive investigation are hydrogen and methanol. Both fuels not only store large amounts of energy, but also have the potential to be renewable. (For example, hydrogen could be obtained from water or methanol and methanol can be obtained from biomass). Automakers hope to have the first fuel cell powered cars on the market by the year 2004. More research remains to be done in order to increase the efficiency and cost-effectiveness of fuel cells. In addition, when designing new technologies, potential environmental impacts must be considered. The questions below will require you to apply concepts that you have learned in general chemistry to addressing some of the issues that fuel cell designers must take into account.

Question: What is the difference between a renewable and a nonrenewable energy source?

SECTION #1:THERMOCHEMISTRY (Questions #1-12), KINETICS **AND EQUILIBRIUM AND BONDING (Questions #13-16)**

COMPARISON OF GASOLINE VS. HYDROGEN
Introduction
In deciding which alternative fuel would be better for use in a car there are a number of different factors that must be considered. One factor is the energy theoretically available from the fuel. Ideally, we would like a fuel to store a large amount of energy in a small

mass and a small volume. A second factor is how efficiently we can actually use the stored energy. A third factor is the potential environmental impact of our choices. Hydrogen is being advocated by many researchers as a possible replacement fuel for gasoline. In this section you consider each of the above factors for hydrogen and for gasoline.

COMPARISON # 1: HOW MUCH ENERGY IS STORED PER GRAM OF FUEL?

One method for comparing potential utility of different energy sources involves comparing the energy that could be produced per gram of fuel burned. In the problems below you will use the standard enthalpies of formation to calculate the energy per gram burned for gasoline, hydrogen.

1) Use the a thermodynamic table in your textbook or the CRC handbook to look up the standard enthalpies of formation for the following substances:

GASOLINE: 2,2,4-trimethlypentane (isooctane), C_8H_{18}

C_8H_{18} Note: gasoline is actually a mixture of different hydrocarbon chains and isomers, however isooctane is the predominant species, so we will use this to estimate a value for gasoline.
CARBON DIOXIDE GAS: CO_2 ; WATER, H_2O (g) – product water will be converted to steam under the conditions of the combustion reaction (vaporization of water therefore using up some of the energy produced from the reaction).

Note: CRC values are in kcal/mol while many textbooks now use kJ/mol. The conversion is: 4.18k J = 1 k cal

2) Write balanced chemical equations for the complete combustion (reaction with O_2) for each potential fuel, isooctane, and hydrogen.

3A) Use the standard enthalpies of formation given in your textbook to calculate out the ∆H of reaction in kJ for isooctane and hydrogen.

3B) Use your answer to 3A and the appropriate coefficients of the balanced equations to calculate the kJ released per mole of fuel burned.

3C) Use your result from 3B and the molar mass of each fuel to calculate the energy per gram for each fuel. Which fuel gasoline or hydrogen, stores more energy per gram for combustion?

COMPARISON 2: HOW MUCH ENERGY CAN YOU ACTUALLY USE? COMPARISON OF ENERGY EFFICIENCY OF GASOLINE COMBUSTION VS. ENERGY RELEASED IN A HYDROGEN FUEL CELL.

<u>Introduction</u>

Today's internal combustion engines utilize the energy released from burning of gasoline. Hydrogen fuel cells utilize energy from oxidation. The difference is that in a fuel cell the chemical energy is essentially converted directly into electrical energy at relatively low temperatures (70° – $80\ ^\circ C$). How does the overall energy efficiency of burning gasoline at high temperatures compare to the efficiency of electrochemically oxidizing hydrogen at lower temperatures?

ENERGY EFFICIENCY OF A TYPICAL GASOLINE COMBUSTION ENGINE

4) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of gasoline is burned. Given 1 gallon = 3.8 L, density of C_8H_{18} = 0.6919 g/mL

5) If 2.9 x 10^4 kJ are actually converted to mechanical energy inside the car engine, calculate the approximate efficiency of the combustion of gasoline for powering a car.

6) Is all of the energy produced by the combustion utilized by the engine? If not what has happened to the energy that has been lost?

EFFICIENCY OF A TYPICAL HYDROGEN FUEL CELL

7A) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of hydrogen GAS is electrochemically oxidized. (Look up density of hydrogen gas in CRC handbook.)

7B) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of LIQUID hydrogen is electrochemically oxidized. Given: 1 gallon = 3.8 L, Look up density of LIQUID hydrogen in CRC handbook. *Note: Not considered in this calculation is the 30% energy penalty that would be required to liquefy hydrogen gas.*

8) To convert the stored chemical energy in a hydrogen fuel cell to mechanical energy of the driving the car requires three steps. Since it is impractical to store a sufficiently large volume of hydrogen gas in a car, a "reformer" is included in most designs. A reformer is a device that can produce hydrogen from a liquid fuel source such as methanol at the time it is needed to operate the fuel cell. Unfortunately, due to the difficulties in preparing pure hydrogen gas for the fuel cell, this process is only about 50% energy efficient. Current fuel cells can be up to 80% efficient. The conversion of electrical energy to mechanical energy in the motor is approximately 80% efficient.

Using the efficiencies for each step given above, calculate an approximate overall efficiency for a reformer fueled hydrogen fuel cell.

9) Is all of the energy produced by the electrochemical oxidation utilized by the engine? If not, what has happened to the energy that has been lost?

COMPARISON OF THE EFFICIENCIES AND CONNECTION TO THE FIRST AND SECOND LAWS OF THERMODYNAMICS

10) Which fuel stores more energy per gallon, gasoline or hydrogen?

11) Does either process operate with efficiencies over 100%? Does either process operate with an efficiency of 100 %? State the first and second laws of thermodynamics and use them to explain these results.

12A) Which system, gasoline combustion or fuel cell oxidation, is more efficient?

ENVIRONMENTAL IMPACT COMPARISON

One major difference between conventional gasoline combustion engines and fuel cells is the operating temperatures. Conventional gasoline combustion engines operate at very high temperatures (approximately 500 ^{o}C) while a hydrogen fuel cell can operate at temperatures of 70-80°C. This temperature difference has important consequences for the production of nitrogen oxides, such as NO and NO_2. Nitrogen oxides can react with moisture in the atmosphere to form acid rain. Nitrogen oxides can react to produce ozone. If ozone production occurs in the lower atmosphere it can cause a number of health problems including respiratory difficulties. The source of oxygen in the oxidation of either a gasoline combustion engine or in a hydrogen fuel cell is air. Air is a mainly mixture of nitrogen, N_2 and oxygen, O_2. Nitrogen monoxide, NO, can form by the reaction of N_2 and O_2 from the air.

$$N_{2(g)} + O_{2(g)} \text{ ---}\rightarrow 2 \text{ NO}$$

Reaction Kinetics

13) Draw Lewis Dot structures for N_2, O_2, and NO.

14) At low temperatures (such as fuel cell conditions) the reaction between N_2 and O_2 is extremely slow.

14A) If the reaction rate at low temperatures is very slow, what does this suggest about the height of the activation barrier for this reaction?

14B) Look at the Lewis Dot Structure for N_2. Can you speculate as to why the activation energy for this reaction is so high?

14C) What will happen to the rate of this reaction at high temperatures (such as those found in gasoline combustion engines)? How does collision theory explain this result?

14D) Once formed in the atmosphere, NO rapidly reacts with oxygen to form nitrogen dioxide, NO_2 a brown gas associated with smog.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

In addition to contributing to the formation of acid rain, NO_2 is associated with the light-catalyzed formation of ozone, O_3, in the lower atmosphere. Ozone in the lower atmosphere is highly undesirable because it can irritate the eyes and is harmful to the respiratory system.

Look at the Lewis Dot structure for NO. What feature of this structure suggests that NO might be highly reactive?

Reaction Equilibrium

15) The equilibrium for the reaction between nitrogen and oxygen lies far to the left at low temperatures.

$$N_{2(g)} + O_{2(g)} + heat \rightarrow 2\ NO_{(g)}$$

15A) If the equilibrium lies far to the left at low temperatures what does this mean about the amount of NO that will be present at equilibrium at fuel cell operating temperatures?

15B) The reaction is endothermic as written. Use Le Chatelier's principle to predict the effect on equilibrium NO concentration of having high temperatures for this reaction.

15C) Overall, which set of conditions will result in a greater production of NO, the conditions in a gasoline combustion engine or the conditions in a hydrogen fuel cell?

16) Look back at the balanced chemical equations you wrote for the combustion of gasoline and for hydrogen in question #1.

16A) What are the products for the combustion of gasoline? What is the product for the combustion of hydrogen?

16B) Which product of the combustion of gasoline is considered to be potentially an environmental concern and why?

16C) Although the fuel cell reaction itself does not produce carbon dioxide, if a carbon-based fuel such as methanol is used in a reformer to produce the hydrogen gas in the fuel

containing fuel is used in the reformer, carbon dioxide will be produced. A typical reformer reaction for methanol is given below:

$$CH_3OH + H_2O \rightarrow CO_2 + 3 H_2$$

Comparing the coefficients of the balanced chemical equation for this reaction and the combustion of isooctane which reaction do you think releases more CO_2?

SUMMARY COMPARISON OF GASOLINE VS. HYDROGEN
AS A FUEL SOURCE FOR CARS

17) Briefly summarize your results as to which process combustion of gasoline or fuel cell hydrogen oxidation:
  A) Stores more energy per gram

  B) Stores more energy per gallon

  C) Is more easily stored?

  D) Can more efficiently utilize its stored energy?

  E) Produces more environmentally friendly emissions?

  18) With all that hydrogen has going for it, why are we not all driving hydrogen powered cars?

SECTION 2: STOICHIOMETRY/ INTERMOLECULAR FORCES/KINETIC MOLECULAR THEORY

COMPARISON OF MASS OF HYDROGEN IN GAS VS. LIQUID FORM

Introduction to this Problem:
    If hydrogen is to be used as a fuel source in a car, an immediate question arises as to how the hydrogen is to be supplied. As you know, hydrogen is a gas at room temperature, while gasoline fuel is a liquid. In the problems below you will explore some issues relating to how to store hydrogen.

1) Which would be easier, dispensing a gas or a liquid? Explain.

2) Compare gaseous H_2 vs. liquid H_2 on the molecular level using four characteristics: *Kinetic Energy, Strength of Intermolecular attractions, Distance between molecules, and molecular organization.*

3A) Use the CRC Handbook of Chemistry and Physics to look up the boiling point of hydrogen gas, and the density values for hydrogen gas and hydrogen liquid.

3B) Calculate, using the density equation, the mass of hydrogen gas that could be stored in a car with a 15-gallon tank. (Recall 1 gallon = 3.8 L.)

3C) Calculate, using the density equation, the mass of hydrogen liquid that could be stored in a car with a 15-gallon tank.

3D) Which phase of hydrogen can store a greater mass? Is the difference close?

3E) What volume of H_2 gas, in liters, and in gallons, would you need to store the same mass of molecules present in 15.0 L of liquid H_2? Is this volume practical for a car?

3F) Consider the boiling temperature of hydrogen at 1 atmosphere pressure. Is storing hydrogen as a liquid in your car a viable option? Explain.

COMPARISON OF THE NUMBER OF HYDROGEN ATOMS IN A LITER OF LIQUID HYDROGEN TO A LITER OF LIQUID METHANOL.

Due the difficulties of storing large amounts of hydrogen as either a gas or a liquid for use in fuel cells, it has been proposed to store hydrogen in other chemical compounds. One molecule which been commonly proposed to store hydrogen is methanol, CH_3OH. Methanol is a liquid at room temperature so it has high energy density compared to hydrogen gas. The hydrogen could then be chemically extracted from the methanol molecules (in a device called a reformer) to produce hydrogen when needed to operate the fuel cell. How much hydrogen can you get from methanol? In the problems below we will compare the number of hydrogen atoms that could be stored in a liter of methanol molecules compared to the number of hydrogen atoms that could be stored in a liter of liquid hydrogen.

Why is a small molecule like methanol a liquid at room temperature?
4) Explain, using principles of bonding /intermolecular forces, why methanol is a liquid at room temperature while H_2 and methane, CH_4 (also a high-energy fuel) are gases?

Comparison of amount of hydrogen in liquid H_2 and CH_3OH

5A) Use the CRC handbook to look up the density of liquid methanol. (See question #3A for density of liquid hydrogen.

5B) Use the density equation to determine the masses in grams of each substance that would be present in 1 liter of pure liquid.

5C) Calculate the # of MOLES OF H_2 MOLECULES and MOLES CH_3OH molecules present in 1 liter.

5D) Calculate the # of H ATOMS present in 1 liter of pure H_2 liquid and 1 liter of pure methanol.

5E) Which contains the greater number of H ATOMS in a liter, pure H_2 liquid or pure methanol liquid? On the basis of amount of hydrogen present, is methanol a reasonable source of hydrogen?

REFORMER REACTION STOICHIOMETRY

A typical reformer reaction, which involves the breakdown of methanol to release hydrogen gas, is given below:

$$CH_3OH + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$$

6) Balance the equation.

7) Calculate the # of grams of H_2 which could be produced by the reaction of 1 gallon of methanol. Density of methanol = 0.79 g/mL; 1 gallon = 3.8 L.

Note: In reality, what you have calculated is a theoretical yield. The actual yield will be lower, in part because of competing reaction pathways (i.e. reactants combining to give different products than those given above compete).

8) Using methanol as a reformer to produce H_2 gas solves the problem of being able to utilize a renewable, easily transferable, high-density liquid fuel, however it also creates other problems.

8A) What do the think the impact will be on the overall energy efficiency of the process of having to run an additional reaction?

8B) What do the think the impact will be on the overall energy efficiency of the process of having to separate the desired product, H_2, from a mixture of other materials?

8C) In a fuel cell with no reformer the only product of the reaction of hydrogen and oxygen is water. In a fuel cell with a reformer reaction for methanol written above

produced CO_2 gas as a product. **What are the potential environmental concerns about releasing more CO_2 into the atmosphere?**

SECTION 3: ELECTROCHEMISTRY

POSSIBLE FUELS FOR CARS OF THE FUTURE

Introduction: Fuel Cells vs. Conventional Batteries

A conventional battery is a system that converts the energy from a chemical reaction directly into electricity. As petroleum supplies diminish, researchers are looking for ways to make existing gasoline powdered cars more efficient and eventually, alternatives to replace gasoline cars altogether. At the present time electric battery powered cars have been produced, however the driving range and power performance of these vehicles is well below the standards consumers have come to expect. Even if advances in engineering are made, it is very unlikely that a vehicle powered only by a conventional battery system will be the solution to our energy needs. Currently, some auto manufacturers such as Honda and Toyota, have introduced hybrid vehicles which are a combination of a gasoline combustion engine and a battery system. The combination of these two designs can produce greatly improved energy efficiency and lower emissions, however hybrid vehicles are still ultimately dependent on gasoline for driving range and power performance. The long-term solution to producing vehicles which are not dependent on non-renewable petroleum products may be hydrogen or methanol fuel cell powered vehicles.

Fuel cells convert most of the energy from oxidation of fuel directly into an electric current instead of releasing the all of the energy as heat as in a combustion reaction. Fuel cells differ from batteries in that the reactants (fuel) are continually resupplied. While the power in a conventional battery will eventually drop and go to zero, a fuel cell will theoretically continue to produce electricity at a constant level as long as fuel is resupplied. Fuel cell systems that are currently being developed have the potential to be far more efficient than gasoline combustion engines, can utilize renewable fuels sources and produce more environmentally friendly emissions. In this module we will investigate some of the electrochemistry of fuel cells.

<u>Hydrogen Fuel Cells</u>
The reaction of hydrogen and oxygen to form water is a leading option to power cars in the future.

$$2 H_2 + O_2 \rightarrow 2 H_2O$$

1) When hydrogen gas is placed in a balloon and a candle is held underneath the balloon, what will happen? Is energy being absorbed or released?

2) What is the difference between carrying this reaction as described above and carrying the same reaction out in a fuel cell?

3) Assign oxidation numbers to H_2, O_2 and the H and O in H_2O.

4) What species is oxidized and what species is reduced is this reaction?

5) One of the half-reactions for this system is $4 H^+ + O_2 + 4e^- \rightarrow 2 H_2O$

5A) Does the above half-reaction represent oxidation or reduction?

5B) Does the process above take place at the anode or the cathode?

5C) Write the other half reaction involving H_2.

5D) Use the table of standard reduction potentials from your textbook to calculate E^o cell for this reaction.

5E) How does the E^o that you calculated above compare to the voltage measured in a working cell with current flowing?

DIRECT METHANOL FUEL CELL

Another option replacing gasoline combustion engines would be a methanol fuel cell. In a methanol fuel cell, methanol, CH_3OH, reacts with oxygen to produce carbon dioxide and water. $2 CH_3OH + 3 O_2 ----\rightarrow 2 CO_2 + 4H_2O$

6) Assign oxidation numbers to the C in CH_3OH and the C in CO_2.

7) Assign oxidation numbers to the O in O_2 and the O in H_2O.

8) What species is being oxidized and what is being reduced in this reaction?

9) Write a balanced half-reactions in acidic solution.

10) If the standard reduction potential for the conversion of CO_2 to CH_3OH is 0.03 V, and the standard reduction potential for the conversion of O_2 to H_2O is 1.23 V, calculate E^o cell.

11) One project being investigated at the National Renewable energy Labs in the possibility of recycling CO_2 by converting it back to methanol.

11A) From an environmental perspective would be the advantages of being able to capture CO_2 exhaust and recycle back to methanol?

11B) A long-term goal is to be able to use a renewable energy source such as solar energy to power this process. What is the theoretical energy in volts, that would have to be supplied to reconvert CO_2 to CH_3OH?

11C) In practice, the actual energy to drive electrolysis reactions is higher than the theoretical voltage. The extra voltage required to drive the reaction is called the overvoltage. The reasons for overvoltage are complex, but one very important factor Is slow kinetics at the electrode. Thus one of the most important research ideas is the development of electrochemical catalysts for the reactions at the anode and the cathode.

What is a catalyst? In general, how does a catalyst work?

SAMPLE SOLUTIONS TO MODULE PROBLEMS

SECTION 1: HYDROGEN VS. GASOLINE

1) GASOLINE: C_8H_{18} Note: gasoline is actually a mixture of different hydrocarbon chains and isomers, however isooctane is the predominant species. (isooctane, 2,2,4, trimethylpentane) ΔH = -53.57 kcal/mol = -223.9 kJ/mol

HYDROGEN: H_2 ΔH^f_o =0 (elemental form)

CO_2 ΔH^f_o = - 94.051 kcal/mol = -393.1 kJ/mol
 H_2O ΔH^f_o = -57.796 kcal/mol = - 241.6 kJ/mol
4.18 kJ = 1 kcal

GASOLINE: C_8H_{18} Note: gasoline is actually a mixture of different hydrocarbon chains and isomers, however isooctane is the predominant species. (isooctane, 2,2,4, trimethylpentane) ΔH = -53.57 kcal/mol = -223.9 kJ/mol

HYDROGEN: H_2 ΔH^f_o =0 (elemental form)

CO_2 ΔH^f_o = - 94.051 kcal/mol = -393.1 kJ/mol
 H_2O ΔH^f_o = -57.796 kcal/mol = - 241.6 kJ/mol
4.18 kJ = 1 kcal

2) Write balanced chemical equations for the complete combustion (reaction with O_2) for each potential fuel.

 Isooctane: $2 C_8H_{18}$ + $25 O_2$ $\rightarrow$ $16 CO_2$ + $18 H_2O$

Hydrogen: $2 H_2$ + O_2 $\rightarrow$ $2 H_2O(l)$

3A) Use the standard enthalpies of formation calculate out the ΔH of reaction in kJ for each of the above fuels.

GENERAL EQUATION: ΔH_o^f rxn $= \sum \Delta H_o^f$ products - $\sum \Delta H_o^f$ reactants

Note: Standard enthalpy for O_2 is all calculations is 0, since it is in its elemental form.

GASOLINE:
  [(16 mol CO_2)(-393.1 kJ/mol) + (18 mol H_2O)(-241.6 kJ/mol)]
– [(2 moles C_8H_{18})(–223.9 kJ/mol)] = - 1.02 x 10^4 kJ

HYDROGEN: (2 mol H_2O)(-241.6 kJ/mol) = -571.2 kJ

3B) Use your answer to 3A and the appropriate coefficients of the balanced equations to calculate the kJ released per mole of fuel burned.

GASOLINE: $\dfrac{- 1.02 \times 10^4 \text{ kJ}}{2 \text{ moles } C_8H_{18}}$ =   - 5.10 x 10^3 kJ/mol

HYDROGEN: Could use value directly from table since H_2O is only product of hydrogen combustion or could calculate:
                    $\dfrac{-571.2 \text{ kJ}}{2 \text{ mol}}$ = -241.6 kJ/mol

3C) Use your result from 3B and the molar mass of each fuel to calculate the energy per gram for each fuel. Which fuel, gasoline or hydrogen, stores more energy per gram for combustion?

GASOLINE: - 5.10 x 10^3 kJ/mol ÷ 115 g/mol = - 44.3 kJ/g

HYDROGEN**:** -241.6 kJ/mol ÷ 2.02 g/mol = - 119.6 kJ/g

HYDROGEN STORES MORE ENERGY PER GRAM. However there is more to the story than just energy per gram. One must also consider how the hydrogen can be stored and how efficiently it can be used. The issues are addressed in subsequent sections.

CRITERIA 2: COMPARISON OF ENERGY EFFICIENCY AND ENVIRONMENTAL IMPACT OF COMBUSTION OF GASOLINE VS. ENERGY RELEASED IN A FUEL CELL.

EFFICIENCY OF A TYPICAL GASOLINE COMBUSTION ENGINE

4) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of gasoline is burned. Given 1 gallon = 3.8 L, density of C_8H_{18} = 0.6919 g/mL

Simplest solution: 3.8 L C_8H_{18} (691.9 g/L) (-44.3 kJ/g) = -1.16 x10^5 kJ

5) If   2.9 x 10^4 kJ are actually converted to mechanical energy inside the car engine, calculate the approximate efficiency of the combustion of gasoline for powering a car.

% efficiency = $\underline{\text{useful energy}}$ x 100% = $\underline{\text{2.9 x } 10^4 \text{ kJ}}$ x 100% = 25 %
                    total energy   1.16 x10^5 kJ

6) Is all of the energy produced by the combustion utilized by the engine? If not what has happened to the energy that has been lost?
NO; 75% of energy is wasted as heat.

EFFICIENCY OF A TYPICAL HYDROGEN FUEL CELL

7A) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of hydrogen GAS is electrochemically oxidized.

3.8 L ((0.08988 g/L) (119.6 kJ/g) = 40.8 kJ

7B) Using your results from problem #3, calculate the energy in kJ that would be released when 1 gallon of LIQUID hydrogen is electrochemically oxidized. Given 1 gallon = 3.8 L, density of H_2 liquid = 70.9 g/L. *Note: Not considered in this calculation is the 30% energy penalty that would be required to liquefy hydrogen gas* 3.8 L (70.9 g/L)(119.6 kJ/g) = 3.2 x 10^4 kJ

8) To convert the stored chemical energy in a hydrogen fuel cell to mechanical energy of the driving the car requires three steps. Since it is impractical to store a sufficiently large volume of hydrogen gas in a car, a "reformer" is included in most designs. A reformer such as methanol, acts as a liquid source to produce hydrogen gas in a chemical reaction at the time it is needed to operate the fuel cell. Unfortunately, due to the difficulties in preparing pure hydrogen gas for the fuel cell this process is only about 50% energy efficient. Current fuel cells can be up to 80% efficient. The conversion of electrical energy to mechanical energy in the motor is approximately 80% efficient.
Using the efficiencies for each step given above, calculate an approximate overall efficiency for a reformer fueled hydrogen fuel cell.

Overall efficiency = product of efficiencies of each step; 0.5 x 0.8 x 0.8 = 0.32 or 32%

9) Is all of the energy produced by the electrochemical oxidation utilized by the engine? If not, what has happened to the energy that has been lost?

NO; About 68% of the energy is lost as heat.

COMPARISON OF THE EFFICIENCIES AND CONNECTION TO THE FIRST AND SECOND LAWS OF THERMODYNAMICS

10) Which fuel stores more energy per gallon gasoline or liquid hydrogen?
GASOLINE; 1.16 x 10^5 J vs. 3.2 x 10^4 (not including 30% energy penalty to liquefy hydrogen). Gaseous hydrogen would have far less than gasoline since gaseous hydrogen has a far lower density (0.0899g/L).

11) Does either process produce operate with efficiencies over 100% ? Does either process operate with an efficiency of 100 %? State the first and second laws of thermodynamics and use them to explain these results.

Both systems operate with efficiencies well under 100%.

First Law of Thermodynamics – (Conservation of Energy) – energy can be neither created nor destroyed.

Translation: You can't win. (You can't get more energy out than you put in).

Second Law of Thermodynamics – entropy (disorder) of the universe for a spontaneous process increases. One implication of this law is that heat energy tends to become more spread out and less concentrated and therefore less available for work.

Translation: You can't even break even, i.e. you always lose. (You can't even get all of the energy that you put in to be converted to useful work. Some of the energy will always be lost as heat.)

Temperatures inside a combustion engine typically approximately 500 $^{\circ}C$. In contrast, it is possible to run a hydrogen fuel cell at a temperature of approximately 70$^{\circ}C$.

12) Which system, gasoline combustion or fuel cell oxidation, is more efficient?
Hydrogen Fuel Cell; Electrochemical fuel cells also intrinsically use the chemical energy from the reaction more directly and efficiently than combustion.

Reaction Kinetics

13) Draw Lewis Dot structures for N_2, O_2, and NO.
N_2 has a triple bond between the N atoms, with 1 nonbonding pair of electrons on each N. O_2 has a double bond between the O atoms, with 1 nonbonding pair of electrons on each O. (Note: Actual bonding in O2 is more complex than is suggested by Lewis Dot structure. The molecular orbital analysis of the bonding correctly predicts the paramagnetic properties of O2 by assigning two unpaired electrons the $2\pi^*$ orbitals.)
NO is a complicated structure to draw an accurate Lewis dot structure for because it has an odd number (11) of valence electrons. There are multiple contributing forms of the resonance hybrid that can be drawn. The two simplest ones to draw (and the ones the students will likely produce are):
1) 3 nonbonding electrons assigned to N, a double bond between the N and O and 4 nonbonding electrons assigned to O.
2) 4 nonbonding electrons assigned to N, a double bond between N and O and 3 nonbonding electrons assigned to O.

Molecular orbital theory calculations, which are confirmed by experiment, suggest that the actual resonance hybrid can be thought as having a bond order of 2.5 between the N and the O.

14) At low temperatures (such as fuel cell conditions) the reaction between N_2 and O_2 is extremely slow.

14A) If the reaction rate at low temperatures is very slow, what does this suggest about the height of the activation barrier for this reaction?

Activation energy must be relatively high.

14B) Look at the Lewis Dot Structure for N_2. Can you speculate as to why the activation energy for this reaction is so high? This reaction will require the breaking of the triple bond between the nitrogen atoms, which requires a great deal of energy.

14C) What will happen to the rate of this reaction at high temperatures (such as those found in gasoline combustion engines? How does collision theory explain this result? As the temperature increases, the fraction of molecules with energy greater than or equal to the activation energy increases, therefore the rate of the reaction will increase.

14D) Once formed in the atmosphere NO rapidly reacts with oxygen to form nitrogen dioxide, NO_2 a brown gas associated with smog.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Look at the Lewis Dot structure for NO. What feature of this structure suggests that NO might be highly reactive?

NO molecule is a free radical, that is, it has an unpaired electron. Species with unpaired electrons are generally highly reactive.

Reaction Equilibrium

The equilibrium for the reaction between nitrogen and oxygen lies far to the left at low temperatures.

$$N_{2(g)} + O_{2(g)} + heat\ \text{--}\rightarrow 2\ NO_{(g)}$$

15A) If the equilibrium lies far to the left at low temperatures what does this mean about the amount of NO that will be present at equilibrium at fuel cell operating temperatures? NO concentration will be very small.

15B) The reaction is endothermic as written. Use Le Chatelier's principle to predict the effect on equilibrium NO concentration of having high temperatures for this reaction. Addition of heat should shift the equilibrium to the right producing more NO.

15C) Overall, which set of conditions will result in a greater production of NO, the conditions in a gasoline combustion engine or the conditions in a hydrogen fuel cell?

Gasoline combustion engine. Current vehicles require a catalyst system to remove nitrogen oxide products from the engine exhaust. The systems are highly efficient, but not perfect. Small amounts of nitrogen oxides are still released to the atmosphere.
 The amounts of nitrogen oxides produced in a hydrogen fuel cell are so trivial that catalyst exhaust systems for removing nitrogen oxides are not needed

16A) What are the products for the combustion of gasoline? What is the product for the combustion of hydrogen? Gasoline: $CO_2 + H_2O$; Hydrogen: H_2O

16B) Which product of the combustion of gasoline is considered to be potentially an environmental concern and why? CO_2; It is a greenhouse gas and increasing atmospheric CO_2 levels have been correlated to an increase in global temperatures.

16C) Although the fuel cell reaction itself does not produce carbon dioxide, if a carbon-based fuel such as methanol, is used in the reformer to produce the hydrogen gas carbon dioxide will be produced. A typical reformer reaction for methanol is given below:

$$CH_3OH + H_2O \rightarrow CO_2 + 3 H_2$$

Comparing the coefficients of the balanced chemical equation for this reaction and the combustion of isooctane which reaction do you think releases more CO_2?

Gasoline combustion will release more CO_2. Each mole of isooctane burned releases 8 moles of CO_2 while each mole of CH_3OH reacted produces one mole of CO_2. This comparison is overly simplified since in reality more methanol moles would have to be reacted than moles of gasoline to produce the energy to run the car. Even correcting for this fact, however, gasoline powered internal combustion engines release more CO_2.

SUMMARY COMPARISON OF GASOLINE VS. HYDROGEN AS A FUEL SOURCE FOR CARS

17) Briefly summarize your results as to which process combustion of gasoline or fuel cell hydrogen oxidation:
    A) Stores more energy per gram. HYDROGEN
    B) Stores more energy per gallon. GASOLINE
    C) Is more easily stored? GASOLINE
    D) Can more efficiently utilize its stored energy? HYDROGEN
    E) Produces more environmentally friendly emissions? HYDROGEN

18) With all that hydrogen has going for it, why are we not all driving hydrogen powered cars? HYDROGEN STORAGE PROBLEM: Hydrogen is a gas. Gases do not have high energy densities. The solutions to the hydrogen storage problem are far from perfect at this point. This issue will be explored further in the next section.
COST; Our infrastructure is still set up to produce gasoline and gasoline burning cars much more cheaply than hydrogen fuel cells. If the efficiency continues to improve for hydrogen fuel cell cars and if gasoline prices continue to climb, hydrogen fuel cell cars will become more cost competitive. Some automakers are projecting marketing hydrogen fuel cell cars in 2004 or 2005.

TEACHER'S SAMPLE SOLUTIONS:

SECTION 2: STOICHIOMETRY/ INTERMOLECULAR FORCES/KINETIC MOLECULAR THEORY

COMPARISON OF MASS OF HYDROGEN IN GAS VS. LIQUID FORM

1) Which would be easier, dispensing a gas or a liquid? Explain.

LIQUIDS. Liquids are much more easily transferred between a storage pump and your car's tank. Gases would require a completely closed system at all times so that the gas molecules wouldn't escape. Also additional safety complications arise in having to consider the dangers of high pressures and the higher flammability of gases vs. liquids.

2) Compare gaseous H_2 vs. liquid H_2 on the molecular level using four characteristics: Average *Kinetic Energy, Strength of Intermolecular attractions, Distance between molecules, and molecular organization.*

	H_2 gas	H_2 liquid
Average Kinetic Energy:	High	Low
Strength of Intermolecular Forces	None (Ideal gas)	Weak (London Attractions Forces) but significant enough To hold molecules together.
Distance between molecules	Very large	Relatively little
Molecular Organization	None (Ideal gas)	"Pockets" of organization

3A) Use the CRC Handbook of Chemistry and Physics to look up the boiling point of hydrogen gas, and the density values for hydrogen gas and hydrogen liquid.
Density of H_2 gas = 0.08988 g/L; Density of H_2 liquid = 70.8 g/L
b.p. of H_2 = -252.7 ^{o}C.
3B) Calculate, using the density equation, the mass of hydrogen gas that could be stored in a car with a 15-gallon tank. (Recall 1 gallon = 3.8 L.)

SOLUTION: 15 gal H_2 $\underline{(3.8\ L)}$ = 57 L ; D = m/V => m = D/V
$\qquad\qquad\qquad$ (1 gal)

H_2 gas: (0.08988 g/L) (57 L) = 5.1 g

3C) Calculate, using the density equation, the mass of hydrogen liquid that could be stored in a 15-gallon tank.

H_2 liquid: (70.8 g/L) (57 L) = 4.0 x 10^3 g

3D) Which method of storing hydrogen would store a greater mass? H_2 liquid

3E) What volume of H_2 gas, in liters, and in gallons, would you need to store the same mass of molecules present in 15.0 L of liquid H_2? Is this volume practical for a car?

V = m/D = 4.0 x 10^3/ 0.08988 g/ L = 4.5 x10^4 L = 12000 gallons. NO ! This is a striking example of the difference in volume between liquid and gas phases!

3F) Consider the boiling temperature of hydrogen at 1 atmosphere pressure. Is storing hydrogen as a liquid in your car a viable option ? Explain.
NO. Since the boiling point of H_2 = -252.7 ^{o}C., only a little over 20 ^{o}C above absolute zero, it would require an enormous energy cost to keep H_2 fuel in the liquid state.

COMPARISON OF THE NUMBER OF HYDROGEN ATOMS IN A LITER OF LIQUID HYDROGEN TO A LITER OF LIQUID METHANOL.

4) Explain, using principles of bonding /intermolecular forces, why methanol is a liquid at room temperature while while H_2 and methane, CH_4 (also a high-energy fuel) are gases?

CH_3OH molecules can hydrogen bond to each other while H_2 and CH_4, as nonpolar molecules, can only form much weaker London Dipole Force attractions.

5A) Use the CRC handbook to look up the densities of liquid hydrogen and liquid methanol.
density of H_2 liquid = 70.8 g/L; CH_3OH = 0.79 g/mL

5B) Use the density equation to determine the masses in grams of each substance that would be present in 1 liter of pure liquid.
Density of H_2 liquid = 70.8 g/L; thus 1 L weighs 70.8 g.
CH_3OH: 0.79 g/mL (1000 mL/ 1 L) = 790 g/L.; thus 1 L weighs 790 g.

5C) Calculate the # of MOLES OF H_2 MOLECULES and MOLES of CH_3OH MOLECULES present in 1 liter.
H_2 liquid: 70.8 g H_2 (1 mole H_2/ 2.02 g H_2) = 35.0 moles H_2

CH_3OH: 790 g CH_3OH (1 mole CH_3OH/ 32.0 g CH_3OH) = 24.7 moles CH_3OH

5D) Calculate the # of H ATOMS present in 1 liter of pure H_2 liquid and 1 liter of pure methanol.

H_2 liquid: 35.0 moles H_2 (6.02 x 10^{23} molecules H_2 / mole H_2)(2 atoms H/ 1 molecule H_2) = _4.21 x 10^{25} atoms of H_

CH_3OH: 24.7 moles (6.02 x 10^{23} molecules CH_3OH / mole CH_3OH)(4 atoms H / 1 molecule CH_3OH) = _5.95 x 10^{25} atoms of H_

5E) Which contains the greater number of H ATOMS in a liter, pure H_2 liquid or pure methanol liquid? On the basis of amount of hydrogen present, is methanol a reasonable source of hydrogen? CH_3OH; YES

REFORMER REACTION STOICHIOMETRY

A typical reformer reaction, which involves the breakdown of methanol to release hydrogen gas, is given below:

$$CH_3OH + H_2O_{(g)} \ \text{--}\rightarrow \ CO_{2(g)} + H_{2(g)}$$

6) Balance the equation. $CH_3OH + H_2O_{(g)} \ \text{--}\rightarrow \ CO_{2(g)} + 3\ H_{2(g)}$

7) Calculate the # of grams of H_2 which could be produced by the reaction of 1 gallon of methanol. Density of methanol = 0.79 g/mL; 1 gallon = 3.8 L.

3.8 L CH_3OH (0.79 g/mL)(1000 mL/L) = 3.0 x 10^3 g CH_3OH

3.0 x 10^3 g CH_3OH (_1 mole CH_3OH_)(_3 moles H_2_)(2.02 g H_2)   = _5.7 x 10^2 g H_2_
                 (32 g CH_3OH)(1 mole CH_3OH)(1 mole H_2)

 8A) What do the think the impact will be on the overall energy efficiency of the process of having to run an additional reaction? Lowers the efficiency; For example H_2O in this process is steam and therefore energy is required to heat water for the reaction.

8B) What do the think the impact will be on the overall energy efficiency of the process of having to separate the desired product, H_2, from a mixture of other materials? A separation of mixtures requires energy expenditure. The use of reformers lowers the overall efficiency of fuel cell.

8C) What are the potential environmental concerns about releasing CO_2?
CO_2 is a greenhouse gas. Most scientists think that it would be wise to reduce our CO_2 emissions to help prevent global warming.

<u>Hydrogen Fuel Cells</u>
The reaction of hydrogen and oxygen to form water is a leading option to power cars in the future.

$$2 \, H_2 + O_2 \rightarrow 2 \, H_2O$$

1) When hydrogen gas is placed a balloon and a candle is held underneath the balloon, what will happen? Is energy being absorbed or released?

An explosion of fire – energy is being released as heat and light.

2) What is the difference between carrying this reaction out as described above and carrying the same reaction out in a fuel cell?

Most of the released chemical energy will be converted directly into electrical energy.

3) Assign oxidation numbers to H_2, O_2 and the H and O in H_2O.
H in $H_2 = 0$; O in $O_2 = 0$; H in $H_2O = +1$; O in $H_2O = -2$.

4) What species is oxidized and what species is reduced is this reaction?
H is oxidized, O is reduced.

5) One of the half-reactions for this system is $4 \, H^+ + \, O_2 + 4e^- \rightarrow 2 \, H_2O$

5A) Does the above half-reaction represent oxidation or reduction?
     Reduction
5B) Does the process above take place at the anode or the cathode?
     Cathode

5C) Write the other half reaction involving H_2.

   $2 \, H_2 \rightarrow \, 4 \, H^+ + 4e^-$

5D) Use the table of standard reduction potentials from your textbook to calculate E^o cell for this reaction.

	E^o
Red: $4 \, H^+ + \, O_2 + 4e^- \rightarrow 2H_2O$	+ 1.23 V
Ox: $2 \, H_2 \rightarrow \, 4 \, H^+ + 4e^-$	0.00 V
Overall: $2 \, H_2 + O_2 \rightarrow 2 \, H_2O$	+1.23 V

5E) How does the E^o that you calculated above compare to the voltage measured in a working cell with current flowing?

The voltage in the working cell with current flowing through it is always less than the theoretical maximum voltage. Current flowing through the cell always loses energy due to resistance. For example, a typical actual voltage of a hydrogen fuel cell might be 0.7 V.

DIRECT METHANOL FUEL CELL

Another option replacing gasoline combustion engines would be a methanol fuel cell. In a methanol fuel cell, methanol, CH_3OH, reacts with oxygen to produce carbon dioxide and water. $\quad 2\ CH_3OH\ +\ 3\ O_2\ ---\!\!\rightarrow 2\ CO_2 + 4H_2O$

6) Assign oxidation numbers to the C in CH_3OH, the C in CO_2.

C in CH_3OH: -2 (Sum must equal zero, each H = +1, O = -2)
C in CO_2: +4 (Sum must equal zero, each O = -2)

7) Assign oxidation numbers to the O in O_2 and the O in H_2O.
O in O_2 = 0; O in H_2O = -2

8) What species is being oxidized and what is being reduced in this reaction?
CH_3OH is being oxidized; O_2 is being reduced.

9) Write a balanced half-reactions in acidic solution.

$\quad\quad$ Ox: $2\ CH_3OH\ + 2H_2O \rightarrow 2\ CO_2 + 12H^+ + 12e^-$
$\quad\quad$ Re: $3\ O_2 +\ 12H^+ + 12e^- \rightarrow 6\ H_2O$
$\quad\quad\quad$ Overall: $2\ CH_3OH\ +\ 3\ O_2\ ---\!\!\rightarrow 2\ CO_2 + 4H_2O$

10) If the standard reduction potential for the conversion of CO_2 to CH_3OH is 0.03 V, and the standard reduction potential for the conversion of O_2 to H_2O is 1.23 V, calculate E^0 cell. $\quad\quad$ 1.23 – 0.03 = 1.20 V

11) One project being investigated at the National Renewable Energy Lab in the possibility of recycling CO_2 by converting it back to methanol.
11A) From an environmental perspective, would be the advantages of being able to capture CO_2 exhaust and recycle back to methanol?

- Limits release of CO_2 a greenhouse gas. Increased atmospheric concentrations of CO_2 have been linked to increases global temperatures.
- Be able to reuse the carbon in the process would reduce the need to produce methanol from petroleum or biomass. Thus fewer resources would be committed to produce fuel.

11B) A long-term goal is to be able to use a renewable energy source such as solar energy to power this process. What is the theoretical energy in volts that would have to be supplied to reconvert CO_2 to CH_3OH?

ANSWER: 1.20 V. This is the reverse described in question #5. (E^ocell = -1.20 V so energy would have to be added to drive the reaction.)

11 C) **What is a catalyst? In general, how does a catalyst work?**

A catalyst accelerates the rate of a chemical reaction without itself being consumed in the reaction. Catalysts work by changing the reaction original reaction pathway to a new pathway with a lower activation energy for the rate-limiting step.

TEACHER'S NOTES:

1) GENERAL INTRODUCTION – the general introductory paragraph could be supplemented or replaced by articles or by having student do research on the Internet for background. The December 2000 issue of Chem Matters has a well-written article entitled "Hydrogen Fuel Cells for Future Cars" by Donald Jones. There are numerous Internet sites. Two good general introductions are "How Fuel Cells Work" by Karim Nice at www.howstuffworks.lycos.com/fuel-cell and "The Future of Fuel Cells" by Ben Wiens at www.benwien.com/energy4.html#energy1.17.

2) REMINDER TO STUDENTS-It is useful to remind students that, in college courses and in real research, it is expected that students will to be able to make connections between different concepts they have learned and be able to apply those concepts to new situations. These problems are designed to give students practice in developing these skills. Also, it is helpful to remind them that, like A.P. exam questions, answers from a previous step may be applied to subsequent problems.

3) DEMONSTRATIONS OR LABS- could certainly be incorporated into the problem modules to increase student interest. Some possible examples:

Energy of hydrogen and oxygen reaction:
• Hydrogen balloon explosion (see Summerlin and Ealy's Chemical Demonstrations, 2nd edition, Volume 1, pp. 25-26, American Chemical Society, 1988.)
• Mini Hydrogen Rockets (see Ehrenkranz and Mauch's Chemistry in Microscale, "Hydrogen and Oxygen Generating, Collecting & Testing", Teacher's Guide pp. 72-80, Micro Mole Scientific, 1990.
• Small- scale hydrogen fuel cells can be purchased commercially or you can make your own (see Bassam Shakhashiri's, Chemical Demonstrations, Vol. 4, pp. 123-129, University of Wisconsin Press, 1991.)

Energy of methanol and oxygen reaction

Methanol cannon demo (see Summerlin and Ealy's <u>Chemical Demonstrations</u>, 2nd edition, Volume 1, pp. 25-26, American Chemical Society, 1988.)

Energy of combustion of hydrocarbon's
Methane combustion (see Bassam Shakhashiri's, <u>Chemical Demonstrations</u>, Vol. 1, pp. 113-116, University of Wisconsin Press, 1983.)