DOCUMENT RESUME

ED 210 505 CE 030 777

TITLE Chemistry for Energy Technology II. Energy Technology Series.
INSTITUTION Center for Occupational Research and Development, Inc., Waco, Tex.; Technical Education Research Centre-Southwest, Waco, Tex.
SPONS AGENCY Office of Vocational and Adult Education (ED), Washington, D.C.
BUREAU NO 498AH80027
PUB DATE Sep 81
CONTRACT 300-78-0551
NOTE 250p.; For related documents see CE 030 771-789 and ED 190 746-761.
AVAILABLE FROM Center for Occupational Research and Development, 601 Lake Air Dr., Waco, TX 76710 ($2.50 per module; $15.00 for entire course).

EDRS PRICE MF01 Plus Postage. PC Not Available from EDRS.
DESCRIPTORS Adhesives; Adult Education; Behavioral Objectives; Ceramics; *Chemistry; Course Descriptions; Courses; *Energy; Energy Conservation; *Fuels; Glossaries; Laboratory Experiments; Learning Activities; Learning Modules; Lubricants; Metals; Nuclear Energy; Plastics; Postsecondary Education; *Power Technology; Solar Radiation; *Technical Education; *Thermodynamics; Two Year Colleges
IDENTIFIERS *Corrosion; Electrochemistry

ABSTRACT

This course in chemistry for energy technology is one of 16 courses in the Energy Technology Series developed for an Energy Conservation-and-Use Technology curriculum. Intended for use in two-year postsecondary technical institutions to prepare technicians for employment, the courses are also useful in industry for updating employees in company-sponsored training programs. Comprised of six modules, the course is designed with a special emphasis on all aspects of chemistry as it relates to the work of an energy technician. Basic chemical information and techniques are presented. (Chemistry for Energy Technology I is available separately as CE 030 773.) Written by a technical expert and approved by industry representatives, each module contains the following elements: introduction, prerequisites, objectives, subject matter, exercises, laboratory materials, laboratory procedures (experiment section for hands-on portion), data tables (included in most basic courses to help students learn to collect or organize data), references, and glossary. Module titles are Corrosion and Electrochemistry; Metals and Ceramics; Thermodynamics and Thermochemistry; Fuels; Plastics, Adhesives, and Lubricants; and Nuclear Chemistry. (YLB)

CHEMISTRY
FOR
ENERGY TECHNOLOGY II

CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT
601 LAKE AIR DRIVE
WACO, TEXAS 76710

SEPT. 81'

PREFACE

ABOUT ENERGY TECHNOLOGY MODULES

The modules were developed by TERC-SW for use in two-year postsecondary technical institutions to prepare technicians for employment and are useful in industry for updating employees in company-sponsored training programs. The principles, techniques, and skills taught in the modules, based on tasks that energy technicians perform, were obtained from a nationwide advisory committee of employers of energy technicians. Each module was written by a technical expert and approved by representatives from industry.

A module contains the following elements:

Introduction, which identifies the topic and often includes a rationale for studying the material.

Prerequisites, which identify the material a student should be familiar with before studying the module.

Objectives, which clearly identify what the student is expected to know for satisfactory module completion. The objectives stated in terms of action-oriented behaviors, include such action words as operate, measure, calculate, identify and define, rather than words with many interpretations, such as know, understand, learn and appreciate.

Subject Matter, which presents the background theory and techniques supportive to the objectives of the module. Subject matter is written with the technical student in mind.

Exercises, which provide practical problems to which the student can apply this new knowledge.

Laboratory Materials, which identify the equipment required to complete the laboratory procedure.

Laboratory Procedures, which is the experiment section, or "hands-on" portion of the module (including step-by-step instruction) designed to reinforce student learning.

Data Tables, which are included in most modules for the first year (or basic) courses to help the student learn how to collect and organize data.

References, which are included as suggestions for supplementary reading/viewing for the student.

Glossary, which defines and explains terms or words used within the module that are uncommon, technical, or anticipated as being unfamiliar to the student.

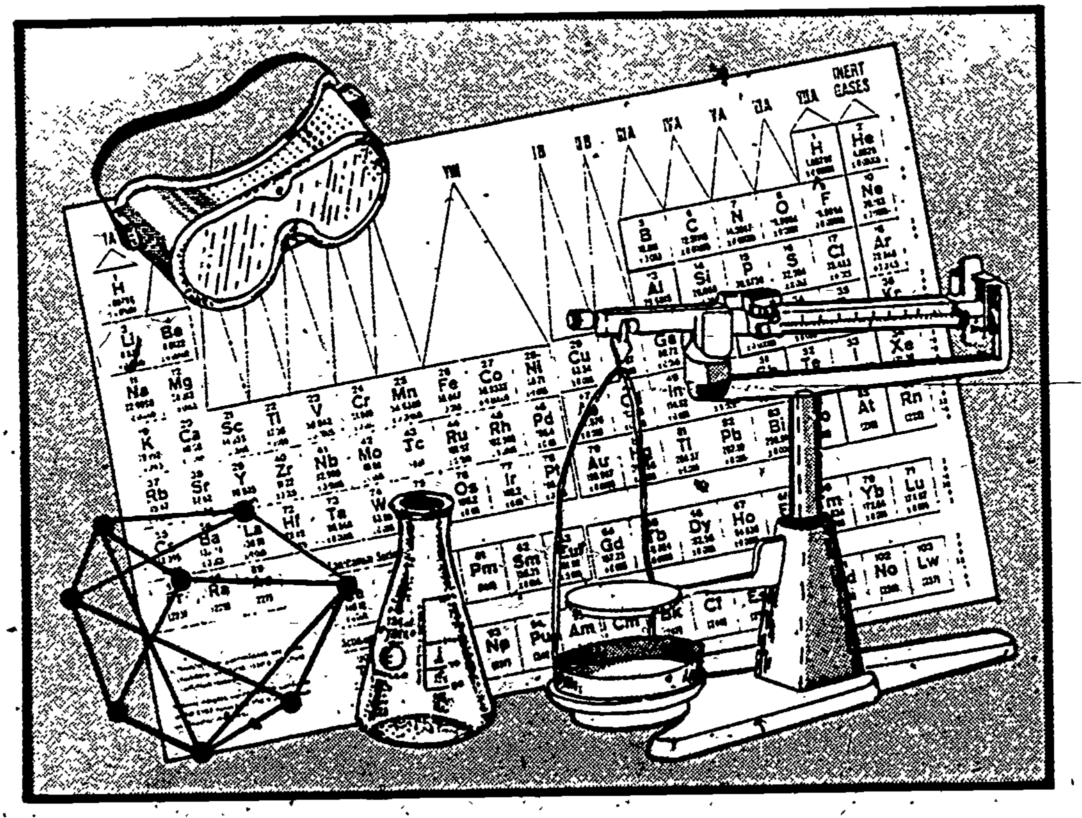
CONTENTS

R

ENERGY TECHNOLOGY

CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-06

CORROSION AND ELECTROCHEMISTRY

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

This work was developed under a contract with the Department of Education. However, the content does not necessarily reflect the position or policy of that Agency, and no official endorsement of these materials should be inferred.

CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

Corrosion is a chemical or an electrochemical process in which a metal is converted to an ionic form, destroying the metal. There are many familiar forms of corrosion: Iron will rust, aluminum will oxidize, silver will tarnish, and even chromium plated steel will lose its luster over a period of time. The damage to metal objects caused by corrosion amounts to a loss of approximately $10 billion each year in the United States. This does not include the millions that are spent in preventing corrosion, such as the $50 million spent each year to prevent automobile radiators from rusting. It is estimated that up to 20% of the iron produced annually in this country is used to replace iron objects that must be replaced because of corrosion damage.

Much can be done to eliminate and reduce the amount of corrosion that occurs. The process of corrosion is explained in this module, as well as some of the means available to control it. In addition, certain aspects of electrochemistry are presented.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of Chemistry for Energy Technology I.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Describe the electrochemical process of corrosion.
2. Explain how cathodic protection can be used to protect a steel tank or a pipeline from the effects of corrosion.
3. Describe how the activity series or the single electrode potentials can be used to predict the relative corrosion of metals.
4. Describe some frequently used cells and batteries.
5. Define the following terms:
   a. Anode.
   b. Cathode.
   c. Cathodic protection.
   d. Corrosion.
   e. Voltaic cell.
   f. Electrolytic cell.
   g. Electrochemistry.
   h. Electrolysis.
6. Describe the electrolytic refining of copper.
7. Describe the importance of magnetite in a boiler.
8. List two objectives of boiler feedwater treatment.
9. List two methods for removing oxygen from boiler feedwater.
10. List four ways to protect metals from corrosion.

CORROSION

Corrosion is the deterioration of a metal caused by a reaction with its environment. Corrosion can result through chemical or electrochemical means. Deterioration by physical causes is not called corrosion but, rather, is described as galling, erosion, or wear. However, chemical and physical deterioration may occur at the same time, as in fretting corrosion or corrosive wear. The term "rusting" is reserved for the corrosion of iron or iron alloys with the formation of the corrosion product iron oxide.

Chemical corrosion is the direct combination of a metal with nonmetallic compounds such as oxygen or sulfur dioxide. This type of corrosion is also called dry corrosion since water or moisture is not involved in the corrosion mechanism. An example of chemical corrosion follows:

$$\begin{array}{ccccccc} Fe & + & SO_2 & \longrightarrow & FeS & + & O_2 \\ \text{Iron} & & \text{Sulfur} & & \text{Iron} & & \text{Oxygen} \\ & & \text{dioxide} & & \text{sulfide} & & \end{array}$$

Although chemical deterioration is one form of corrosion, the principal type of corrosion involves an electrochemical process. In this form of corrosion a metal is converted to an ionic form with a passage of an electrical current. Electrochemistry and electrochemical corrosion are considered in the following sections of this module.

ELECTROCHEMISTRY

Electrochemistry is the field of chemistry concerned with chemical changes produced by an electric current and with the production of electricity by chemical reactions. In electrolytic cells, electricity is used to produce desired chemical changes, such as in the electrolysis of water to produce oxygen and hydrogen gases or in the production of aluminum. In voltaic cells, chemical reactions are used to produce electricity, such as in the automobile battery. Electrochemical processes are widely used in industry, which is a large consumer of electricity; therefore, these processes are of importance to an energy technician.

ELECTRODE POTENTIALS

When a metal such as zinc is placed in water, there is a tendency for the zinc atoms to lose electrons and pass into solution as zinc ions, as follows:

$$Zn \longrightarrow Zn^{++} + 2\ e^-$$

The zinc ions move into the solution, leaving their electrons behind. The metal, therefore, becomes negatively charged. This potential, or voltage, can be measured; for zinc it is found to be +0.76 volts when the concentration of zinc ions is one molar. This voltage is called the standard electrode potential for zinc; it is a measure of the tendency of zinc to lose electrons and form ions. By measuring the standard electrode potentials of different metals in solutions of their ions at a concentration of one molar, an activity series may be developed. Table 1 gives the standard electrode potential for a number of metals.

TABLE 1. STANDARD ELECTRODE POTENTIALS.

Element	Electrode Reaction	Standard Electrode Potential (volts)	
Potassium	$K \longrightarrow K^{+} + e^{-}$	Increasing Activity ↑	2.93
Calcium	$Ca \longrightarrow Ca^{++} + 2\ e^{-}$		2.87
Sodium	$Na \longrightarrow Na^{+} + e^{-}$		2.71
Magnesium	$Mg \longrightarrow Mg^{++} + 2\ e^{-}$		2.37
Aluminum	$Al \longrightarrow Al^{+3} + 3\ e^{-}$		1.66
Zinc	$Zn \longrightarrow Zn^{++} + 2\ e^{-}$		0.76
Chromium	$Cr \longrightarrow Cr^{+3} + 3\ e^{-}$		0.74
Copper	$Cu \longrightarrow Cu^{++} + 2\ e^{-}$		-0.34
Gold	$Au \longrightarrow Au^{+} + e^{-}$		-1.68

Table 1 is often called the electromotive series, or activity series. The metals at the top of Table 1 (such as potassium) are very reactive, whereas the metals lower in Table 1 (such as gold) are more stable. Gold can be found in nature in the elemental state, whereas potassium cannot. The reduced form of any element will reduce the oxidized form of any element below it in the series. For example, metallic zinc will reduce copper (II) ions according to the following reaction:

$$Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$$

This reaction is utilized in a voltaic cell, called the Daniell cell, in order to produce electricity. The voltage of the cell is found by subtracting (algebraically) the potential of the copper electrode from that of the zinc electrode. The voltages are given in Table 1.

$$\begin{aligned} \text{Cell voltage} &= 0.76 - (-0.34) \\ &= 0.76 + 0.34 \\ &= 1.10 \text{ volts} \end{aligned}$$

Standard electrode potentials, abbreviated E°, do not take into account changes in concentration. As was previously stated, the <u>standard electrode</u> potentials are found by measuring the voltages in a cell with a one-molar concentration. The Nernst equation makes it possible to calculate voltages at other concentrations. The Nernst equation for a cell at 25°C is as follows:

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{Molar concentration of products}}{\text{Molar concentration of reactants}}$$

Equation 1

where:

E = The voltage for the cell.
E° = The standard electrode potential (from Table 1).
n = The number of electrons involved in the reaction.

EXAMPLE A: VOLTAGE MEASUREMENT.

Given: A 0.1 M solution of $ZnSO_4$.

Find: The voltage of a strip of zinc immersed in the solution.

Solution: $Zn \longrightarrow Zn^{++} + 2\ e^-$

(The value of 1 is assigned as the concentration for all elements.)

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{Molar concentration of products}}{\text{Molar concentration of reactants}}$$

$$= 0.76 - \frac{0.059}{2} \log \frac{0.1}{1}$$

$$= 0.76 - (0.0295)\ (-1)$$

$$= 0.76 + 0.0295$$

$$E = 0.789.$$

Although standard electrode potentials are useful for predicting the corrosion of metals, other factors are important. Some metals display an unusual inactivity called passivity. Passivity can be considered to be the reason a metal does not corrode when it should according to its standard electrode potential. For example, according to its standard electrode potential, one would expect aluminum to be a very reactive metal; yet, it possesses good corrosion resistance. Aluminum quickly forms a surface coating of aluminum oxide, which stops further corrosion. In addition, chromium should be more reactive than iron (according to their electrode potentials). However, chromium actually is used to protect iron (steel) from corrosion in applications such as chromium-plated automobile bumpers. Passivity is usually caused by the formation of thin, adherent metallic oxide coatings.

ELECTROLYSIS

Electrolysis is the process in which electric current is passed through a solution of ions to produce desired chemical reactions. Electrolysis of a solution of sodium chloride in water is depicted in Figure 1. When sodium chloride, NaCl, is dissolved in water, the solution will contain hydrogen ions and hydroxide ions from the water, sodium and choride ions from the sodium chlorine, and many molecules of water. When two electrodes (composed of an inert material such as graphite) are placed in the solution and connected to a battery, the negative ions (Cl^- and OH^-) move toward the positive electrode, called the anode, where they may lose electrons and be oxidized. The possible oxidation reactions are as follows:

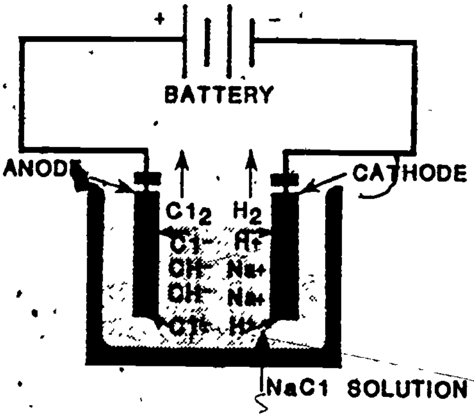


Figure 1. Electrolysis of Aqueous Sodium Chloride.

$$2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$$

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4\ e^-$$

One would expect that chlorine gas, Cl_2, or oxygen gas, O_2, would be emitted at the anode. Chlorine will be produced in a concentrated solution of sodium chloride. The positive ions (H^+ and Na^+) migrate to the negative electrode, called the cathode, where they may gain electrons and be reduced. Possible reduction reactions at the cathode are as follows:

$$Na^+ + e^- \longrightarrow Na$$

$$2\ H_2O + e^- \longrightarrow H_2 + 2\ OH^-$$

Water is more easily reduced than sodium ion; therefore, hydrogen gas is produced at the cathode. The net overall reaction for electrolysis of aqueous sodium chloride is obtained by adding the two half-reactions as follows:

$$\begin{array}{rcl} 2\ H_2O + 2\ e^- & \longrightarrow & H_2 + 2\ OH^- \\ 2\ Cl^- & \longrightarrow & Cl_2 + 2\ e^- \\ \hline 2\ H_2O + 2\ Cl^- & \longrightarrow & H_2 + Cl_2 + 2\ OH^- \end{array}$$

The hydroxide ions, OH^-, combine with sodium ions, Na^+, to form sodium hydroxide. Electrolysis of aqueous sodium chloride is an important commercial process for production of hydrogen, chlorine, and sodium hydroxide.

Another example of the application of electrolysis to commercially produce chemicals is the electrolysis of an aqueous solution of sulfuric acid. Sulfuric acid, consisting of hydrogen ions and sulfate ions, does not decompose during the electrolysis process. The following reactions occur:

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4\ e^- \quad \text{(at the anode)}$$

$$4H^+ + 4\ e^- \longrightarrow 2\ H_2 \quad \text{(at the cathode)}$$

$$2\ H_2O \longrightarrow 2\ H_2 + O_2 \quad \text{(net reaction)}$$

The net reaction shows that water is decomposed by the electric current into hydrogen and oxygen gases. This method gives very pure hydrogen and oxygen. However, it is expensive, and its industrial use is limited to conditions where purity of gases is important – such as in the production of oxygen for breathing purposes.

ELECTROLYTIC REFINING (METALS)

An important application of electrochemistry is <u>electrolytic refining</u> of metals. In this process, impure metals are converted to highly pure forms of the metals. Copper – an important metal – is refined on a large scale by electrolytic methods. The primary use of copper as electrical wire requires a metal of high purity – which can be obtained through electrolytic refining. Gold, silver, nickel, lead, and zinc are successfully refined by electrolysis of aqueous solutions; and aluminum is produced by electrolysis of a fused (melted) solution. The main advantages of electrolytic refining are:

- greater purity of the primary metal
- and recovery of by-product metals (especially precious metals).

By-product metals are present in very small amounts. In electrolytic refining, an impure form of the metal to be refined (such as copper) is made the anode; and it is suspended in a suitable electrolyte (as in Figure 2). The anodic reaction is therefore, $Cu \longrightarrow Cu^{++} + 2e^-$. A thin

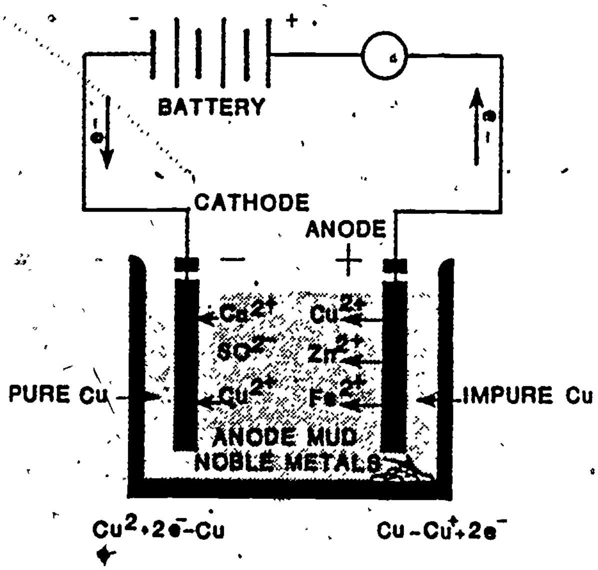


Figure 2. Electrolytic Refining of Copper.

sheet of the pure metal is made the cathode. The cathodic reaction is $Cu^{++} + 2e^- \longrightarrow Cu$. The conditions of concentration and temperature are carefully regulated so that the deposited metal has a high purity. The less active metals (such as gold and silver, which are found in impure copper) do not dissolve; they fall to the bottom of the electrolysis cell and form a mud or slime from which they are recovered.

LAW OF ELECTROLYSIS

In 1832, Michael Faraday discovered that the quantity of substances undergoing chemical change at each electrode during electrolysis is directly proportional to the quantity of electricity that passes through the electrolytic cell. Experimental results show that one electron reduces one silver ion; whereas two electrons are required to reduce one copper (II) ion, as follows:

$$Ag^{+} + e^{-} \longrightarrow Ag$$
$$Cu^{++} + 2e^{-} \longrightarrow Cu$$

Since one electron is required to reduce one Ag^+, and two electrons are required to reduce one Cu^{++}, it follows that one mole of electrons is required to reduce one mole of silver ions, and two moles of electrons are required to reduce one mole of copper (II) ions. The electrical charge of a mole of electrons, called a "faraday," is equal to 96,500 coulombs.

$$1 \text{ Faraday} = 6.023 \times 10^{23} \text{ electrons}$$
$$= 1 \text{ mole of electrons}$$
$$= 96{,}500 \text{ coulombs}$$

A coulomb is the quantity of electrical charge passing through a given point in the cell in one second, at a current of one ampere:

Coulombs = Amperes x seconds

EXAMPLE B: WEIGHT CALCULATION, USING LAW OF ELECTROLYSIS.

Given: A cathodic reduction of copper (II) ions, during which 1.60 amperes of current passes for one hour.

Find: Calculate the weight of copper produced.

Solution: Coulombs = Amperes x seconds

= 1.60 amps x 60 min/hr x 60 sec/min

= 5760

96,500 coulombs will reduce $\frac{63.54 \text{ g}}{2} = 31.77$ g

5760 coulombs will reduce 31.77 g x $\frac{5760}{96{,}500} = 1.89$ g of copper

ELECTROCHEMICAL MACHINING

Electrochemical machining (milling) is becoming more and more important in that it is replacing mechanical machining of complex designs in metals. The process is illustrated in Figure 3. The metal to be machined is made the anode, and the piece that determines the final shape (die) is made the cathode. The current is largest where the two electrodes come in closest contact. As a result, the most metal is removed from the object where the die comes closest to the material being formed. Thus, the object being machined gradually takes the shape of the die.

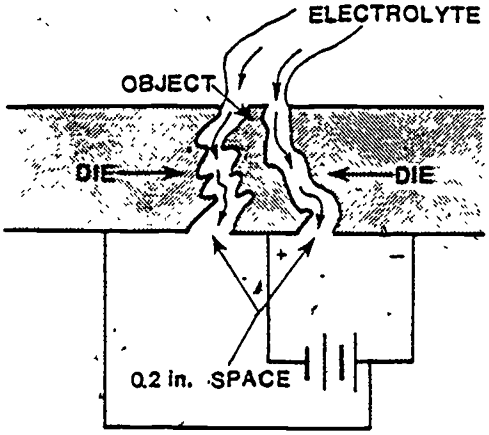


Figure 3. Electrochemical Machining.

The electrolyte, usually a 5 to 10% solution of a salt, is passed at high velocity through the gaps between the object being machined and the die in order to keep the parts cool and remove the electrode reaction products. The cathode reaction at the die is the evolution of hydrogen, rather than the plating of a metal. Current densities used in electrochemical machining are high (1000 to 1500 amp/ft^2) and voltages are low (less than 20 V). Under these conditions, the removal rate for aluminum, tungsten, titanium, nickel, iron, chromium, and copper is about two cubic centimeters per minute. Electrochemical milling or machining is used to shape complex parts used in automobile transmissions. One advantage of electrochemical machining is that the product does not have the stresses that are always present in mechanically machined parts.

VOLTAIC CELLS

Voltaic cells, also called galvanic cells, produce an electrical current through chemical reactions. These cells may be primary or secondary. Primary cells cannot be recharged, whereas secondary cells can. The most familiar primary voltaic cell is the dry cell. (This cell is not actually dry; if it were, it could not conduct a current.) The electrolyte consists of a thick paste of $ZnCl_2$, NH_4Cl, and MnO_2. The center, positive pole is made of graphite, and the contents are sealed in zinc, which acts as the negative pole of the cell. Zinc, which has a higher electrode potential than carbon, supplies the electrons that flow from the zinc to the carbon pole (Figure 4). The following reactions occur at the anode and cathode:

$$\begin{array}{rll} Zn & \longrightarrow Zn^{++} + 2\,e^- & \text{(anode)} \\ 2\,NH_4^+ + 2\,e^- & \longrightarrow 2\,NH_3 + H_2 & \text{(cathode)} \\ \hline Zn + 2\,NH_4^+ & \longrightarrow Zn^{++} + 2\,NH_3 + H_2 & \text{(net cell reaction)} \end{array}$$

The manganese dioxide in the cell oxidizes the hydrogen as it is formed in order to produce water. Otherwise, the hydrogen gas would accumulate on the cathode and stop the action of the cell.

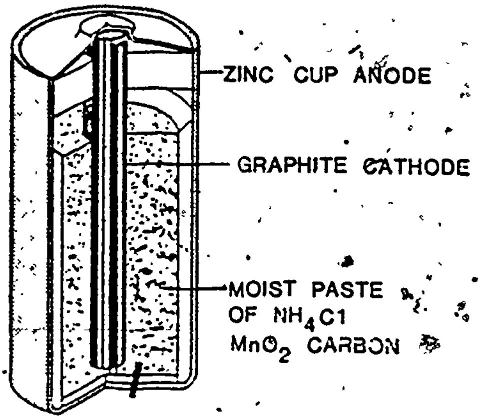


Figure 4. Cross-Section of a Dry Cell.

A secondary voltaic cell is one that is reversible (that is, it can be recharged). The most common battery is the lead storage battery used in automobiles. A battery is a combination of two or more cells in an assembly. The 12-volt automobile battery consists of six cells, each of which supplies two volts. The cathode is composed of lead dioxide, PbO_2, and the anode is composed of lead, Pb. Both anode and cathode are immersed in a solution of sulfuric acid, with a density of approximately 1.30 g/cm^3. A hydrometer can be used to readily determine the condition of the battery. When the density of the sulfuric acid falls below 1.20 g/cm^3, the battery needs recharging or replacing. The electrode reactions that occur during discharge of the battery are as follows:

$$\begin{array}{rcll} Pb + SO_4^{-2} & \longrightarrow & PbSO_4 + e^- & \text{(anode)} \\ PbO_2 + SO_4^{-2} + 4\,H^+ + 2\,e^- & \longrightarrow & PbSO_4 + 2\,H_2O & \text{(cathode)} \\ \hline Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{-2} & \longrightarrow & PbSO_4 + 2\,H_2O & \text{(net reaction)} \end{array}$$

As can be seen from the net reaction, during discharge, lead is consumed through conversion to lead sulfate. The sulfuric acid also is consumed through conversion to lead sulfate and partially to water – which is the reason for the decrease in density of the sulfuric acid solution as the battery discharges. During recharge, the lead and sulfuric are regenerated. A discharging cell is depicted in Figure 5.

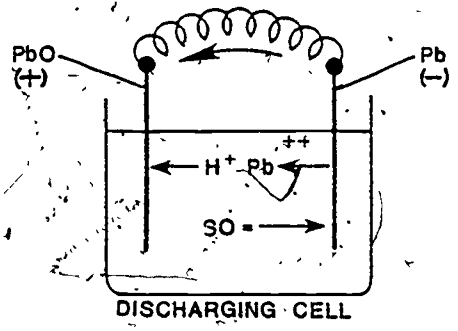


Figure 5. Discharging Lead-Acid Storage Battery.

ELECTROCHEMICAL CORROSION

In electrochemical corrosion, a metal is converted to an ionic form in the presence of water with a passage of an electrical current. Corrosion of iron is depicted in Figure 6.

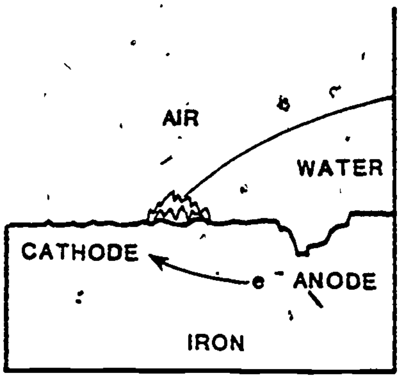


Figure 6. Corrosion of Iron.

One region on the surface of the iron serves as an anode at which the iron is oxidized:

$$Fe \longrightarrow Fe^{++} + 2\,e^- \quad E° = 0.44 \text{ volts (anode)}$$

The electrons produced at the anode migrate to another region on the surface of the piece of iron where they are available to reduce oxygen according to the following reaction:

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \quad E° = 1.23 \text{ volts (cathode)}$$

Corrosion is enhanced by the presence of salts or other ions, which assist in carrying the current through a moisture coating. This enhanced corrosion is evident on automobiles in areas where there is heavy salting of roads during winter to remove ice and snow. Ultrapure iron is not very susceptible to corrosion because the anodic and cathodic sites are not available; however, ordinary iron has impurities or defects which can become cathodic or anodic sites, allowing electrochemical corrosion to proceed. Even stress introduced during the manufacturing process can provide an environment for corrosion.

BOILER CORROSION

Boilers are widely used to produced steam which may be used to generate electricity, provide space heating, or provide heat for industrial processes. Corrosion of boilers can occur on the water side of the boiler – that is, inside the boiler tubes, the superheater, and condensing equipment. Corrosion can also occur on the heated (fire) side of the equipment. High pressure boilers that drive steam turbines operate on a recirculatory system and use "make-up" quantities of water that has been carefully treated. Low pressure boilers that provide hot water or process steam often use less of this treated water.

Boilers are constructed of a low-carbon (mild) steel or low-alloy steel. At temperatures above 250°C, water attacks steel to form a surface layer of magnetite (Fe_3O_4), according to the following reaction:

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2$$

The magnetite film is ~~highly~~ desirable since it protects the steel from further oxidation. The growth of the protective magnetite film inside a boiler is accelerated by using alkaline boiler water, whereas excessive acidity removes the film. Therefore, boiler water is usually maintained at a pH between 8.5 and 9. The protective magnetite film is also weakened by oxygen in the boiler feedwater, causing the corrosion of the underlying steel. Oxygen is commonly removed by mechanical or chemical methods.

Condensers and heat exchangers are made of copper, brass, bronze, and copper-nickel alloys. Cooling water used with condensers and heat exchangers normally is untreated. This water may vary from fairly pure river or lake water to highly polluted water from harbors and bays. The polluted waters often contain hydrogen sulfide, causing rapid deterioration of copper and its alloys. The primary means of limiting corrosion in condensers and heat exchangers is through careful selection of the materials of construction.

BOILER WATER TREATMENT

The main objectives of feedwater treatment are the prevention of corrosion and the prevention of scale formation. This scale, which is a deposit of calcium carbonate and magnesium hydroxide on the metal surface, is a poor conductor of heat and interferes with the normal heat transfer in the boiler. Scaling can cause a large increase in the operating costs of boilers. If steam is used for power production, concentrations of silica and silicates in feedwaters must be reduced in order to minimize the volatilization of SiO_2 with steam — which can cause formation of damaging deposits on turbine blades.

Water hardness (that is, the concentration of calcium and magnesium ions) is reduced by precipitation, distillation, or ion-exchange. The addition of lime and soda is used to precipitate the calcium as carbonate and the magnesium as hydroxide. This procedure will reduce the water hardness to 10 ppm or less. Water can be distilled to remove calcium and magnesium ions. Distillation can reduce the dissolved solids to 0.1 ppm. In the ion-exchanger method, synthetic ion-exchange resins remove the calcium and magnesium ions, replacing them with less harmful ions such as sodium or hydrogen ions. The ion-exchange method, often called "polishing the water," is very effective. By proper control of water hardness, the formation of scale in boilers can largely be eliminated.

Oxygen removal from boiler feedwater is important to control corrosion. This removal may be accomplished by mechanical or chemical methods. The oxygen, along with carbon dioxide, can be removed mechanically by spraying preheated water into an evacuated chamber. The oxygen content of boiler feedwater can also be reduced (to about 2 ppm) by storing it for 30 minutes at a temperature just below boiling.

For use in high pressure boilers, water should have an oxygen content less than 0.005 ppm. Treatment with hydrazine can be used to accomplish this oxygen reduction according to the following reaction:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2\ H_2O$$

Some of the hydrazine is decomposed by heat to form ammonia and nitrogen. The ammonia is useful since it reacts with CO_2, thereby removing the CO_2 from the water. Another chemical used as an oxygen "scavenger" is sodium sulphite. Sodium sulphite reacts with oxygen according to the following reaction:

$$2\ Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4$$

One disadvantage of using sodium sulphite to remove oxygen is the formation of sulfates. These sulfates can react with free calcium ions to form scale. Still another method of reducing the oxygen content of boiler water is with an ion-exchange resin. This method can reduce the concentration of oxygen to less than 0.01 ppm.

As indicated earlier, it is desirable to maintain the pH at a value of 8.5 to 9 to ensure that a protective layer of magnetite is formed and maintained. This requires the addition of chemicals to raise the pH. Ammonia, cyclohexylamine, or morpholine are commonly used for pH control. Amines may also be used to form a protective film over the metal surface. Octadecylamine is the most commonly used filming amine.

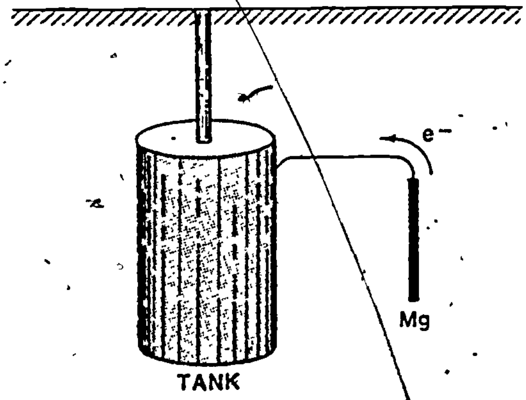
PROTECTION OF METALS FROM CORROSION

Several widely used methods of protecting metals from corrosion are listed below:

- Cathodic protection
- Metallic coatings, such as from galvanizing or electroplating
- Inorganic coatings, such as phosphates
- Organic coatings, such as paints

Underground pipelines or tanks are often protected by a cathodic protection method — which makes them similar to cathodes in a voltaic cell. A more active metal, such as zinc or magnesium, is buried adjacent to the pipe or tank and connected by means of a wire or cable. The active metal is converted to its ionic form (rather than the iron in the pipe), thereby protecting the pipe. For continued protection, the sacrificial anode can be replaced at intervals. The protection of an iron tank from corrosion using a sacrificial magnesium anode is depicted in Figure 7.

Figure 7. Cathodic Protection of an Iron Tank.



A similar type of protection is given by the process known as galvanizing. In this process, a thin coating of zinc is applied to the iron object. If this coating is broken, allowing moisture and oxygen to contact the exposed iron, the remainder of the zinc acts as a large anode, at which oxidation occurs more readily than at the iron surface.

Phosphatizing is a common method for corrosion prevention. First, the surface of the metal is grit- or sand-blasted to clean and roughen it. Then, the article is dipped in a phosphoric, acid-phosphate salt solution for 5 to 50 minutes. Since the phosphate coatings created in this process are very adherent, they prevent electrical conduction along the surface of the metal. Phosphate coatings are often coated with paint to form an effective corrosion barrier.

The process of applying a thin coating of metal to some article when immersed in an electrolyte is called electroplating. Generally, the article to be plated is another metal, but plastics are also plated. Many knobs in automobiles are made of chromium-plated plastic because plastic is less expensive than metal and it also reduces the weight of the knobs. Four advantages of electroplating are as follows:

1. Cheap metal objects are coated with an expensive metal (like gold or silver) to increase their value or improve their appearance.
2. Metal coatings of nickel or chromium are used for their decorative effect or for combining improved appearance with increased wearing qualities.
3. Zinc plating protects other metals from corrosion.
4. Chromium plating of bearings in machinery greatly increases their ability to withstand mechanical wear.

Some metal plating is conducted without an electric current. This type of plating process is called immersion, or electroless plating. A specially formulated bath that has phosphate and nickel in the coating is used to plate electroless nickel. This coating is extremely hard and wear-resistant. Much gold plating (especially of jewelry) is conducted by dipping the object to be plated in an electrolyte containing gold ions. The amount of metal deposited can be controlled to some extent by the length of the immersion. The metal object to be plated is usually made of brass.

In electroplating, the object to be plated is made the cathode, and the metal to be plated is supplied by the electrolyte. In some processes, a bar of the metal to be plated out is used as the anode. This type of arrangement serves to keep the concentration of metallic ions in solution constant. The object to be plated must be properly prepared prior to electroplating.

The selection of a proper material for a given application is all-important. The corrosion-resisting property of alloys is often far superior to pure metals. An important consideration in the selection of proper materials is to make certain that metals that have widely differing activities are not placed in direct contact with each other. For example, steel bolts should not be used to fasten brass plates since the "battery" formed will cause severe corrosion.

LABORATORY MATERIALS

Laboratory 1

Clean, bright nails
Test tubes
0.1 M NaOH
0.1 M $Na_2Cr_2O_7$
0.1 M NaCl
0.1 M HCl
0.1 M KOH
0.1 M Na_2CO_3
0.1 M KNO_3
0.1 M HNO_3
0.1 M Na_3PO_4
0.1 M KSCN
0.1 M $Na_2C_2O_4$
0.1 M H_2SO_4
ph paper
Test tube rack
0.1 M potassium hexacyanoferrate, $K_3Fe(CN)_6$
0.1 M iron (II) sulfate
Agar
Burner
1% phenolphthalein indicator
Petri dish
Copper wire
Zinc strip or mossy zinc

Laboratory 2

Test tubes
Small funnel
Stirring rod
Bunsen burner
Calcium sulfate
Magnesium sulfate
Sodium carbonate
Lime water
Distilled water
Soap solution (40 ml of liquid soap in 160 ml distilled water
250 ml graduate
Aluminum sulfate solution (20 g/liter)
Fine clay

LABORATORY PROCEDURES

LABORATORY 1. CORROSION OF IRON.

Corrosion is a complex process in which a metal is converted to its oxide. For exmample, iron corrodes to form iron oxide as follows:

$$4\ Fe + 3\ O_2 \longrightarrow 2\ Fe_2O_3$$

Many factors influence the rate of corrosion of iron, such as the presence of salts, contact with other metals, and the pH of the solution. Iron will not rust in water unless oxygen is present. On the other hand, iron will not rust in a substance such as oil if there is absolutely no water present – even if oxygen is present. Each year, corrosion of iron costs industry in the United States billions of dollars. It is estimated that 20% of the iron produced annually in this country is used to replace iron objects that have been discarded because of excessive rust damage. In this experiment, some of the factors involved in the corrosion of iron are investigated.

PROCEDURE

Carefully record all data in Data Table 1.

1. Put a small, clean, bright nail in each of 13 test tubes. Hold the test tube at an angle and gently slide the nail into the tube to avoid breaking the tube.

2. Using the reagents listed in Data Table 1, fill each of the tubes with enough liquid just to cover the nail. All the solutions (except water) should be 0.1 M.
3. For each solution, determine whether it is acidic, basic, or neutral by using litmus paper. Record findings in Data Table 1.
4. Leave the nails in the solutions overnight. Observe and record any changes that have taken place.
5. To test for the presence of iron ions (Fe^{+++}) in the solutions, add several drops of 0.1 M potassium hexacycanoferrate, $K_3Fe(CN)_6$, and record any observations. In some cases, a metal in contact with iron will cause the iron to rust much faster than it would without being in contact with the metal. In other cases, the iron is protected because the second metal corrodes in preference to the iron. Magnesium is often used to protect iron tanks in a process called cathodic protection.
6. Prepare about 100 ml of agar mixture by heating 100 ml of distilled water to its boiling point, removing it from the burner, and stirring in one gram of powdered agar. Heat again until the agar is evenly dispersed throughout the solution.
7. Add 10 drops of 0.1 M potassium hexacyanoferrate and 10 drops of 1% phenolphthalein indicator to the agar mixture, and stir thoroughly.
8. Place one nail on one side of a petri dish. Bend another nail sharply with a pair of pliers and place it on the other side of the dish. Do not let the nails touch each other.

9. Twist a clean piece of copper wire around a third nail. (If the copper wire is not bright and shiny, or if it has a coating, sandpaper the wire until the coating is removed.) Place this nail in a second petri dish.
10. Twist a clean piece of zinc metal around a fourth nail, and place it in the second petri dish with the nail wound with the copper wire. Do not allow the nails to touch each other.
11. When the agar mixture has cooled, but while it is still a liquid, pour it carefully into the petri dishes until the nails and attached metals are covered.
12. Observe the nails during the class period and the next day. Record any observations in Data Table 1.

LABORATORY 2. PURIFICATION OF WATER.

This experiment investigates the differences between soft water, hard water, and permanent hard water; and it determines the effect of these waters upon a soap solution. It also investigates the use of alum to purify water by coagulation.

PROCEDURE

Note: Ordinary soaps are sodium salts of complex organic acids. Sodium stearate ($NaC_{18}H_{35}O_2$) is present in many common soaps.

1. Add a drop or two of soap solution (40 ml liquid soap in 160 ml distilled water) to a test tube half filled with distilled water, and shake the tube. Are lasting suds produced? Distilled water is "soft water," and the results are characteristic of these waters.
2. Add a drop or two of soap solution to a test tube half filled with tap water, and shake the tube. Is the tap water soft water? (Tap water varies in different localities; it may range from very soft to very hard.)
3. Place a small amount of magnesium sulfate into a test tube half filled with distilled water. Shake the tube to dissolve the magnesium sulfate. Add a few drops of the soap solution and shake the tube. Do suds form? The precipitate that is formed is magnesium stearate. Water that gives precipitates with soap solution is called "hard water."
4. Continue adding soap solution and shaking the tube until permanent suds form. Enough soap solution must be added until all the magnesium ion is removed. Why does it cost more to wash with hard water than with soft water.
5. Make another test tube of hard water by adding some magnesium sulfate to a half-filled test tube of distilled water.
6. Boil the water in the test tube.
7. Add a few drops of soap solution. Do lasting suds form? Did the boiling of the water affect its hardness?. A hard water that is not softened by boiling is known as a "permanent" hard water. These waters usually contain magnesium or calcium sulfate; they cannot be softened by heating, but they may be softened by adding a solution of sodium carbonate.

8. Make a test tube of hard water by adding some calcium sulfate to a half-filled test tube of distilled water. Shake the mixture and then filter it into another test tube.
9. To the clear filtrate, add a solution of sodium carbonate as long as a precipitate continues to form.
10. Filter, then add some soap solution to the filtrate. Was the addition of the sodium carbonate solution effective in softening the hard water?
11. Add some calcium bicarbonate to a half-filled test tube of distilled water.
12. Test this solution for hardness. Is the calcium bicarbonate solution hard or soft?
13. Make another test tube of calcium bicarbonate solution and heat it until it boils.
14. Filter the solution and test the filtrate with a few drops of soap solution. Has the water solution of calcium bicarbonate been softened? This type of hard water is called a "temporary" hard water. Temporary hard water can also be softened by the addition of lime or lime water.

Note: The following steps concern purification of water by coagulation.

15. Make 25 ml of a dilute solution of aluminum sulfate, $Al_2(SO_4)_3$.
16. Add 50 ml of lime water. The reaction is as follows:

$$Al^{+3} + 3\ OH^- \longrightarrow Al(OH)_3$$

Describe the precipitate of aluminum hydroxide formed.

17. Add water to a graduated cylinder until it is approximately two-thirds full. Add some fine clay and stir.
18. Add 10 ml of aluminum sulfate solution and mix.
19. Without stirring, slowly add 20 ml of lime water.
20. Allow the water to stand and observe from time to time.

Aluminum sulfate, or "alum" as it is called, is commonly used as a flocculating agent in water treatment. When alum is added to water, aluminum hydroxide forms as a spongy, gelatinous precipitate. The aluminum hydroxide precipitate has an overall positive charge. Since most of the suspended particles (such as clay) have a negative charge, the suspended particles are attracted to the precipitate of aluminum hydroxide and are carried down with it. In this way, almost all finely divided matter is removed from the water.

DATA TABLE 1. CORROSION OF IRON

Reagent	pH	Reaction (yes or no)	Iron Ion Present (yes or no)
KOH			
NaOH			
NCl			
HNO_3			
H_2SO_4			
NaCl			
$Na_2Cr_2O_7$			
Na_2CO_3			
KNO_3			
Na_3PO_4			
$Na_2C_2O_4$			
KSCN			
Water			

a. The first two reagents above are bases, the next three are acids, and the remainder are salts. Are any regularities observed in the corrosion of iron in the presence of the solutions?

Data Table 1. Continued.

b. Record any observations concerning the iron nails in the agar mixture:

(1) Straight nail:

(2) Bent nail:

c. What effect does stress (placed in the nail by bending) have on the nail's corrosion resistance?

(1) Copper wound nail:

(2) Zinc wound nail:

d. A coating of zinc is often placed on iron to form galvanized iron. Relate any observations concerning this practice.

REFERENCES

Bosich, Joseph F. Corrosion Prevention for Practicing Engineers. New York: Barnes and Noble, Inc., 1970.

Butler, G. and Ison, H.C.K. Corrosion and its Prevention in Waters. New York: Reinhold Publishing Corp., 1966.

Higgins, R. A. Materials for the Engineering Technician. London: The English Universities Press Ltd., 1972.

Metal Finishing Guidebook and Directory, 47 Annual Edition. New Jersey: Metals and Plastics Publications, Inc., 1979.

GLOSSARY

Anode: The positive electrode in an electrolysis cell.

Cathode: The negative electrode in an electrolysis cell.

Corrosion: The deterioration of a metal because of a reaction with its environment.

Electrochemistry: The field of chemistry concerned with chemical changes produced by an electric current, and the production of electricity by chemical reactions.

Electrode potential: A measure of the tendency of a metal to go into solution.

Electrolysis: The process in which electric current is passed through a solution of ions to produce desired chemical reactions.

Electrolytic cells: Devices in which electricity is used to produce desired chemical changes.

Electrolytic refining: A process in which metals are purified by electroplating them.

Electroplating: A process in which a thin coating of metal is applied to an object, using an electric current.

Galvanizing: A process in which a thin coating of zinc is applied to an iron object to prevent it from corroding.

Passivity: An unusual inactivity of metals which helps keep them from corroding.

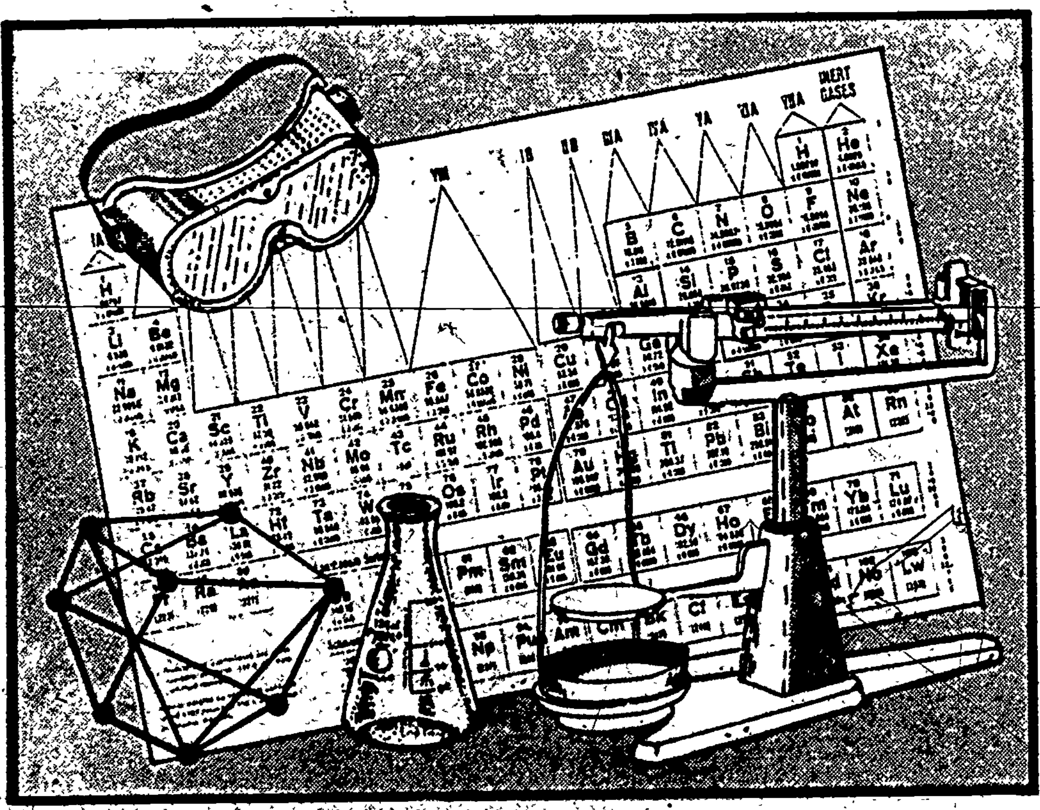
Voltaic cells: Devices in which chemical reactions are used to produce electricity.

ecut

ENERGY TECHNOLOGY

CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-07

METALS AND CERAMICS

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

Approximately three-fourths of the earth's elements are metals. Many of these metals are important to civilization; in fact, it is difficult, if not impossible, for people to go through their daily lives without relying upon products made from metals: coffee pots, toasters, refrigerators, automobiles, tools, doorknobs, and countless other items. A number of important properties of metals and alloys will be considered in this module.

Ceramics are also studied in this module. Ceramics and metals comprise two of the three major materials families. The third member of the materials families, plastics, will be studied in Module CH-10. Ceramics have high compression strength and good heat and thermal-shock resistance. The ceramics family is large and varied. It includes ceramics, glass, brick, cement, and porcelain. Uses of these materials range from common tableware to temperature resistance nose cones for rockets.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of Chemistry for Energy Technology I and Module CH-06 of Chemistry for Energy Technology II.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Explain the differences between crystalline and amorphous solids.
2. List some of the advantages of alloys over pure metals.
3. Match the types of steel with their chemical composition or physical properties.
4. List the three major materials families.
5. Describe the type of bonding that occurs in metals.
6. List four members of the ceramics family.
7. Describe the process for making cermets and list some of their uses.
8. List some of the mechanical properties of materials that are commonly determined through testing.
9. Define the following terms:
    a. Freezing point.
    b. Melting point.
    c. Sublimation.
    d. Density.
    e. Specific gravity.
    f. Elasticity.
    g. Fatigue limit.
    h. Tensile strength.
    i. Compressive strength.
    j. Hardness.
    k. Impact strength.
    l. Creep.
    m. Ductility.
    n. Malleability.
    o. Alloy.
    p. Cermets.

SUBJECT MATTER

SOLIDS

All metals, except mercury, are solids at room temperature. Solids are less compressible than liquids and much less compressible than gases. In fact, solids often are said to be incompressible. Solids retain their volume and their original shape when placed in a container. At the molecular level, the molecules or ions are in rapid motion; but this motion generally is restricted to vibration about a fixed point. The individual molecules or ions are not mobile; they stay in place. These particles arrange themselves in regular geometric patterns, or lattices — not randomly as is characteristic of liquids or gases.

BONDING

Solids may be classified into four groups, based on the type of bonding that occurs in the crystal: the ionic lattice, the covalent lattice, the molecular lattice, and the metallic lattice. An example of the ionic lattice is sodium chloride. This crystal consists of alternate positive and negative ions. The bonding, or force, hold~~ing~~ the crystal together is the attractive forces between oppositely charged ions. These strong, attractive forces cause the crystals to be hard and brittle with a high melting point. Ionic lattice crystals do not conduct an electrical current when solid, but will conduct a current when they are melted.

In some solids, the atoms are bound together by shared pairs of electrons to form a covalent molecule. There are no independent molecules in these solids; they are continuous. Diamonds and sand, which are composed of carbon and silicon dioxide respectively, are examples of covalently bonded solids. These solids generally have very high melting points, are very hard, and are nonconductors of electricity.

Some solids are composed of independent, covalently bonded molecules. The only binding forces between the molecules are relatively weak polar attractions. These solids have low melting points, and the crystals are soft. Dry ice (which is carbon dioxide) and liquid oxygen are examples of this type of solid.

Solid metals are composed of networks of positive ions interspersed with clouds of loosely bound electrons. These mobile electrons account for the high electrical and thermal conductivity of metals.

MELTING POINT

The temperature at which solid and liquid states can exist together is known as either the <u>melting point</u> or the <u>freezing point</u>, depending upon the direction of change occurring. If the amount of solid in equilibrium with the liquid is increasing, the temperature is referred to as the freezing point; if the amount of solid is decreasing, the temperature is known as the melting point. Melting occurs when the crystal has absorbed enough energy to allow the particles to overcome the strong forces holding them together. For crystalline solids, this temperature is a very definite one and may be used to identify unknown solids or to check their purity. Some solids, such as glass and plastics, do not have a regular, geometric lattice pattern. These amorphous solids can be viewed as supercooled liquids, that is, they have an irregular arrangement of the particles comprising the solid. Amorphous solids do not have a sharp, fixed, melting point; rather, they soften and melt over a range of temperatures.

SUBLIMATION

When heated, certain solids are converted directly to the gaseous state without passing through the liquid state — a process known as sublimation. Dry ice, naphthalene, iodine, and camphor are solids that undergo sublimation at ordinary atmospheric pressure. Even solids that can form a liquid phase can sublime. For example, the vapor pressure of ice is 4 mm of mercury at 0°C. Even at the freezing temperature (or below), ice will gradually be converted to water vapor through the sublimation process. On a cold, winter day, even with the temperature below freezing, ice will "disappear" from streets and trees through the sublimation process.

PROPERTIES OF METALS

Metals have a number of properties that are important in the selection of a metal for a particular application. These properties include physical properties, such as density, electrical conductivity, thermal conductivity, and luster. The mechanical properties are strength, hardness, and ductility. Mechanical properties are determined by application of force. They indicate suitability of a metal for mechanical service or use.

DENSITY

<u>Density</u>, defined as "weight per unit volume," is shown by the following equation:

$$D = \frac{W}{V}$$

where:

D = Density.
W = Weight.
V = Volume.

Density is often measured in terms of grams per cubic centimeter. Density of metals is receiving increased attention because of the many applications and uses of metals where weight is an important factor. For example, engineers are constantly seeking metals of high strength and low weight for use in airplanes and automobiles. In fact, metals are being displaced by low-density plastics in many applications.

<u>Specific gravity</u> is the weight of a volume of a material compared with an equal volume of water. The specific gravity of the most dense metal, osmium, is approximately 40 times that of the lightest metal, lithium. The specific gravity and strength-to-weight ratios of some metals and alloys are given in Table 1. The strength-to-weight ratio is the tensile strength in pounds per square inch divided

by the density. The effect of forming an alloy on the strength of a metal is clearly shown from the data for iron and steel. The strength-to-weight ratio for iron is increased nearly 10 times by alloying it with other metals to form steel (from 125,000 to 1,100,000).

TABLE 1. SPECIFIC GRAVITY AND STRENGTH-TO-WEIGHT RATIOS OF METALS AND ALLOYS.

Material	Specific Gravity	Strength-To-Weight Ratio (tensile strength/density)
Magnesium	1.7	545,000
Beryllium alloy	1.8	1,100,000
Aluminum alloy	2.6	800,000
Titanium alloy	4.6	1,100,000
Steel	7.8	1,100,000
Iron	7.9	125,000
Copper	8.9	87,000
Nickel	8.9	140,000

THERMAL PROPERTIES

Metals exhibit a few characteristics that are regarded as their thermal properties: specific heat, thermal conductivity, and thermal expansion. Specific heat for a given substance is defined in the metric system as "the number of calories required to raise the temperature of one gram of that substance one degree Celsius." Generally, metals have strikingly low specific heats. For example, gold has a specific heat of 0.032, and lead has a specific heat of 0.034; whereas, in contrast, water has a specific heat of 1.0, and ethyl alcohol has a specific heat of 0.581.

Thermal conductivity is the rate at which heat is transmitted through a material. Metals usually transfer heat by electron transfer and, sometimes, by vibrations of the atoms. The high thermal conductivity of metals is due to their free electrons, which nonmetals do not have.

Metals generally increase in volume when they are heated. This expansion usually is defined as "the change in length of the metal when its temperature is changed one degree." The coefficient of expansion of some metals is given in Table 2, and an example of thermal expansion is given in Example A.

TABLE 2. LINEAR COEFFICIENT OF THERMAL EXPANSION OF METALS.

Material	Linear Coefficient of Thermal Expansion (in/in/°F)
Lead	0.0000163
Magnesium	0.0000151
Aluminum	0.0000133
Iron	0.0000065
Titanium	0.0000047

EXAMPLE A: THERMAL EXPANSION.

Given: A 100-foot bridge span made of steel (iron).

Find: Calculate the increase in length when the temperature increases from 0°F to 100°F.

Solution: 100 ft x 12 in/ft = 1200 in
1200 in x 0.0000065 in/in/°F x 100°F
= 0.78 in.

The 100-foot steel span increased approximately three-fourths of an inch with a change in temperature to 100°F. Therefore, it is apparent that an engineer must consider the thermal expansion of materials in designing structures that are subjected to changes in temperature.

ELECTRICAL CONDUCTIVITY

Metal atoms have valence electrons that are not firmly associated with one particular atom. A measure of the ease with which these electrons flow through the metal lattice is called electrical conductivity, whereas the interference which a metal offers to the passage of electrons is called electrical resistivity. Increasing the temperature of a metal increases the vibrational activity of its ions, thereby interfering with electron flow and decreasing conductivity. Adding alloying elements to a metal also decreases conductivity because this adds a greater amount of imperfections to the metal lattice. Lowering the temperature of metals will increase conductivity: at a temperature near absolute zero, the metal may become super-conductive. Some electrical devices are kept cold to increase their electrical conductivity.

MECHANICAL PROPERTIES AND TESTING

Strength, hardness, ductility, and toughness are mechanical properties of metals. These properties make them useful in many applications. When metals are compressed or stretched, the atoms of the crystal are either pushed together or pulled apart; but when the force, or load, causing the deformation is removed, the metal returns to its original dimension. This property is called elasticity. The most common test to identify the strength of a metal is to pull a specially constructed specimen of the metal until it breaks. The value obtained, called tensile strength, is dependent upon the orientation and size of the grains that comprise the metal. The tensile strength gives the ultimate point at which a structure would break under a load. Therefore, in designing a structure, engineers make certain that the tensile strength is not approached closely.

Dynamic, or cyclic, loading is also a very important part of the study of the strength of metals. For instance, a load applied repeatedly can cause fracture in a metal at a much lower value than ultimate tensile strength. Most steels have a fatigue limit of approximately 50% of their tensile strength.

At elevated temperatures, the strength of metals decreases because the activity of the atoms increases and their attraction decreases. For example, the tensile strength of steel is 80,000 psi at ordinary temperatures, but it is reduced to 30,000 psi at 900°F (482°C).

Compressive strength is the ability of a material to resist a load that is pressing downward upon it without breaking. High compressive strength is required for foundations, supports, and pillars, such as those used in bridges.

The hardness of a metal is a measure of its resistance to indentation or penetration. The three most common hardness measurement tests are as follows: Brinell, Vickers, and Rockwell. The Brinell hardness determination consists of applying a load of 3000 kg for 30 seconds to a hard steel ball that is 10 mm in diameter as it rests on the smooth surface of the steel to be tested. Then the diameter of the impression made by the ball is measured, and the Brinell number is calculated. The Vickers test is similar; however, a diamond pyramid is used instead of a ball. In the Rockwell test, the indentation made by a diamond cone under a load of 150 kg is measured. Since the relationship between hardness and tensile strength in steel is very consistent, and the hardness tests are nondestructive, hardness tests are often used to give an estimate of tensile strength. This is a convenient method of checking on heat-treatment procedures. However, true tensile strength can be determined only through destructive testing.

Impact strength is another important consideration in material selection. A metal may be strong, as indicated by a high tensile strength, but may have a low impact strength — that is, it is relatively brittle. Impact strength, or toughness, of a material is its capacity for resisting mechanical shock. In determining impact strength, the test specimen is placed where it may be struck by a heavy pendulum that is released from a fixed height.

When stressed over a long period of time, some metals extend very gradually, and they may fail at a stress well below the tensile strength of the metal. This phenomenon is known as <u>creep</u>. Such slow extension is common at high temperatures. The effects of creep must be considered in steam turbines, boilers, and other equipment subjected to continual high temperatures.

Additional metal properties that are important are ductility and malleability. <u>Ductility</u> is a measure of the ability of a metal to be drawn into a wire. <u>Malleability</u> is a measure of the ability of a metal to be rolled out or hammered into thin films. Copper, silver, and gold are metals that exhibit a high degree of ductility and malleability.

The metal tests just considered are called destructive tests since test pieces are made and tested until a failure occurs. This type of test is adequate if the test piece is representative of the production material. In materials such as rolled steel and drawn rod — which are uniform in properties throughout a large batch of material — destructive testing can accurately predict the properties of a final product. However, in individually produced parts — such as castings and welded joints — the quality may vary widely. In such cases, non-destructive tests can be used. Non-destructive tests include X-ray methods, gamma-ray methods, ultrasonic testing, magnetic particle inspection, and dye penetrant examinations.

ALLOYS

An alloy is usually composed of two or more metals; or it can be one metal and a nonmetal, such as carbon, phosphorous, or silicon. Although there are several reasons for making alloys of metals, the primary one is to improve the mechanical properties of the principal metal. For example, it may be desirable to increase the hardness, tensile strength, ductility, or toughness of a metal. Other reasons for forming an alloy include the following:

- To improve the corrosion resistance of the principal metal.
- To improve the casting, hot working, weldability, or other processing or fabrication characteristics.

CLASSIFICATIONS

Alloys can be grouped into three classifications based upon their structures.

1. The alloy may be a simple mixture in which the component metals are insoluble in each other and the elements retain their identify. For example, tin and lead (in plumbers solder) are insoluble in each other in the solid state.
2. The alloying element also can be dissolved into the crystal lattice of the major metal to form a solid solution.
3. In intermetallic compounds the atoms of the components of the alloys appear in definite atomic ratio, such as copper-zinc alloy Cu_5Zn_8.

The composition, uses, and properties of some common elements are given in Table 3. Some of the alloys, such as stainless steel, may have variable compositions – that is, there is a variety of steels that are labeled "stainless."

TABLE 3. COMMON ALLOYS.

Name	Composition	Properties	Uses
Stainless steel	80.6% Fe, 0.4% C 18% Cr, 1% Ni	Resists corrosion	Kitchen fixtures, tableware
Pewter	85% Sn, 6.8% Cu 6% Bi, 1.7% Sb	Corrosion resistant	Utensils
Dental amalgam	70% Ag, 25% Pb 3% Cu, 2% Hg	Easily worked	Dental fillings
Monel	69% Ni, 33% Cu, 7% Fe	Resists corrosion, bright surface	Kitchen fixtures
Sterling silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Yellow brass	67% Cu, 33% Zn	Easily polished, ductile	Hardware items
Wood's metal	50% Bi, 25% Pb, 2.5% Sn, 12.5% Cd	Melts at 70°C	Fuse plugs, automatic sprinklers
Silver coins, U.S.	90% Ag, 10% Cu	Resists corrosion, shiny	Coins
18 carat, yellow gold	75% Au, 12.5% Ag, 12.5% Cu	Bright, shiny	Jewelry
Nickel, U.S.	75% Cu, 25% Ni	Corrosion resistant, shiny	Nickel coin

TYPES OF STEEL

The most important alloys are those of iron which are called "steels." Iron and steel can be classified as follows: (1) pig iron, (2) cast iron, (3) wrought iron, (4) metal powder-sintered iron, (5) carbon steel, (6) alloy steel, (7) high-alloy steel, and (8) tool steel. Each of these classes are discussed briefly in the following paragraphs.

Pig Iron

Pig iron is not used directly to produce finished articles, but is used as a raw material in producing more highly refined iron or steel. Interestingly, "pig iron" received its name because it was thought that the rounded backs of the bars – as they were cast for later remelting – resembled a herd of pigs. Pig iron contains 4% carbon; therefore, it is very hard and brittle. Pig iron is the product obtained from a blast furnace – which is the method used to reduce approximately 90% of the iron ore to metallic iron. A blast furnace consists of a steel shell that is approximately 30 feet in diameter, up to 150 feet high, and lined with refractory firebrick. Iron ore (iron oxide), limestone (calcium carbonate), and coke (carbon) are introduced through the top of the furnace. Air that has been preheated to 1200°F is introduced through the bottom of the furnace. Thus, the iron oxide is reduced by the carbon to form pig iron, which is removed from the bottom of the furnace at intervals. Large quantities of oxygen are used in blast furnaces since the addition of about 5% oxygen to the air yields an additional 20% output of iron.

Cast Iron

Cast iron is produced by heating coke, pig iron, scrap steel, and limestone in a furnace. Although the composition of cast iron varies, it usually is high in carbon content (approximately 3%). Cast iron is the metal of the foundry; it is valued because of its good casting properties, ease of shaping, and desirable mechanical- and corrosion-resistant properties.

Wrought Iron

Although wrought iron is decreasing in popularity, it still is used in making pipe. Wrought iron consists of approximately 0.01% silicone, 0.02% sulfur, 0.10% phosphorus, 0.05% manganese, and 0.03% carbon. Iron, which is the remaining element, makes up the balance.

Powdered Iron

Powdered iron can be converted into many useful products of complex shapes by the technique called "powder metallurgy." Powdered iron is placed in a mold and then compacted somewhat. The article is then sintered, or heated, near the melting point of iron. The sintering occurs in a controlled-atmosphere furnace in order to prevent excessive oxidation.

Carbon Steel

The term "carbon steel" is used to denote those steels having a carbon content of from 0.005% up to approximately 1.0%. Increasing the carbon content leads to marked increases in hardness and strength of steel. These steels have specific names, such as mild steel, low-carbon steel, medium-carbon steel, and high-carbon steel. Carbon steels are used to make the following: railroad rails, springs, machine parts, auto frames, and steel for galvanizing and enameling. Carbon steels may contain small amounts of other elements, such as manganese, sulfur, copper, and silicon.

Alloy Steels

It was determined by accident that steels with higher than normal quantities of alloying elements had markedly different characteristics than regular carbon steel. The most commonly-used alloying metals in steel are copper, vanadium, nickel, chromium, molybdenum, and manganese. Since many alloys can have approximately the same combination of properties, it is common practice for designers or engineers to specify the properties desired of a steel and leave the composition up to the producers. A common use of alloy steels is in applications calling for a high tensile strength steel, such as in the manufacture of cranes, truck frames, and railroad cars. This tensile strength is greatly improved by careful heat-treating of the steel. Alloy steels generally have a low concentration of carbon. Steels for use at elevated temperatures (up to 1100°F) usually contain as much as 9% chromium. For low temperature applications, alloy steels containing as much as 9% nickel are used.

High-Alloy Steel

When the combined amount of chromium, manganese, or nickel in steel is 10% or higher, the material is called a "high-alloy" steel. The stainless steels are one major class of high-alloy steel. There are more than 30 standard stainless steels. These are noted for their corrosion resistance, as well as their non-magnetic and outstanding low-temperature characteristics. Unfortunately, stainless steels may cost 10 times as much as carbon steel. An important application for high-strength, heat-resisting alloys is in steam-piping and super-heater tubing in a high-pressure-steam, electrical-power generating plant. A high chromium-nickel alloy is used to withstand the 1100°F operating temperatures in these plants.

Tool Steel

There is a family of steels manufactured specifically for making tools. These tool steels range from carbon steels (which are used for their exceptional hardness) to alloy steels. Some tool steels are used in high-strength structures, such as airframes of aircraft.

EXAMPLES OF OTHER ALLOYS

A greater variety of changes can be made in the mechanical properties of iron by alloying with carbon than by alloying with any other element. Carbon can form a true solution with iron, or it may form the compound iron carbide.

Iron carbide is a material of extreme hardness that accounts for much of the hardening effect of carbon in steel. Manganese generally is added to steel as an alloying element to combine chemically with the oxygen or sulfur that may be present. It also promotes greater strength by increasing the hardness of the steel. In high percentages, phosphorus is detrimental to steels; it causes them to be brittle. However, in amounts up to approximately 0.10%, phosphorus improves strength and machinability of steels. Sulfur and selenium, in quantities of up to 0.30%, are added to some steels to improve their machining properties. These elements apparently lubricate the tip of the machining tool, thereby preventing it from galling or seizing with the material being machined. Silicon is used primarily to remove an excess amount of oxygen from steel, but it also improves the hardness and strength of the steel. As much as 4% copper may be added to steel to retard corrosion and increase its hardening ability. Chromium, the basic element in stainless steels, is added primarily for its hardening effect and its outstanding corrosion resistance. An interesting application of nickel in steel is in the manufacture of invar, which contains 35-45% nickel. Invar has an extremely low thermal expansion characteristic and is used in glassblowing applications where metal-glass seals are required. Molybdenum normally is added to steels for service at elevated temperatures. It greatly increases the high-temperature strength and creep-resistance of alloy steels. Lead is added to many types of steel to improve their machinability, thereby allowing parts to be machined at greater speeds with consequent savings in costs.

CERAMICS

Metals comprise one of the three major materials families. The other two are the organic plastics and the ceramic materials. The inogranic ceramic family is large and varied. It includes glass, brick, cement, porcelain, and ceramics.

Ceramics, as a class, have low tensile strength and are relatively brittle. Ceramics have a much higher compressive strength than tensile strength. In fact, the widespread use of cement is attributed primarily to its high compressive strength. One of the major distinguishing characteristics of the ceramic family – as compared to metals – is their almost total absence of ductility. Ceramic materials – in general – are considerably harder than most other materials, making them especially useful as wear-resistant parts and for abrasives and cutting tools.

Ceramics have the highest known melting points of any materials. Hafnium carbide, for example, has a melting point slightly above 7000°F compared to 2600°F for the metal tungsten. Because of their excellent temperature resistance, ceramics are used in linings of furnaces for making glass and steel. Ceramics are relatively low in thermal conductivity and thermal-shock resistance compared to metals.

Almost all ceramic materials have excellent chemical resistance. They are inert to all chemicals except hydrofluoric acid. Ceramics have relatively few free electrons and, therefore, are nonconductive, as well as being good electrical and thermal insulators.

The composition of ceramics varies widely. Ceramics contain metals such as aluminum, silicon, magnesium, beryllium, titanium, and boron, combined with non-metals such as carbon or nitrogen. Some ceramics contain only one compound, whereas others contain a combination of two or more compounds. Alumina (Al_2O_3) and magnesia (MgO) are two of the most common ceramic compounds that are single compounds.

The basic steps in producing ceramic products are (1) preparing the ingredients for forming, (2) shaping or forming the part, (3) drying, and (4) firing or sintering. Ceramics can be formed by a large number of methods in either the dry or liquid state. Parts may be made by casting, molding, pressing, or extrusion. Drying is conducted to remove any moisture prior to firing. During firing, chemical reactions occur. These reactions produce the final bonding.

Ceramics have many technical uses because of their high temperature and chemical, electrical, and abrasion resistance. They are used in gas turbines, jet engines, nuclear reactors, and for high temperature processes. Some widely used ceramics and their applications are considered in the following paragraphs.

Refractory ceramics are produced from clays. Alumina (aluminum oxide) is the most widely used refractory ceramic. It is relatively low in cost, is plentiful, and has good mechanical properties. Alumina is widely used as an electrical insulator and in applications utilizing its excellent chemical resistance. Beryllia (beryllium oxide) is noted for its high thermal conductivity, which is about 10 times the conductivity of alumina and three times the conductivity of steel. Because of this high thermal conductivity, combined with excellent electrical resistance, beryllia is used for transisters, resistors, and in other electrical applications to distribute heat. Unfortunately, beryllia is costly, difficult to work with, and its dust is toxic, requiring special handling and precautions. Cordierite is a mixed oxide used in heating elements, thermocouples, radiant elements in furnaces, and as furnace refractory brick.

There are three commonly used carbides: silicon carbide, tungsten carbide, and titanium carbide. These carbides have the highest melting points of all materials. Silicon carbide is commonly known as carborundum; it is used in wear and abrasion applications. Tungsten carbide is used mainly for cutting tips and tools.

Ferrites are mixed metal oxide ceramics that contain high electrical resistivity and strong magnetic properties. Ferrites are used as memory cores for computers; in permanent magnet motors in automobiles, small appliances, and portable electric tools; and as the phonograph pickup device.

Glass is an important member of the ceramic family. It is one of the oldest and most widely used materials. Glass is made from the most abundant resource on the earth – silica, or sand. Many types of glass are produced. Soda-lime glass is the least expensive. It is commonly used for bottles, kitchenware, windowpanes, and plate glass and accounts for about 90% of the glass used in this country. Soda-lime glass is made from soda ash (Na_2CO_3), lime (CaO), and high-purity sand (SiO_2). Lead glass is made by utilizing the additives lead oxide and potash (K_2CO_3). Lead glass has excellent optical properties and is widely used for lenses in spectacles and optical instruments. It is also used for cut glass, tableware, and vases. Lead glass is often called "crystal," although, like all glasses, it has no crystalline structure. Borosilicate glasses have excellent chemical durability, as well as resistance to heat and thermal shock. One variety, known as Pyrex, is used in ovenware. Another variety, known as Kovar, can be used to form glass-to-metal seals.

Borosilicate glasses are used in gauges, sights, piping, electronic tubes, pump impellers, and laboratory glassware. Borosilicate glass contains approximately 18% boron oxide. Fused quartz is composed of pure silicon dioxide and is used in scientific applications such as prisms, solar-cell covers, lasers, and radar.

Ceramics generally have high melting points and good high temperature strength; however, they are brittle and have poor resistance to mechanical shock. To overcome some of the deficiencies of ceramics, combinations of metals and ceramics have been developed. These materials, known as cermets, are made by powder metallurgy methods. Powders of suitable particle size that contain a mixture of metal and ceramics are compressed in dies under high pressure. The powder undergoes a degree of cold-welding and will hold its shape when removed from the die. It is then sintered or heated to a temperature near the melting point of the metal to allow knitting of the metal particles. Then, the cermet is composed of hard rigid ceramic particles bonded in a tough metallic matrix. The proportion of ceramic-to-metal can be varied to produce cermets with a range of properties. Cermets are used in heating elements, bearings, gas-turbine parts, rocket-engine and jet-engine parts, lamp filaments, cutting tools, and grinding tools.

LABORATORY MATERIALS

Laboratory 1

10 test tubes
Test tube rack
5 strips of copper, approximately 2 x 1/2 inch
5 strips of zinc, approximately 2 x 1/2 inch
Glass rod
Lead nitrate, 5% solution
Zinc nitrate, 5% solution
Mercurous nitrate, 5% solution
Silver nitrate, 5% solution
Copper nitrate, 5% solution

Laboratory 2

100 ml beaker
Test tubes, small
HCl, 6 M
$AgNO_3$, 0.1 M
$Hg_2(NO_3)_2$, 0.1 M
$Pb(NO_3)_2$, 0.1 M
Medicine dropper
K_2CrO_4, 0.1 M
NH_4OH, 6 M
HNO_3, 6 M
Unknown solution containing any combination of silver, lead, or mercury ions

LABORATORY PROCEDURES

LABORATORY 1. REACTIONS OF METALS WITH SALT SOLUTIONS.

In this experiment, strips of zinc and copper are reacted with various salt solutions. Equations are to be written in the Data Tables for those cases where reactions occur. Metals are to be arranged in an activity series.

PROCEDURE

Carefully record all data in Data Table 1.

1. In separate test tubes, place solutions of copper nitrate, silver nitrate, mercurous nitrate, zinc nitrate, and lead nitrate.
2. Put a strip of zinc in each test tube. Bend the end of the strip so that it hangs on the edge of the test tube.
3. In five additional test tubes, place solutions of copper nitrate, silver nitrate, mercurous nitrate, zinc nitrate, and lead nitrate.
4. Put a strip of copper in each of these test tubes. Bend the end of the strip so that it hangs on the edge of the test tube.
5. Let the metal strips stand in the solutions for at least five minutes.
6. Remove the zinc strip that has been in the solution of mercurous nitrate.
7. Rinse the strip, then rub it with a finger. Bend the strip and examine the broken edge. (1) What metal has been deposited on the strip? Record the answer in Data Table 1.

8. Remove the copper strip from the solution with mercurous nitrate. Rinse and rub with a finger. (2) What has been deposited on the copper? Record the answer. (3) What does the color of the solution that remains in the test tube indicate? Record the answer.
9. Remove the zinc strip from the silver nitrate solution and remove the deposit. (4) What metal was deposited on the zinc strip? Record the answer.
10. Examine the zinc strip placed in the copper nitrate solution. (5) What was deposited? Record the answer.
11. Examine both of the test tubes in which zinc nitrate was placed. (6) Was there a reaction? Record the answer. (7) What occurred? Record a description.
12. Complete the equations in Data Table 1 for those reactions that occurred.
13. Use the data to arrange the metals in an activity series.

LABORATORY 2. QUALITATIVE ANALYSIS OF METALS.

Analytical chemistry involves the methods of determining the composition of substances and mixtures of substances and solutions. When chemical analysis is restricted to finding which ions are present, the analysis is qualitative. However, when the precise amounts of the ions are determined, the analysis is quantitative. Obviously, qualitative analysis must precede quantitative, that is, what is present in a substance (the composition) must be known before how much of a particular component that is present (the quantity) can be determined.

In identifying a substance such as KCl, one does not isolate the potassium in order to recognize this metal. Nor is chlorine gas obtained from the compound. This type of approach would be accurate; but, in many cases, it would be difficult to carry out. A more convenient and equally reliable procedure consists of taking the substance into solution and, by adding appropriate reagents, forming characteristic insoluble compounds of each of the ions. Thus, in the case of KCl, the presence of Cl^- would be indicated by adding $AgNO_3$ to part of the solution. The formation of a white, curdy precipitate would indicate the presence of chloride. To another part of the original solution, some $Na_3CO(NO_2)_6$ could be added. A yellow precipitate would show the presence of potassium ion. A systematic procedure can be established to positively identify all of the metals, as well as all of the non-metals. In this experiment, the scheme for identifying silver, mercurous, and lead ions is used.

PRELIMINARY PROCEDURES

Note: The following procedures contain preliminary experiments. The purpose of preliminary experiments is to determine the main reactions of the ions. These reactions are utilized later in the schemes of analyses.

Lead Ion

Carefully record all data in Data Table 2.

1. In a small test tube, add two drops of dilute HCl to two drops of the test solution of Pb^{++}. (1) Note the nature and color of the precipitate and record these findings in Data Table 2. (2) Write the ionic equation for the formation of the precipitate in Data Table 2.
2. Allow the precipitate to settle in the test tube (or centrifuge the solution if possible). Decant, or draw off, the liquid with a medicine dropper. Discard the solution.
3. Add several drops of water and stir, then remove the water.
4. To the washed precipitate (from Step 3), add five drops of water. Then place the tube in a boiling water bath. Stir while heating. (3) Does the precipitate dissolve? (Silver and mercurous chlorides are insoluble in hot water.) Record the answer.
5. Add one drop of acetic acid and one drop of K_2CrO_4 to the solution. (4) What reaction is observed? Record the answer.

   This test confirms the presence of lead ion in a solution.

Silver Ion

Carefully record all data in Data Table 2.

1. Add two drops of dilute HCl in a small test tube that contains two drops of the test solution Ag^+. (5) Note

the nature and color of the precipitate and record these findings in Data Table 2. (6) Write the ionic equation for the formation of the precipitate in Data Table 2.

2. Allow the precipitate to settle in the test tube (or centrifuge the solution if possible). Decant, or draw off, the liquid with a medicine dropper. Discard the solution.
3. Wash the precipitate by adding two drops of water, stirring, and centrifuging. Discard the washings.
4. Treat the residue of AgCl with five drops of dilute NH_3(NH_4OH) and stir until the solution takes place.
5. Add dilute HNO_3 – drop-by-drop – and stir the mixture after each addition until it is acid. To check for the acid condition, touch the wet stirring rod on dry, blue litmus paper. If the paper turns red, the solution is acid. (7) What happens? Record the answer.

Mercurous Ion

Carefully record all data in Data Table 2.

1. In a test tube, treat two drops of the test solution of Hg_2^{++} with two drops of dilute HCl. (8) Note the nature and color of the precipitate and record these findings in Data Table 2. (9) Write the equation for the formaation of the precipitate in Data Table 2.
2. Allow the precipitate to settle in the test tube (or centrifuge the solution if possible). Decant, or draw off, the liquid with a medicine dropper. Discard the solution.
3. Wash the residue with two drops of water. Discard the washings.

4. Add two drops of dilute NH_3 to the residue and stir the precipitate. (10) What is the color of the precipitate? Record the answer.
5. Centrifuge and reject the solution.
6. Add aque regia (one drop of concentrated HNO_3, four drops concentrated HCl) and set the tube in a water bath. Heat and stir until solution is complete.
7. Transfer the solution to a 5 ml beaker and carefully boil down just to dryness. (Do not allow it to become completely dry.)
8. Add two drops of water. Transfer the clear solution to a test tube and add one drop of reagent $SnCl_2$. (11) What is observed? Record the answer.

PROCEDURE

Analysis of Silver, Lead, and Mercury Ions

Carefully record all data in Data Table 2.

1. Add two drops of dilute HCl to 1 ml of a test solution containing silver, lead, and mercury ions. Stir vigorously and allow the precipitate to settle.
2. Add one more drop of dilute HCl.
3. To the residue, add three drops of dilute HCl and stir. Remove the washings and discard.
4. Add 1 ml of water to the precipitate and place it in a boiling water bath. Stir for several minutes.
5. Separate the solution from the residue, transferring the clear solution to a test tube. The solution may be Pb^{++}.

6. Add a drop of acetic acid and five drops of K_2CrO_4 to the solution. A yellow precipitate shows the presence of Pb^{++}.
7. The residue may be AgCl, Hg_2Cl_2, and some undissolved $PbCl_2$. To remove the $PbCl_2$, add 10 drops of water, set the tube in a boiling water bath, and stir for one minute. Separate the solution and discard.
8. Add 10 drops of dilute NH_3 to the residue. Stir for several minutes and separate the residue and solution.
9. Transfer the solution to a clean test tube. Add another 10 drops of NH_3 to the residue and stir. Then combine the solutions.
10. The solution may contain Ag^+. Add dilute HNO_3 and stir until the mixture becomes acid. A white precipitate (or cloudiness) proves the presence of Ag^+.
11. If the residue is black, the presence of Hg_2^{++} is confirmed. However, to ensure confirmation of Hg_2^{++}, add five drops of aqua regia (four drops of concentrated HCl and one drop of concentrated HNO_3). Stir; then set in a water bath and stir until the solution is complete.
12. Transfer the solution to a 5 ml beaker. Then, under hood, carefully boil this down almost to dryness to destroy the excess aqua regia.
13. Add four drops of water and stir.
14. Transfer the clear solution to a test tube and add one or two drops of $SnCl_2$. A white, grey, or black precipitate proves the presence of Hg_2^{++}. (12) Obtain an unknown containing Ag^+, Pb^{++}, and/or Hg_2^{++} and analyze it. Record the answer in Data Table 2.

DATA TABLES

DATA TABLE 1. REACTIONS OF METALS WITH SALT SOLUTIONS.

(1) ____________________

(2) ____________________

(3) ____________________

(4) ____________________

(5) ____________________

(6) ____________________

(7) ____________________

Complete the following equations in the cases where a reaction occurred:

$AgNO_3 + Zn$

$AgNO_3 + Cu$

$Hg_2(NO_3)_2 + Zn$

$Hg_2(NO_3)_2 + Cu$

$Pb(NO_3)_2 + Zn$

$Pb(NO_3)_2 + Cu$

$Cu(NO_3)_2 + Zn$

$Zn(NO_3)_2 + Cu$

Activity Series

____________ (metal replaced by all others)

____

____

____

____

____________ (metal not replaced by any other)

DATA TABLE 2. QUALITATIVE ANALYSIS OF METALS.

(1) ____
(2)
(3) __________________________________
(4) __________________________________
(5) __________________________________
(6)
(7) __________________________________
(8) __________________________________
(9)
(10) __________________________________
(11) __________________________________
(12) Ions present in unknown: ________________________

REFERENCES

Bachmann, H.G. "The Origin of Ores." *Scientific American* 202 (June 1960): p. 146.

Cottrell, A.H. "The Nature of Metals." *Scientific American* 218 (September 1967).

Mott, Sir Nevill. "The Solid States." *Scientific American* 217 (September 1967).

Pascoe, K.J. *An Introduction to the Properties of Engineering Materials*. New York: Interscience Publishers, Inc., 1961.

Rogers, Bruce A. *The Nature of Metals*. Ames, IA: Iowa State University Press, 1964.

Starfield, Martin J. and Arthur M. Shrager. Introductory Materials Science. New York: McGraw-Hill Book Company, 1972.

Tottle, C.R. The Science of Engineering Materials. New York: Chemical Publishing Co., Inc., 1966.

Van Vlack, L.H. Elements of Material Science. Reading, MA: Addison-Wesley Publishing Co., Inc., 1959.

GLOSSARY

Alloy: A metal composed of two or more metals or a metal and a non-metal.

Ceramic: A temperature resistant material composed of a metal such as aluminum, silicon, magnesium, beryllium, titanium, or boron, combined with a non-metal such as oxygen, carbon, or nitrogen.

Cermet: A material formed from metal and ceramic powders.

Compressive strength: The ability of a material to resist a compressive load without breaking.

Creep: The slow extension of a material.

Density: The weight per unit volume of a material.

Ductility: The ability of a metal to be drawn into a wire.

Elasticity: The property of a material that allows it to regain its original dimension after being deformed by a force.

Ferrite: A metal oxide ceramic that has strong magnetic properties.

Freezing point: Temperature at which solid and liquid states exist together and the proportion of solid is increasing.

Glass: A member of the ceramic family that is comprised primarily of silicon dioxide.

Hardness: A measure of a material's resistance to indentation or penetration.

Impact strength: The capacity of a material for resisting mechanical shock.

Malleability: A measure of the ability of a metal to be rolled or hammered into thin films.

Melting point: Temperature at which solid and liquid states exist together and the proportion of solid is decreasing.

Specific gravity: The weight of a volume of material compared with an equal volume of water.

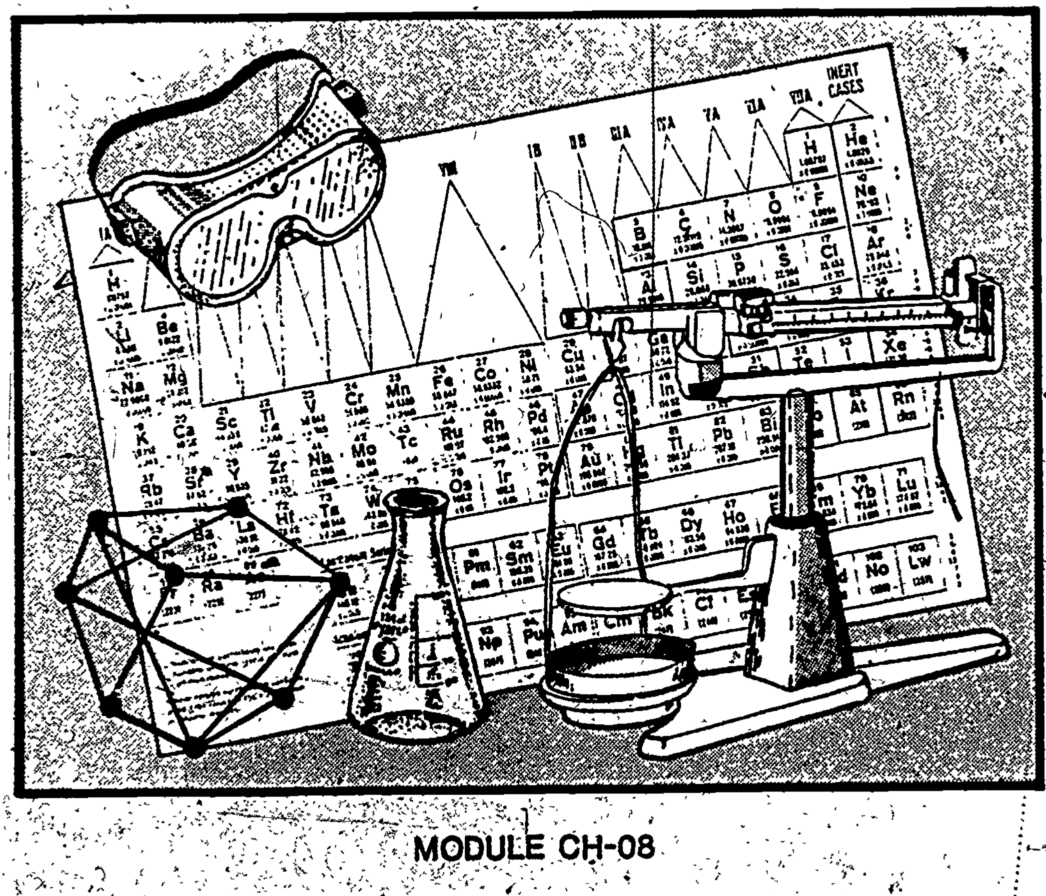
Sublimation: The direct conversion of a solid into a vapor without passing through the liquid state.

Tensile strength: The strength of a material that is exhibited when it is pulled apart.

ENERGY TECHNOLOGY

CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-08

THERMODYNAMICS AND THERMOCHEMISTRY

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

Thermodynamics is the study of the relationships between heat energy and other forms of energy called work. The principles of thermodynamics are important in power plants, refrigeration, and other devices that use heat to produce power or that use engines to add or remove heat. Heat, specific heat, refrigeration capacity, heats associated with changes of state, and solar energy storage are some of the thermodynamic topics considered in this module. Heat transfer, heat pipes, and heat engines are also discussed.

Thermochemistry is the study of the heat that accompanies chemical reactions. Calorimetry, a method of measuring the heat effect of fuels, is presented in this module, as well as the relationship between matter and energy.

Thermodynamics and thermochemistry are important to the energy technician because they are topics that relate to heat and, therefore, to the fuels that produce heat.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of <u>Chemistry for Energy Technology I</u> and Modules CH-06 and CH-07 of <u>Chemistry for Energy Technology II</u>.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Describe the relationship between potential energy and kinetic energy.

2. Use specific heats to calculate heat gains and losses.
3. Use specific heats to calculate refrigeration capacity.
4. Calculate the amount of heat required for phase changes such as fusion or vaporization.
5. Calculate the enthalpy (total heat) involved in the heating of a substance.
6. Discuss the importance of high specific heat and high density for materials to be used for solar energy storage.
7. Identify three mechanisms of heat transfer.
8. Briefly describe the operation and uses of a heat pipe.
9. Given the low and high temperatures, calculate the efficiency of a heat engine.
10. Define the following terms:
    - a. Calorimetry.
    - b. Heat of combustion.
    - c. Thermodynamics.
    - d. Energy.
    - e. Potential energy.
    - f. Kinetic energy.
    - g. Work.
    - h. Btu.
    - i. Calorie.
    - j. Specific heat.
    - k. Latent heat.
    - l. Heat of fusion.
    - m. Heat of vaporization.
    - n. Sensible heat.
    - o. Enthalpy.
    - p. Superheated vapor.
    - q. Conduction.
    - r. Convection.

s. Radiation.
t. Exothermic.
u. Endothermic.
v. Heat engine.

THERMODYNAMICS

Thermodynamics is the science of the relationships between heat energy (thermo) and other energy forms called work (dynamics). Because of the energy crisis, thermodynamics has gained in popularity, since better utilization of the energy that is stored in fuels is needed. Many of the principles of thermodynamics are used in refrigeration. Electrical energy is used to run a compressor that extracts heat from the air. Thus, refrigeration is not the manufacture of cold air, but it is the removal of heat. A refrigeration system is a heat pump that pumps heat from a low-temperature level to a higher-temperature level. From this higher-temperature level, the heat can be rejected to air or water. An understanding of heat, energy, work, and power is important to the field of refrigeration and, therefore, to the energy technician.

Energy is the capacity to do work. Energy can be found in many different forms, such as mechanical, chemical, electrical, light, or heat. Energy may also be classified as either potential or kinetic. Potential energy is the energy that an object possesses by virtue of its position or composition. For example, water stored behind a dam has potential energy because of its position. A combustible chemical has potential energy because of its composition. Kinetic energy is energy of motion. The magnitude of the kinetic energy of an object is given by the following relationship:

$$E_k = \frac{1}{2} mv^2 \qquad \text{Equation 1}$$

where:

E_k = Kinetic energy.
m = Mass.
v = Velocity.

Thus, the larger the mass of a moving object and the greater its speed, the more energy the object possesses. Work is accomplished when a force moves a mass across a distance. Work is defined by the following mathematical expression:

$$W = f \times d \qquad \text{Equation 2}$$

where:

W = Work.
f = Force.
d = Distance.

The English or engineering unit of work is the foot-pound (ft-lb). One foot-pound is the amount of work resulting from the movement of an object with a mass of one pound through a distance of one foot.

EXAMPLE A: CALCULATION OF WORK.

Given: Water weighs 8.3 lb/gal.

Find: Amount of work done in pumping 500 gal of water to a height of 100 ft.

Solution:

$$\begin{aligned} W &= f \times d \\ &= 500 \text{ gal} \times 8.3 \text{ lb/gal} \times 100 \text{ ft} \\ &= 415{,}000 \text{ ft-lb.} \end{aligned}$$

HEAT

All matter is composed of atoms and molecules that are in constant motion. When heat is added to matter, the atom and molecules increase in motion or vibration. Heat is a form of energy that cannot be measured directly. However, the intensity of heat can be measured with a thermometer that gives the temperature of a substance. Temperature is a relative value: a substance is either hot or cold in relation to another object. For example, boiling water is hot compared to ice, but is cold compared to molten iron. Heat and temperature should not be confused. Heat is a measure of a quantity, and temperature is a measure of degree or intensity. For example, if both a one-gallon and a two-gallon container contained boiling water, the two gallons of water would contain twice as much heat as the one gallon of water, even if both had the same temperature of 100°C.

The British thermal unit (Btu) is the unit of heat quantity normally used in refrigeration and other engineering work. The Btu is the amount of heat energy necessary to raise the temperature of one pound of water 1°F. For example, it takes 10 Btu to raise the temperature of one pound of water from 85 to 95°F.

The calorie is the unit of heat quantity used in scientific work. The calorie is the heat energy necessary to raise the temperature of one gram of water 1°C. One Btu equals 252 gram calories.

SPECIFIC HEAT

Specific heat is the amount of heat required to raise the temperature of one pound of any substance 1°F. Thus, the specific heat of water is one Btu per pound. The specific heat of some common substances is given in Table 1.

TABLE 1: SPECIFIC HEAT OF COMMON MATERIALS.

Material	Specific Heat (Btu/lb)
Aluminum	0.226
Brass	0.090
Copper	0.094
Ice	0.49
Lead	0.031
Oil	0.43
Steel	0.11
Tin	0.053
Water	1.00
Zinc	0.096

In refrigeration work, specific heat is used to determine how much heat must be removed to refrigerate various products, such as meat, milk, and bananas. The specific heats of foods are relatively high because of their moisture content.

The amount of heat necessary to change the temperature of a material is given by the following equation:

$$H = W\,c\,(t_2 - t_1) \qquad \text{Equation 3}$$

where:

W = Weight, in lb.
c = Specific heat, in Btu/lb.
t_2 = Second temperature.
t_1 = Initial temperature.

EXAMPLE B: SPECIFIC HEAT.	
Given:	Five pounds of steel at 70°F.
Find:	Amount of heat required to raise the temperature to 300°F.
Solution:	From Table 1, the specific heat of steel is 0.11. $H = W c (t_2 - t_1)$ $= 5 \text{ lb} \times 0.11 \text{ Btu/lb} (300 - 70)$ $= 126 \text{ Btu.}$

In Example B, 126 Btu are required to raise the temperature of steel from 70° to 300°F. A hotter object would be required to transfer the 126 Btu to the steel. Any heat gain in one substance is offset by an equal heat loss by another substance. This concept, which is the basis for heat transfer calculations, is illustrated in Example C.

EXAMPLE C: HEAT GAIN AND LOSS.

Given: Ten pounds of steel at 400°F dropped into three gallons of water at 65°F.

Find: Final temperature of steel and water, neglecting any heat gain or loss by the container walls.

Solution: Heat gain in water, H_w, equals heat loss in steel, H_s.

$$H_w = W_w c_w (t_f - t_1) = H_s = W_s c_s (t_2 - t_f).$$

The final temperature, t_f, of the water and steel will be equal.

$$3 \text{ gal} \times 8.3 \text{ lb/gal} \times 1 \text{ Btu/lb } (t_2 - 65°) = 10 \text{ lb} \times 0.11 \text{ Btu/lb } (400 - t_f)$$

$$t_f = 79°F.$$

REFRIGERATION UNITS

Air conditioning and refrigeration equipment is rated in Btu/hr, in horsepower, and in tons of refrigeration. Chilling to temperatures below freezing requires much more refrigeration capacity than simply cooling air. One ton of refrigeration is equivalent to the cooling effect of one ton of ice per 24 hours. The heat required to melt one ton of ice is 2000 lb (one ton) x 144 Btu/lb = 288,000 Btu. Therefore, one ton of refrigeration is equivalent to 288,000 Btu/day or 12,000 Btu/hr or 200 Btu/min. The relationships of specific heat and cooling capacity are given in Example D.

EXAMPLE D: REFRIGERATION CAPACITY.

Given: One ton of beef at 100°F, with a specific heat of 0.77.

Find: Tons of refrigeration required to cool the beef to 40°F in 24 hours.

Solution: $H = W\ c\ (t_2 - t_1)$

$= 2000\ \text{lb} \times 0.77\ (100° - 40°)$

$= 92{,}400\ \text{Btu}$

$$\text{Tons of refrigeration} = \frac{92{,}400\ \text{Btu}}{288{,}000\ \text{Btu/ton}} = 0.32.$$

CHANGES OF STATE

Evaporation and condensation of liquids were briefly considered in Module CH-05 of Chemistry for Energy Techology I. Matter can exist in three states: solid, liquid, and gas. Changes from one state to another, such as evaporation and condensation, require heat energy. The heat energy associated with the physical change in the state of a material is known as latent heat. The Latin word "latent" means hidden; thus, the latent heat is hidden since it causes no temperature change. For example, one pound of ice at 32°F will melt with the addition of 144 Btu; and the resulting water will still have a temperature of 32°F. The value 144 Btu/lb ~~is the~~ latent heat of fusion of water. It is the amount of heat required to melt or freeze one pound of ice or water at 32°F. The latent heat of fusion for different materials has been determined experimentally and may be found in various tables. In the metric system, the heat of fusion of water is 80 cal/g.

The quantity of heat absorbed or given off at the melting point of a solid is given by the following equation:

$$H = W \times h_L \qquad \text{Equation 4}$$

where:

H = Quantity of heat, in Btu.
W = Weight, in lb.
h_L = Latent heat, in Btu/lb.

The use of this equation is illustrated in Example E.

EXAMPLE E: HEAT OF FUSION.	
Given:	Twenty pounds of ice at 32°F. The heat of fusion of ice is 144 Btu/lb.
Find:	The amount of heat required to melt the ice.
Solution:	$H = W \times h_L$ $= 20\ \text{lb} \times 144\ \text{Btu/lb}$ $= 2880\ \text{Btu}.$

Just as there is a specific quantity of heat associated with freezing or melting, there is also a specific quantity of heat associated with vaporization or condensation. The quantity of heat that one pound of a liquid absorbs when changing into the vapor state is known as the <u>latent heat of vaporization</u>. The word "latent" is used once again since vaporization is a constant temperature process and the heat is hidden. The heat of vaporization is found by using the same equation as for heat of fusion. The latent heat of vaporization of water is 970 Btu/lb.

EXAMPLE F: HEAT OF VAPORIZATION

Given: Five gallons of water at 212°F.

Find: The amount of heat required to vaporize the water.

Solution: $H = W \times h_L$

$= 5 \text{ gal} \times 8.3 \text{ lb/gal} \times 970 \text{ Btu/lb}$

$= 40{,}255 \text{ Btu}.$

EXAMPLE G: STEAM CONDENSATION.

Given: Ten thousand Btu are removed from 15 lb of steam at 212°F.

Find: The amount of steam that will condense into water.

Solution: $H = W \times h_L$

$$W = \frac{H}{h_L}$$

$$= \frac{10{,}000 \text{ Btu}}{970 \text{ Btu/lb}}$$

$$= 10.3 \text{ lb}.$$

Heat has the ability to bring about a change in the physical state of a material (such as freezing or vaporization), as well as the ability to cause a change in temperature. The heat that brings about a change in state has been defined as latent heat. When heat is absorbed or rejected by a substance, with a change in temperature, the heat transferred is known as sensible heat. The term "sensible" is used because the heat causes a change that can be sensed by the sense of touch, or by a device such as a thermometer.

Total heat is the sum of the sensible and the latent heats of a substance. These measurements begin at 32°F for water and -40°F for refrigerants in order to avoid the large numbers obtained if absolute zero is used. Total heat is also known as enthalpy. Calculations used in refrigeration often involve the use of enthalpy. Enthalpy is given by the following equation:

$$E = W\,c\,(t_2 - t_1) + W\,h_L \qquad \text{Equation 5}$$

where:

E = Enthalpy.
W = Weight of substance, in lb.
c = Specific heat.
t_2 = Final temperature.
t_1 = Initial temperature.
h_L = Latent heat.

The calculation of total heat on enthalpy is illustrated in Example H.

EXAMPLE H: CALCULATION OF ENTHALPY (TOTAL HEAT).

Given: Ten pounds of ice at 10°F; specific heat of ice, 0.5; specific heat of water, 1.

Find: The total heat required to convert the ice to steam at 212°F.

Solution: First there is a sensible heat change (H_1) from 10°F to 32°F, the melting point of ice.

$$H_1 = 10 \times 0.5\ (32 - 10) = 110 \text{ Btu.}$$

Next, there is a latent heat change (H_2) from ice at 32°F into water at 32°F.

$$H_2 = 10 \times 144 = 1440 \text{ Btu.}$$

Next, there is a sensible heat change (H_3) from water at 32° to water at 212°F.

$$H_3 = 10 \times 1\ (212 - 32) = 1800 \text{ Btu.}$$

Finally, there is a latent heat change (H_4) to convert the water at 212° to steam at 212°F.

$$H_4 = 10 \times 970 = 9700 \text{ Btu.}$$

$$\begin{aligned} E_{total} &= H_1 + H_2 + H_3 + H_4 \\ &= 110 + 1440 + 1800 + 9700 \\ &= 13{,}050 \text{ Btu.} \end{aligned}$$

Temperature-enthalpy relationships for water are shown in Figure 1. This figure shows graphically what happens when one pound of ice is heated from 0°F to steam at 400°F. The first step in the process is the heating of ice at 0°F to ice at 32°F. Since the specific heat of ice is 0.5 Btu/lb, it takes 16 Btu to increase the temperature to 32 degrees.

When 144 more Btu are added to the ice, it will be converted to water at 32°F. The latent heat of fusion of ice is 144 Btu/lb. It takes 180 Btu to go from point B (32°F) to point

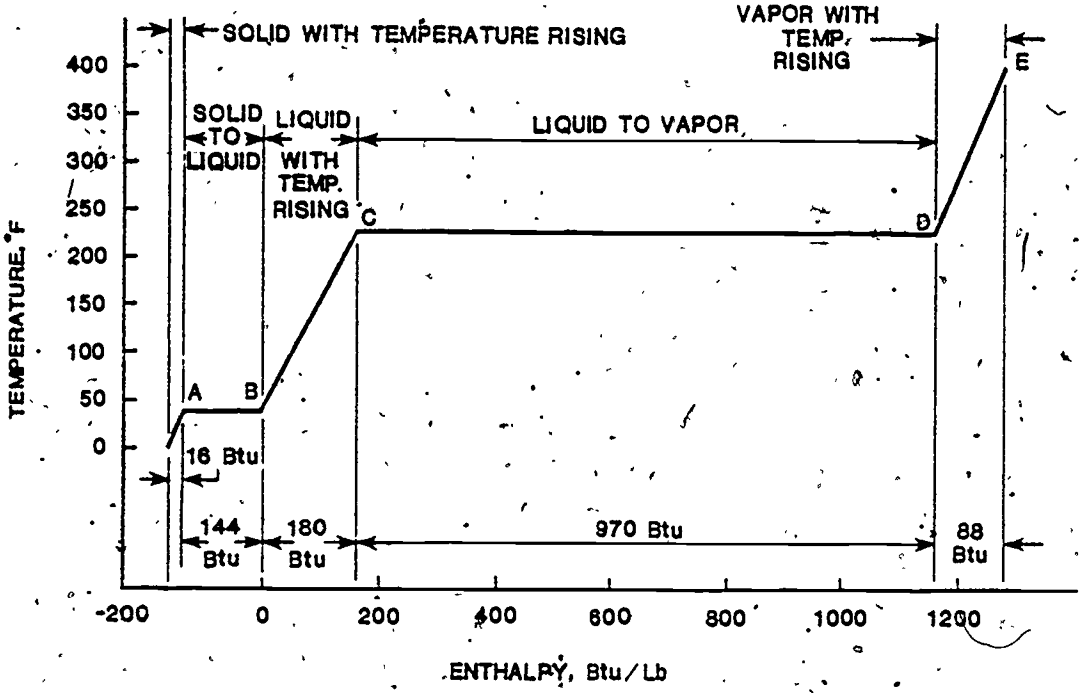


Figure 1. Temperature-Enthalpy Relationships for Water.

C (212°F) since the specific heat of water is one Btu/lb, and 212 minus 32 is 180. At point C (212°F), the water vaporizes, requiring the heat of vaporization of water, which is 970 Btu/lb. At point D, all of the water has been converted into steam. Additional heat causes the temperature of steam to increase. The specific heat of steam is 0.47 Btu/lb. Therefore, it would require an additional 88 Btu to raise the temperature of the one pound of steam from 212 to 400°F (400 - 212 = 188 and 188 x 0.47 = 88). A vapor such as steam, which is above the vaporization temperature of the liquid, is said to be superheated. Properties of superheated steam and other superheated vapors are found in many handbooks. The tables indicate the temperature, pressure, volume, and heat content relationships of the vapors.

SOLAR ENERGY STORAGE

Solar energy can only be collected when the sun is shining. Some of the energy must be stored for use at night and during cloudy periods. The material used for the heat storage is important to the efficient operation of the solar system. The primary materials in current use are water, stone, and concrete. The specific heat of a material is an important consideration in its use as a solar energy storage medium. Some of the important properties of materials used for storage are given in Table 2. As can be seen in Table 2, water is the most effective heat storage material. Water has the capacity to store nearly twice as much heat per cubic foot as stone or concrete. High specific heat and high density are desirable for heat storage. Certain salts that

TABLE 2. PROPERTIES OF COMMON SOLAR STORAGE MATERIALS.

Material	Specific Heat (Btu/lb)	Density (lb/ft^3)	Heat Capacity (Btu/ft^3)
Water	1	62.5	62.5
Stone	0.21	180	36
Concrete	0.27	140	38

store heat by melting rather than by getting hotter are being developed. These materials store heat of fusion at a constant temperature. Experimental development of these materials and others that rely upon heat of reaction (such as the heat of reaction between sulfuric acid and water) is underway.

HEAT TRANSFER

Heat always flows from a warmer object to a colder object. The rate of heat flow depends on the temperature difference between the two objects. The transfer of heat from one place to another occurs in three ways: (1) conduction, (2) convection, and (3) radiation. Conduction is the flow of heat through an object. For conductive heat transfer between two objects, they must be in contact. Some materials, such as metal, conduct heat readily; others, such as glass, wood, and cork, do not conduct heat readily. These nonconductors of heat are called insulators. Convection is the flow of heat by the use of a fluid, either gas or liquid. The fluids most often used for convective heat transfer are air and water. A heated fluid is less dense and rises, whereas a cool fluid is more dense and falls. This causes a continuous movement of the fluid, giving rise to natural convection. If the fluid currents are caused by a pump or fan, the term "forced convection" is used. Radiation is the transfer of heat by wave motion. The waves may be light waves or radio frequency waves. The heat felt in front of a fireplace or in direct sunlight is an example of radiant heating. The air between the objects is not heated, just the object itself.

HEAT PIPE

As indicated above, the rate of heat transfer by conduction is proportional to the difference in temperature of the two objects. A relatively new (1964) device has been developed for transmitting heat at a high rate over a considerable distance and with an extremely small temperature drop. The heat pipe is especially attractive since it requires no external pumping power. The heat pipe is a closed tube with inner surfaces that are lined with a porous capillary wick. The wick is saturated with the liquid phase of a fluid, and the remaining volume of the tube contains the vapor phase of the fluid. Heat applied at one end (the evaporator end) by an external heat source vaporizes the fluid in that section of the pipe. The resulting difference in pressure drives vapor from the evaporator to the condenser end of the pipe where it condenses and releases the latent heat of vaporization to a heat sink in that section of the pipe. Depletion of the liquid by evaporation in the evaporator end of the pipe causes liquid to enter into the wick surface. Then, capillary pressure pumps the condensed liquid back to the evaporator for revaporization. Thus, the heat pipe indefinitely transports the latent heat of vaporization from the evaporator to the condenser. The amount of heat that can be transported as latent heat of vaporization is usually several orders of magnitude larger than that which can be transported as sensible heat in a conventional convective system. The heat pipe can transport a large amount of heat with a small pipe size and a small temperature differential. Heat pipes have been developed which are more effective than the most conductive metals. Heat pipes are used to recover heat from the exhausts of industrial boilers, furnaces, and kilns. Heat pipes are also used for heat recovery from HVAC (heating, ventilation, air conditioning) systems.

HEAT ENGINES

The basic principle of a heat engine is illustrated in Figure 2. A certain amount of heat, q_h, is absorbed by the working fluid of the engine at a high temperature, T_h. The heat is partly converted to work, w, and the remainder of the heat, q_1, is rejected to the surroundings at a lower temperature, T_1. The temperatures must be expressed on the absolute (Kelvin) scale. The efficiency of the heat engine, an important value, is given by the following equation:

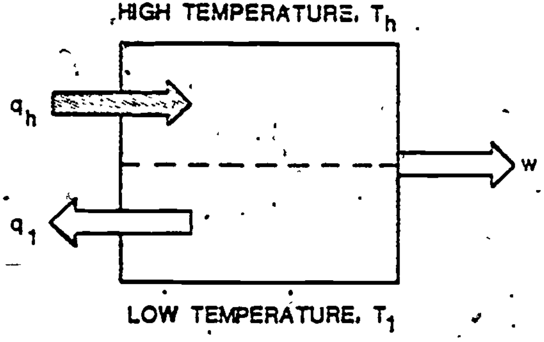


Figure 2.
Heat Engine.

$$\text{Efficiency} = \frac{T_h - T_1}{T_h} \qquad \text{Equation 6}$$

If the two temperatures, inlet temperature and outlet temperature, are the same, the efficiency of the heat engine is zero. A steam engine operating between 100°C (the boiler temperature) and 25°C (the condenser temperature) would have an efficiency as calculated below:

$$\text{Efficiency} = \frac{373 - 298}{373} = 0.20$$

The efficiency of this engine is only 20%. The waste heat is 80%, a tremendous loss in heat. To improve efficiency, modern power plants operate under high pressure, using superheated steam. Nevertheless, most power plants operate at less than 40% efficiency. Thus, more than half of the heat is wasted.

THERMOCHEMISTRY

Thermochemistry is concerned with the heat that accompanies chemical reactions. Thermochemical equations indicate the state of the materials. Solids, liquids, and gases are designated by (s), (l), and (g), respectively. For the combustion of carbon the following reaction is used:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94{,}052 \text{ cal/mole}$$

This reaction indicates that solid carbon burns in gaseous oxygen to form gaseous carbon dioxide. The ΔH is the heat of reaction, or enthalpy change. The negative sign indicates that heat is evolved in the burning of carbon. Most chemical reactions give off heat and have a negative enthalpy. These reactions are <u>exothermic</u> reactions. Those reactions in which heat is absorbed are endothermic reactions. They have a positive enthalpy change.

In most combustion or exothermic reactions, the products are of secondary importance. What is more important than the products is the energy being produced. In contrast, most endothermic reactions are conducted because the products are of primary importance – that is, energy is utilized to form useful products.

RELATIONSHIP BETWEEN MATTER AND ENERGY

Energy may be transformed or changed from one type to another. Chemical energy may be converted to heat energy, heat energy to electrical energy, mechanical energy to electrical, and so forth. However, in none of these changes is there a change in the total amount of energy – that is, the sum of all forms of energy remains constant. The law of conservation of energy states the following: Energy cannot be created or destroyed, although it can be changed in form. Likewise the law of conservation of matter states that there is no change in the quantity of matter during an ordinary chemical change. This law is the basis for all analytical calculations and determinations.

These two laws concerning conservation of energy and conservation of matter are only applicable for ordinary chemical reactions. In 1905, Albert Einstein first proposed the relationship between matter and energy. This relationship, usually referred to as Einstein's Equation, is as follows:

$$E = mc^2 \qquad \text{Equation 7}$$

where:

E = Energy of a reaction.
m = Mass being changed to energy.
c = A constant, the speed of light.

This relationship between matter and energy is significant only in nuclear reactions. The laws of conservation of energy and matter may be combined and stated as follows: Matter and energy can be neither created nor destroyed, but they can be transformed, one to the other.

CALORIMETRY

Measurement of heat effects of chemical and physical changes is called calorimetry. One of the most common calorimetric measurements is the heat of combustion of materials. Fuels, such as coal, gasoline, oil, and gas, vary in the amount of heat that different samples of each will produce. When buying fuels such as coal, it is important to know the amount of heat that a given fuel will produce. The price of coal and other fuels depends upon their grade, which is assigned by a calorimetric measurement.

The heat evolved in the complete oxidation of a substance is known as the heat of combustion. Heats of combustion of various substances are given in Table 3. The values are in kcal per gram of substance burned to H_2O and CO_2 at constant pressure and 25°C. In the English system, heats of combustion are reported in units of Btu/lb.

TABLE 3. HEATS OF COMBUSTION.

Substance	Heat of Combustion (kcal/g)
Hydrogen	-33.9
Carbon	-7.8
Carbon monoxide	-2.4
Methane	-13.3
Propane	-12.0
Octane	-11.4
Acetylene	-11.9

Heats of combustion are measured in a bomb calorimeter. A schematic of a bomb calorimeter is shown in Figure 3.

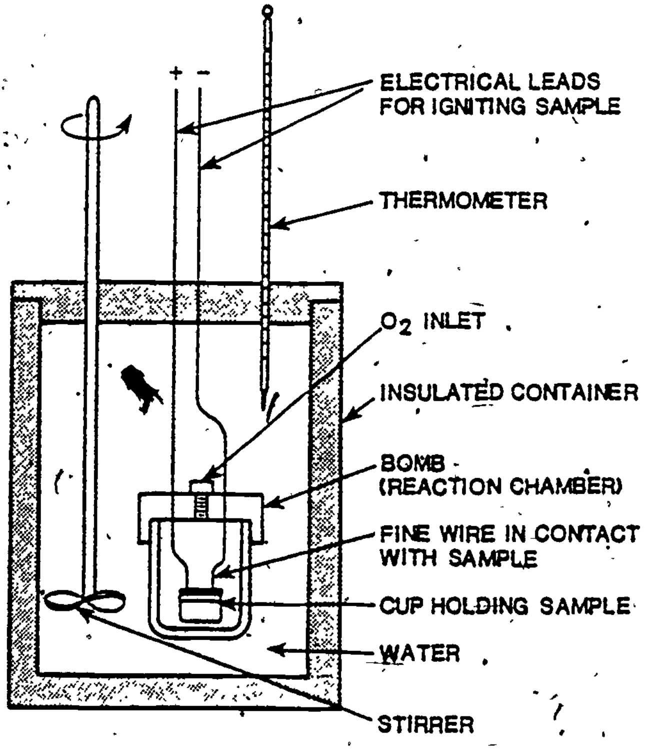


Figure 3.
Bomb Calorimeter.

To determine the heat of combustion in a bomb calorimeter, the following procedure is used. The sample (usually 1 g) is weighed and mounted on a holder inside a thick, stainless steel bomb. The bomb is sealed, and oxygen gas is added through a valve to a pressure of 25 atmospheres. In an atmosphere with this elevated amount of oxygen concentration, complete combustion of most fuels is assured. The sealed bomb is placed in a container, and exactly 2000 g of water is added to the container. This container is then placed inside an insulating container. A thermometer and a stirrer are placed in the water surrounding the immersed bomb. The water is stirred at a constant rate until temperature equilibrium is attained. Then the sample inside the bomb is electrically ignited. The rise in temperature is measured carefully and can be used to calculate the heat of combustion of the sample.

To standardize the apparatus, the calorimeter constant must be obtained. A known weight of a standard, such as a very pure benzoic acid, is combusted. From the known amount of heat absorbed by the calorimeter, and the measured rise in temperature of the water, a calorimeter constant is calculated, using the following equation:

$$\text{Calorimeter constant} = \frac{\text{Known heat of combustion}}{\text{Measured change in temperature}}$$

Equation 8

The heat of combustion of a unknown substance can be determined by burning a comparable weight of a sample and multiplying the rise in temperature by the calorimeter constant.

Since many fuels contain nitrogen and sulfur, a correction must be made to obtain the true heat of combustion. Usually 1 ml of water is placed in the bomb prior to combustion in order to absorb the sulfur oxides and nitrogen oxides formed. The reaction with water forms acids that are titrated with standard sodium hydroxide to obtain a measure of the amount of sulfur or nitrogen impurity in the sample.

LABORATORY MATERIALS

Laboratory 1

- Calorimeter (two polystyrene "coffee" cups, cardboard cover)
- Thermometer
- Lead shot
- Iron shot
- Clock or watch with second hand
- 600 ml beaker
- Burner
- Balance
- Test tube

Laboratory 2

- Calorimeter (same as Lab 1)
- Thermometer
- KCl
- 1.0 M NaOH
- 1.0 M HCl
- Magnesium ribbon
- Sandpaper

LABORATORY PROCEDURES

LABORATORY 1. SPECIFIC HEAT OF A SOLID ELEMENT.

Procedure

Record all data in Data Table 1.

1. Assemble the calorimeter, as shown in Figure 4.
2. Put about 300 ml of water into a 600 ml beaker and heat to boiling.
3. Measure the temperature and record as T_b.
4. Using a triple-beam or top-loading balance, weigh 100 g of lead shot into a test tube.
5. Place the test tube in the boiling water and allow the tube to remain in the boiling water for five minutes. (The lead should now be at temperature T_b.)

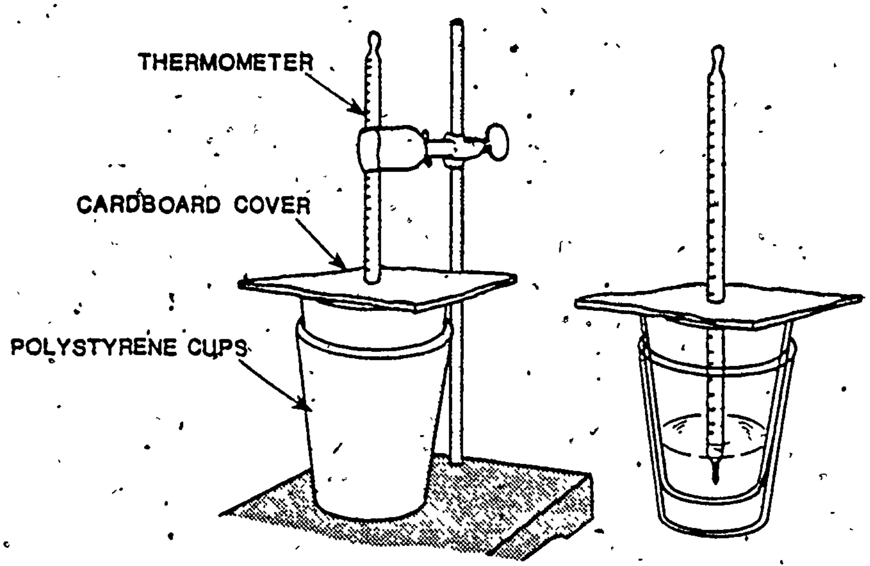


Figure 4. Calorimeter.

6. Pour 100 ml of water into the inner cup of the calorimeter.
7. Measure the temperature of the calorimeter water and record as T_i.
8. Remove the test tube from the heating bath and quickly pour the lead shot into the calorimeter water and cover with the cardboard top.
9. Stir for 30 seconds and record the maximum temperature as T_f.
10. Repeat the procedure, using iron shot.

The amount of heat absorbed by the calorimeter is given by the following equation:

$$\text{Heat absorbed} = (T_f - T_i) \times 100\ \text{g} \times 1\ \text{cal/g-°C}$$

The heat absorbed is equal to the heat added from the hot lead or iron.

$$\text{Heat delivered} = 100\ \text{g} \times (T_b - T_f) \times \begin{matrix}\text{Specific heat}\\ \text{of metal}\end{matrix}$$

Equating the two equations,

$$100\ \text{g} \times (T_b - T_f) \times \begin{matrix}\text{Specific heat}\\ \text{of metal}\end{matrix} = (T_f - T_i) \times 1.$$

Solving for specific heat,

$$\text{Specific heat} = \frac{(T_f - T_i) \times 100\ \text{g} \times 1\ \text{cal/g-°C}}{100\ \text{g} \times (T_b - T_f)}$$

11. Using this equation, calculate the specific heats of lead and iron and compare the values of those found in a handbook.

LABORATORY 2. HEATS OF REACTION.

Chemical and physical changes are usually accompanied by the liberation or absorption of heat. When a salt is dissolved in water, the resulting solution may be either warmer or colder than the water was. The heat of solution of a substance is the heat change when one mole of the substance is dissolved in a large amount of solvent. The heat of solution, ΔH, of potassium chloride will be determined in this experiment.

When a strong acid and a strong base are mixed, a considerable quantity of heat is given off. In this experiment, the heat that is liberated when hydrochloric acid and sodium hydroxide are mixed is determined. This quantity is called the heat of solution.

Finally, magnesium metal is dissolved in hydrochloric acid and the heat of reaction is measured.

PROCEDURE

Heat of Solution

Record all data in Data Table 2.

1. Assemble the calorimeter, as shown in Figure 4.
2. Measure 75 ml of water with a graduated cylinder and transfer the water to the inner polystyrene cup of the calorimeter.
3. Accurately weigh a quantity of potassium chloride between 1.5 and 2.5 g. Record.
4. Measure the initial temperature of the water. Record.
5. Add the weighed amount of KCl to the water and swirl the cup gently to dissolve the salt. Observe the temperature and, when it is constant, record the value.
6. Calculate the number of calories involved in the reaction. (1 ml of water weighs 1 g. A calorie is the amount of heat required to raise the temperature of 1 g of water 1 degree C.) Record.
7. Calculate the number of moles of KCl which were dissolved. Record.
8. Calculate how many calories would be involved if one mole of KCl were dissolved in water. (This is the heat of solution.) Record.

Heat of Neutralization

Record all data in Data Table 2.

1. Measure 50 ml of 1 M HCl with a graduated cylinder and transfer it to the inner cup of the calorimeter.
2. Measure the temperature of the HCl in the calorimeter. Record.
3. Measure 50 ml of 1 M NaOH with a graduated cylinder and add it to the HCl in the cup.
4. Mix the HCl and NaOH and record the temperature when it becomes constant.
5. Calculate the number of calories involved in the reaction. Record.
6. Calculate the number of moles of HCl that were neutralized. Record.
7. Calculate the number of calories which would be involved if one mole of HCl were neutralized. (This is the heat of neutralization.) Record.

Heat of Reaction

Record all data in Data Table 2.

1. Clean a piece of magnesium ribbon (weighing about 0.1 g) with sandpaper, and then weigh the metal accurately. Record.
2. Add 75 ml of 1 M HCl to the inner cup of the calorimeter.
3. Record the temperature of the acid.
4. Place the magnesium ribbon in the acid and swirl the cup.
5. Record the temperature when it becomes constant.
6. Calculate the number of calories of heat given off in the reaction. Record.

7. Calculate the number of moles of magnesium used. Record.
8. Calculate the heat of reaction that would have been observed if one mole of magnesium had been dissolved.
9. The accepted value for the heat of this reaction is 110 kcal/mole. Calculate the percent difference between the accepted and the observed values. Record.

DATA TABLES

DATA TABLE 1. SPECIFIC HEAT OF A SOLID ELEMENT.

Step	Procedure	Lead	Iron
3.	Temperature, T_b		
7.	Temperature of water, T_i		
9.	Maximum temperature, T_f		
11.	Calculated value of specific heat		
	Handbook value of specific heat		

111

DATA TABLE 2. HEATS OF REACTION.

Heat of Solution:

Step

3. Weight of KCl ____________
4. Initial temperature of water ____________
5. Final temperature of water ____________
6. Number of calories liberated ____________
7. Number of moles of KCl used ____________
8. Heat of solution (cal/mole) ____________

Heat of Neutralization:

Step

2. Temperature of HCl ____________
4. Final temperature of HCl-NaOH mixture ____________
5. Number of calories liberated ____________
6. Number of moles of HCl used ____________
7. Heat of neutralization (cal/mole) ____________

Heat of Reaction:

Step

1. Weight of Mg ribbon ____________
3. Temperature of acid ____________
5. Final temperature of mixture ____________
6. Number of calories of heat given off ____________
7. Number of moles of Mg used ____________
8. Heat of reaction (cal/mole) ____________
9. % difference between accepted and experimental values ____________

REFERENCES

Babits, George F. Applied Thermodynamics. Boston: Allyn and Bacon, Inc., 1968.

Chi, S.W. Heat Pipe Theory and Practice. Washington: Hemisphere Publishing Corporation, 1976.

Davies, Clive. Calculations in Furnace Technology. London: Pergamon Press, 1966.

Emswiler, J.E. and Schwarts, F.L. Thermodynamics. New York: McGraw-Hill Book Company, Inc., 1943.

Strauss, Howard J. Handbook for Chemical Technicians. New York: McGraw-Hill Book Company, Inc., 1976.

GLOSSARY

Btu: The amount of heat necessary to raise the temperature of one pound of water 1°F.

Calorie: The amount of heat necessary to raise the temperature of one pound of water 1°C.

Calorimetry: The measurement of heat effects in chemical reactions.

Conduction: The flow of heat through an object.

Convection: The flow of heat by use of a fluid.

Endothermic: Absorbs heat.

Energy: The capacity to do work.

Enthalpy: The total heat of a substance.

Exothermic: Gives off heat.

Heat engine: A system that relies upon differences in temperature at the inlet and outlet.

Heat of combustion: The heat evolved in the complete oxidation of a substance.

Heat of fusion: The amount of heat required to melt a substance.

Heat of vaporization: The amount of heat required to vaporize a substance.

Heat pipe: A device for transferring heat that does not require a large difference in inlet and outlet temperatures.

Kinetic energy: Energy due to motion of an object.

Latent heat: The heat associated with a change of state of a material at constant temperature.

Potential energy: The energy that an object has by virtue of its position or composition.

Radiation: The transfer of heat by wave motion.

Sensible heat: Heat absorbed or rejected by a substance, with a change in temperature.

Specific heat: The amount of heat required to raise the temperature of one pound of any substance 1°F.

Superheated: A vapor that is above its vaporization temperature.

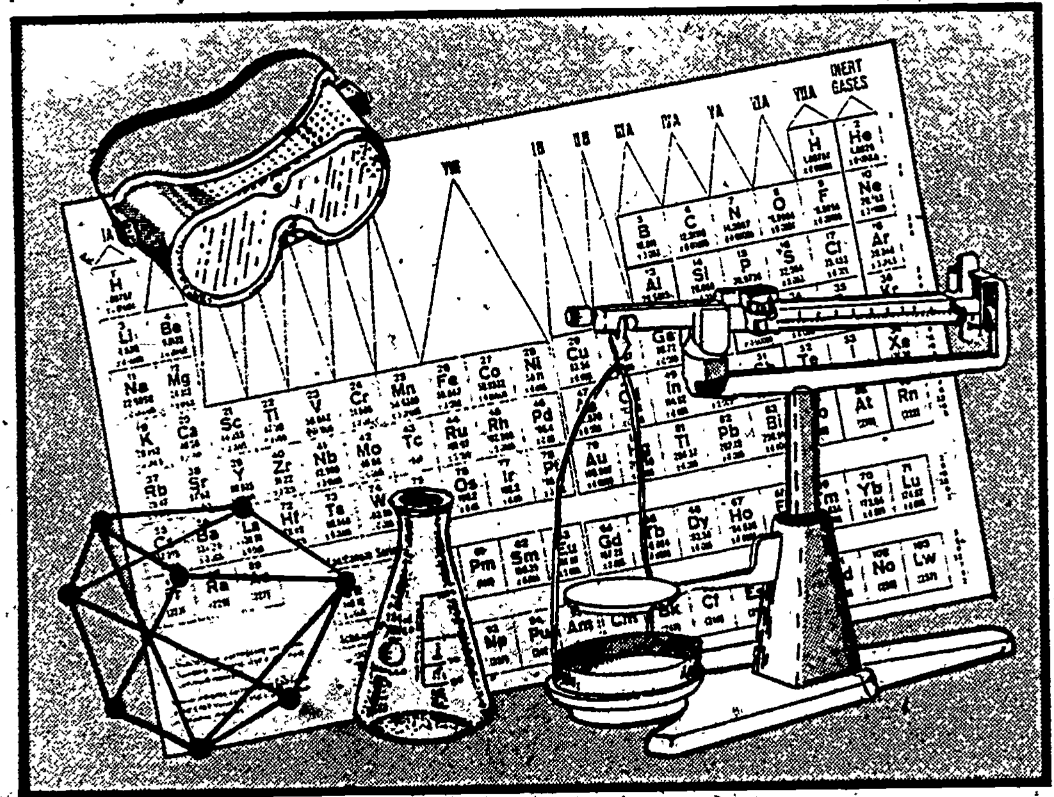
Thermochemistry: The branch of chemistry concerned with the heat that accompanies chemical reactions.

Thermodynamics: The study of the relationships between heat energy and other forms of work.

Total heat: The sum of the sensible and the latent heats of a substance (also known as enthalpy).

ENERGY TECHNOLOGY
CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-09
FUELS

ORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

The energy crisis is possibly the greatest problem facing society. In the United States, the use of energy is increasing, whereas the availability of energy is decreasing. Energy consumption has been increasing at the rate of approximately 3.5% over the last few years. This energy is currently being supplied by petroleum, coal, natural gas, water power, and nuclear power.

Energy use has increased as society has become less agricultural and more industrialized. As recently as the 1940s, more than three-fourths of the world's population was at a primitive agricultural level, requiring relatively little energy. Today, one-third of the world's population lives in an industrialized society, consuming 80% of the world's energy production. The United States, with 6% of the world's population, uses one-third of the yearly energy production. As more and more of the populace become significant energy users, the competition for energy will become very severe.

Most of the energy production throughout the world depends upon fossil fules: coal, petroleum, and natural gas. These fuels were formed millions of years ago from buried plant material. These fuels are not replaceable; therefore, alternate fuels must be sought as the fossil fuels are depleted. The fossil fuels, in addition to being used for fuels, are used as the raw material to produce chemicals. This secondary use compounds the shortage of fuels and makes it vital that alternate energy sources be developed.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of Chemistry for Energy Technology I and Modules CH-06, CH-07, and CH-08 of Chemistry for Energy Technology II.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    - a. Petroelum.
    - b. Octane number.
    - c. Cracking.
    - d. Antiknock agent.
    - e. Refining.
    - f. Polymerization.
    - g. Hydrocarbon.
    - h. Isomer.
    - i. Alkane.
    - j. Alkene.
    - k. Alkyne.
    - l. Aromatic hydrocarbon.
2. List the characteristics of a good fuel.
3. Compare the composition, properties, and fuel values of anthracite, bituminous, and lignite coal.
4. Identify the major constituents of gasoline.
5. Write the chemical reactions for the combustion of fuels.
6. List the major fractions obtained in petroleum refining.
7. List and explain the purposes of the processes used to increase the yield of gasoline.

8. Identify several nonconventional or alternate energy sources.
9. List the general differences between organic and inorganic compounds.
10. Name two factors that account for the large number of organic compounds.
11. List the names of the first eight members of the alkane series of hydrocarbons.
12. Match the formula of an organic radical with its name.
13. Identify functional groups in the major classes of substituted hydrocarbons.

CHARACTERISTICS OF FUELS

A fuel is any combustible substance that is burned to produce useful heat energy. Fossil fuels were – and are – produced by the sun's energy in the photosynthesis of growing plants. These fuels include wood, coal, oil, and natural gas. To meet the demand for energy, more direct ways of utilizing solar energy must be developed.

There are a number of desirable characteristics in fuels. A fuel should produce a large amount of heat energy in proportion to its weight. Fuels must be low in cost and available in large quantities. They must not produce combustion products that are dangerous, and they should not leave large amounts of residue after combustion. Finally, it is important that fuels can be easily produced, handled, and transported. Oil and natural gas are the closest to having all of these desirable characteristics and, therefore, are the most popular fuels. They are easily transported, are fairly inexpensive, and leave virtually no residue after burning.

The heat content of coal, petroleum, and natural gas is given in Table 1. As shown, natural gas has a relatively high heat content; it contains 70% more heat energy than coal.

TABLE 1. HEAT CONTENT OF FOSSIL FUELS
AND USAGE IN THE UNITED STATES.

Fuel	Heat Content (kcal/gram of fuel)	Usage
Coal	7.8	21%
Petroleum	11.4	45%
Natural gas	13.2	34%

SOLID FUELS

Historically, wood has been the most important fuel, although its current use as a fuel is rather limited. Most of the world's production of wood is used in the construction industry, in the manufacture of paper and textiles, and in the production of a variety of products through destructive distillation. The destructive distillation of wood produces wood alcohol (methyl alcohol), acetic acid, acetone, creosote, wood tar, charcoal, and several combustible gases.

There are several important forms of coal. Anthracite, or "hard" coal, contains about 80% carbon; whereas bituminous, or "soft" coal, contains about 60% carbon. In spite of the lower carbon content, bituminous coal has a higher heat value than does anthracite, because the bituminous coal contains a considerable amount of volatile hydrocarbons that have a high heat value. Anthracite burns with a clear flame that produces little soot. Lignite contains even less carbon than bituminous coal. This brown coal exhibits much of the structure of the wood from which it was derived. Lignite is found in veins near the surface and is strip mined. Peat is compressed moss that has undergone some of the processes that formed coal.

Coal is the most abundant fossil fuel. It was estimated that, at present consumption rates, coal could last for up to 500 years. Unfortunately, the rate of consumption is increasing 3.5% each year. Two of coal's major drawbacks are that it is a relatively dirty fuel and it is difficult to handle. The atmospheric pollution caused by coal, especially sulfur-containing coal, is severe. In addition, deep coal mining is dangerous and unhealthy to miners; and strip mining can have a serious ecological impact.

In spite of the severe problems connected with coal, it must supply the major energy needs for the next decades. Coal can be used directly to produce heat upon combustion, as follows:

$$C + O_2 \longrightarrow CO_2 + 94 \text{ kcal/mole}$$

Extensive research and development efforts are being made to convert coal to gas or liquid prior to its use. Coal gasification can be used to convert coal into a relatively clean burning fuel. In this process, coal is reacted with hot air or steam. The reaction with hot air produces a gaseous mixture called power gas, which contains as much as 50% nitrogen. Since nitrogen does not burn, power gas has a very low heating value. The reaction is as follows:

$$\underset{\text{Coal}}{C} + \text{air} \longrightarrow \underset{\text{(Power gas)}}{CO + H_2 + N_2}$$

If the coal is reacted with steam, a mixture of carbon monoxide and hydrogen, known as coal gas, is obtained:

$$\underset{\text{Coal}}{C} + \underset{\text{Steam}}{H_2O} \longrightarrow \underset{\text{(Coal gas)}}{CO + H_2}$$

The carbon monoxide and hydrogen from either power gas or coal gas will burn to produce heat:

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O + \text{Heat}$$
$$2\ CO + O_2 \longrightarrow 2\ C + \text{Heat}$$

Coal can also be reacted with hydrogen to produce methane by the following reaction:

$$\underset{\text{Coal}}{C} + \underset{\text{Hydrogen}}{2\ H_2} \longrightarrow \underset{\text{Methane}}{CH_4}$$

The methane can then be burned. This process is not fully developed, but it is promising since the coal can be burned in a central processing plant and the methane then piped inexpensively through the existing natural gas lines to the customer. Liquid fuels can also be made from coal by several liquification processes. Liquid fuels from coal can possibly be used as a substitute for gasoline. Since coal is predominately carbon, additional hydrogen is added to form petroleumlike hydrocarbons. The hydrogenation of coal must take place at high temperatures and pressures, thus making the process a difficult challenge. The most promising methods operate on the principle of contacting crushed coal with selective solvents that act as hydrogen donors to aid in converting it to a liquid phase. Final hydrogenation is then conducted in the presence of a catalyst.

GASEOUS FUELS

Generally, gaseous fuels are relatively easy to transport; and they burn cleanly. As indicated previously, coal can be reacted with steam to produce coal gas. One ton of bituminous coal can produce as ~~much~~ as 12,000 cubic feet of coal gas, as well as 1200 pounds of coke, 120 pounds of coal tar, and ammonia. The coal tar is rich in valuable aromatic compounds.

The composition of natural gas varies from source to source. Some natural gases have a carbon dioxide content as high as 30% or more. Other natural gases contain high percentages of hydrogen sulfide, nitrogen, or helium. Prior to being sold, natural gas is processed to remove much of the nonfuel component since these materials will not burn. Although the processed gas will vary in composition, a typical composition of natural gas sold as fuel is shown in Table 2.

TABLE 2. COMPOSITION OF NATURAL GAS AFTER PROCESSING FOR SALE.

Component	Percent
Methane	80
Nitrogen	10
Ethane	5.9
Propane	2.9
n-Butane	0.71
Isobutane	0.26

Bottled gas, or liquified petroleum gases (LPG), is a mixture of propane, C_3H_8, and butane, C_4H_{10}. Propane and butane are extracted from natural gas or obtained as by-products of petroleum refining. These gases are compressed until liquified and then "bottled" in steel cylinders. The liquified gas readily reverts to the gaseous form when the pressure is reduced and the gas is consumed. Bottled gas is used in rural areas for cooling and heating, on house trailers, and on recreational vehicles.

Acetylene is a gaseous fuel that burns in an atmosphere of pure oxygen to produce extremely high temperatures (3000°C). The high temperature from the reaction of oxygen and acetylene is used in the oxyacetylene torch — a torch that is useful for welding and cutting metals. The reaction is as follows:

$$2\ H-C\equiv C-H + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O + 620\ \text{kcal}$$

In addition to being used as a fuel, acetylene (ethyne), C_2H_2, is widely used in polymerization reactions to form plastics. Acetylene is made by reacting calcium carbide with water. The first step in the production of acetylene is the heating of limestone in a kiln to produce calcium oxide:

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\text{Heat}} \underset{\text{Calcium oxide (quicklime)}}{CaO + CO_2}$$

A mixture of the calcium oxide and coke is then heated in an electric furnace to produce calcium carbide:

$$\underset{\text{Coke}}{2\ C} + \underset{\text{Calcium oxide}}{CaO} \xrightarrow{2000^\circ C} \underset{\text{Calcium carbide}}{CaC} + CO$$

Finally, the calcium carbide is reacted with water to produce acetylene and calcium hydroxide:

$$\underset{\text{Calcium carbide}}{CaC_2} + 2\ H_2O \longrightarrow \underset{\text{Acetylene}}{H-C\equiv C-H} + Ca(OH)_2$$

LIQUID FUELS

The important liquid fuels – gasoline, kerosene, and fuel oil – are obtained from petroleum. Petroleum, as it comes from the oil well, is called crude oil. It consists of a complex mixture of different types of hydrocarbons (compounds of carbon and hydrogen). Petroleum is found in porous rocks and sands; it is never found in underground pools or lakes. A variety of methods are used to remove the oil from the porous rocks and sands.

Crude oil is shipped by tanker or underground pipeline to a refinery for processing. In the refinery, crude oil is heated to vaporize and separate it into fractions according to boiling point. This fractional distillation process is much the same as that which will be used in one of the laboratories in this module.

The principal fractions obtained from the refining of petroleum will now be considered. The first materials to come out of the fractionating tower are gases. These gases are soluble in the crude petroleum and, therefore, are in the liquid state. When separated in the refining process, they are free to remain in the gaseous state at normal temperatures and pressures. These gases, which are mainly propane and butane, can be liquified and sold as bottled gas. These low-boiling gaseous hydrocarbons are also the building blocks for making many chemical compounds. The second fraction is aviation gasoline, automobile gasoline, and solvents. Kerosene, the next fraction, consists of compounds having from 10 to 16 carbon atoms. Most of the kerosene is converted to gasoline by cracking the larger molecules into smaller ones. Kerosene's major use today is for jet aircraft. Fuel oil contains more carbons than the kerosenes.

Fuel oil is used for industrial and home furnaces. Diesel fuel is produced from the fuel oil fraction. Following fuel oils, the next fractions are lubricating oils and greases. The material obtained from the bottom of the distillation tower consists of asphalt, waxes, and coke. The petroleum fractions and their main uses are given in Table 3.

TABLE 3. PETROLEUM FRACTIONS.

Fractions	Composition	Principal Uses
Gas	$C_1 - C_4$	Fuel
Gasoline	$C_6 - C_9$	Automobile fuel, solvent naphtha
Kerosene	$C_{10} - C_{16}$	Jet fuel, fuel oil, diesel fuel
Oil	$C_{16} - C_{18}$	Diesel fuel, cracked to gasoline
Wax oil	$C_{18} - C_{20}$	Lubricants, mineral oils
Paraffin wax	$C_{21} - C_{40}$	Wax paper, candles
Asphalt		Roofing, road material

Gasoline production through the refining process will be considered later in this module.

ORGANIC CHEMISTRY

All of the fuels considered so far in this module, solid, gaseous, and liquid, are organic compounds, that is, compounds which contain carbon. Organic chemistry is the study of these carbon-containing compounds. There are several differences between organic and inorganic compounds, including the following:

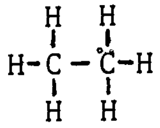
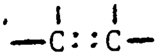
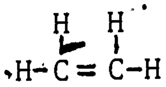
- All organic compounds contain carbon, and most contain hydrogen. In addition, organic compounds can contain nitrogen, oxygen, and the halogens (chlorine, fluorine, bromine, and iodine). Although organic compounds are comprised of only these few elements (plus several others occasionally), inorganic compounds can contain almost any of the more than 100 elements.
- Many organic compounds are either combustible or decomposed by heat; most inorganic compounds will not burn and are stable when heated.
- Most bonding in organic compounds is covalent; most of the bonding in inorganic compounds is ionic.
- Water is a poor solvent for organic compounds; however, it is a good solvent for many inorganic compounds.
- In comparison to inorganic compound reactions, reactions involving organic compounds generally proceed more slowly, and they do not go to completion.

Since so few elements are found in organic compounds it would be logical to assume that there are relatively few organic compounds. However, there are actually hundreds of thousands of organic compounds. Two principal reasons for this large number of organic compounds are as follows:

1. Carbon has the unusual ability to bond to itself by covalent bonding, thus forming long chains and rings. Each of two adjacent carbon atoms furnishes one or more electrons to form an electron pair or pairs in the covalent bond. Because of this bonding ability, there are long series of compounds, with each successive compound containing one more carbon than its

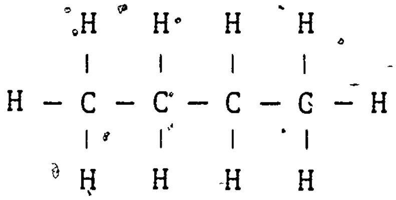
predecessor. Examples of these series are alkanes, alkenes, and alkynes. The three types of bonding found in organic compounds are summarized in Table 4.

TABLE 4. BONDING IN ORGANIC COMPOUNDS.

Type of Bond	Electron Dot Structure	Series	Example	Proper Name	Common Name
Single bond	 $-\overset{\vert}{\underset{\vert}{C}}:\overset{\vert}{\underset{\vert}{C}}-$	Alkane	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	Ethane	Ethane
Double bond	 $-\overset{\vert}{C}::\overset{\vert}{C}-$	Alkene	 $H-\overset{H}{C}=\overset{H}{C}-H$	Ethane	Ethylene
Triple bond	$-C:::C-$	Alkyne	$H-C\equiv C-H$	Ethyne	Acetylene

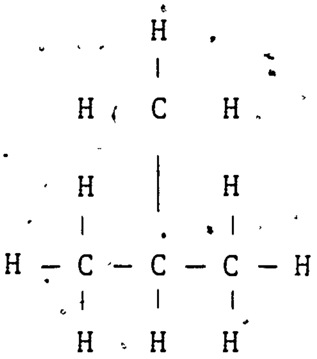
2. The same kinds and numbers of atoms can be arranged differently to form different compounds called <u>isomers</u>. Isomers are compounds having the same composition and molecular weight, but different properties (because of different arrangements of the atoms). For example, in the gaseous hydrocarbon butane, which has the formula C_4H_{10}, carbon atoms must have four bonds, and each hydrogen must have one bond.

The following examples are two ways that four carbons and 10 hydrogens can be arranged:



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Normal butane



$$\begin{array}{ccccccccc} & & & & H & & & & \\ & & & & | & & & & \\ & & H & & C & & H & & \\ & & & & | & & & & \\ & & H & & | & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Isobutane (methylpropane)

The first structure is called normal butane. It has a continuous straight-chain structure, with each carbon bonded to no more than two other carbons. The second compound is called isobutane, or methylpropane.

One of the carbon atoms in isobutane is bonded to three other carbons. These are two distinct compounds (isomers) — as indicated by their boiling points, as well as other properties. (Isobutane has a boiling point of -11.7°C, whereas normal butane has a boiling point of 0.5°C.) Table 5 illustrates the tremendous number of isomers possible in organic chemistry. For instance, there are 62 trillion possible isomers of tetracontane.

TABLE 5. NUMBER OF POSSIBLE ISOMERS OF SELECTED ALKANES.

Molecular Formula	Name	Number of Possible Isomers
CH_4	Methane	0
C_2H_6	Ethane	0
C_3H_8	Propane	0
C_4H_{10}	Butane	2
C_5H_{12}	Pentane	3
C_6H_{14}	Hexane	5
C_7H_{16}	Heptane	9
C_8H_{18}	Octane	18
$C_{12}H_{26}$	Dodecane	355
$C_{20}H_{42}$	Eicosane	366,319
$C_{40}H_{82}$	Tetracontane	62,491,178,805,831

The molecular formula does not give enough information to be very useful in working with organic compounds; therefore, "structural formulas" are used. A dash (–) is used to represent a bond between pairs of atoms rather than using two dots to represent the two electrons. The following formulas can be used to represent butane:

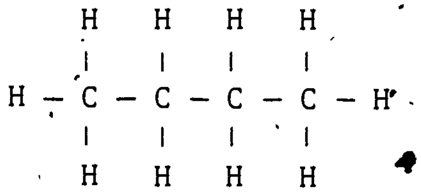
1. A simple molecular formula:

$$C_4H_{10}$$

2. A simplified structural formula:

$$CH_3 - CH_2 - CH_2 - CH_3$$

3. A full structural formula:



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

When first starting to study organic chemistry, it is best for one to use the full structural formula. After some familiarity with writing structures, however, the simplified structure is sufficient. The simple molecular formula normally is not very useful.

CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds can be classified into two general groups: aliphatic compounds and aromatic compounds. Aliphatic compounds are straight-chain compounds, although a few cyclic (or ring) compounds that chemically resemble straight-chain compounds can be straight-chain or branched. Aromatic compounds have a special six-member hexagonal carbon ring called the benzene ring. The aromatic hydrocarbons form three common series: the benzene, the naphthalene, and the anthracene series. The aliphatic hydrocarbons also form three series: the alkanes, the alkenes, and the alkynes. The sources, chemical reactions, physical properties, and nonmenclature of some of the members of these series will now be considered.

ALKANE SERIES

The alkane series of hydrocarbons are the simplest organic compounds. They contain only single bonds and only two elements: carbon and hydrogen. The series is also called the methane series (after the first member of the series) and the paraffin series (because of the stability of members of the series which resembles paraffin — one of the highest members of the series). The members of this series have the general formula of C_nH_{2n+2}, where n can be any number. If n = 1, the compound is CH_4; if n = 2, the compounds is C_2H_6; if n = 3, the compound is C_3H_8, and so on.

The first member of the alkanes is methane (CH_4), a colorless, nearly odorless gas. About 90% of the gas in natural gas is methane. Methane is formed by the decomposition of organic matter, such as in marshes; therefore, the gas is sometimes called marsh gas. It also is formed in coal mines (coal gas), where it can form a dangerous, explosive mixture with air. Since methane is almost odorless, mercaptans are added to give natural gas a detectable odor so that it is safer.

The first four members of the alkane family are gases. Alkanes containing 5 to 17 carbon atoms are liquids at room temperature, whereas those having 18 or more carbon atoms are solids.

The alkanes, all of which are obtained from petroleum, are usually consumed as mixtures.

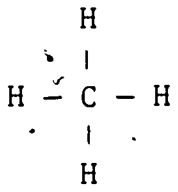
NOMENCLATURE

Many of the more common organic compounds were named long ago. As the number of known compounds grew, however, a systematic means of naming compounds became necessary. As early as 1892, a committee of chemists met at Geneva, Switzerland, to develop this method. The most recent group to propose names met in Amsterdam in 1949. This system of naming organic compounds, known as the IUPAC (International Union of Pure and Applied Chemistry) system, is currently in use. Unfortunately, both the common name and the proper name for many compounds are widely used; therefore, both must be learned.

The first four members of the alkanes have only common names: methane, ethane, propane, and butane. (Note that all of the alkanes end with the suffix -ane.) The next members follow a system in which the number of atoms present in a continuous chain is indicated by a Greek prefix, followed by the -ane (or -ne) suffix. The following are examples:

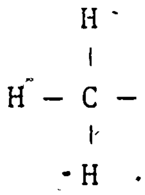
C_5H_{12} is pentane (penta is 5).
C_6H_{14} is hexane (hexa is 6).
C_7H_{16} is heptane (hepta is 7).
C_8H_{18} is octane (octa is 8).

The unbranched, or continuous, chain alkanes are called "normal," and the prefix n- is used (for example, n-butane). Alkyl groups, or radicals, have no independent existence, but they are used in naming organic compounds. Removal of one hydrogen from an alkane gives an alkyl group, which is named by replacing the -ane of the alkane with -yl. The following are examples:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

becomes

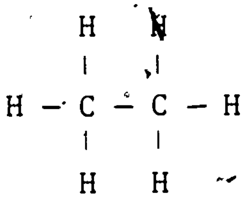


$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$$

or CH_3-

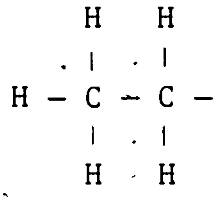
Methane

Methyl



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

becomes



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$$

or C_2H_5-

Ethane

Ethyl

The following are examples of using the alkyl groups in naming compounds:

CH_3Br	Methyl bromide
C_2H_5OH	Ethyl alcohol
$CH_3-CH_2-CH_2-I$	n-Propyl iodide

The following IUPAC rules are helpful in naming organic compounds:

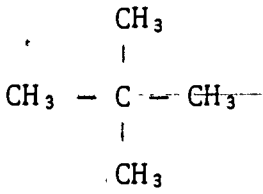
1. Determine the longest continuous carbon chain in the compound and name it as an alkane. The name of this chain is the basic name of the compound.
2. Number the carbon atoms in the chain from one end or the other so that the alkyl groups or other atoms have the smallest possible numbers.
3. The position of each substituent is designated by the number of the carbon atom to which it is attached. Hyphens are used to separate numbers from names of substituents.

4. If identical groups appear more than once, the number of the carbon to which each is bonded is given each time. If identical groups appear on the same carbon, the number is repeated. Numbers are separated from each other by commas. The number of identical groups is indicated by prefixes: di-, tri-, tetra-, and so on.

5. The name is written in a continuous manner (that is, there are no spaces left in the name).

6. If more than one alkyl group is present, they are named in alphabetical order (for example, ethyl before methyl).

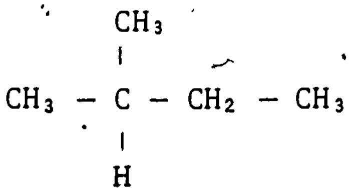
The preceding rules are illustrated below:



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2,2-Dimethylpropane

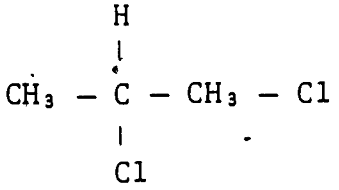
The longest carbon chain is three; therefore the basic name is propane. Two methyl groups are on carbon number 2; therefore 2,2-di- is used.



$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

2-Methylbutane

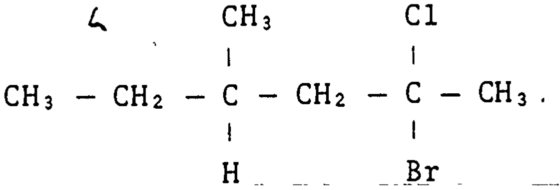
The longest carbon chain is four; therefore the basic name is butane. Numbering from left to right would place the methyl group on carbon number 2. (Numbering from right to left would place the methyl group on carbon number 4. Since four is larger than two, 4-methylbutane would be incorrect.)



$CH_3 - \underset{Cl}{\overset{H}{C}} - CH_3 - Cl$

1,2-Dichloropropane

The longest carbon chain is three; therefore the basic name is propane. Numbering from right to left gives the smallest numbers (1 and 2), rather than 2 and 3. One chlorine is on carbon number 1 and one chlorine is on carbon number 2. Since there are two chlorines, di- is used.



$CH_3 - CH_2 - \underset{H}{\overset{CH_3}{C}} - CH_2 - \underset{Br}{\overset{Cl}{C}} - CH_3$

2-Bromo,2-chloro,
4-methylhexane

The longest carbon chain is six; therefore the basic name is hexane. Numbering from right to left gives the smallest numbers. Both bromine and chlorine are on carbon number 2. (Bromo appears in the alphabet before chloro.) A methyl group is on carbon number 4.

The most important use of the alkanes, as indicated earlier, is for fuel. As an illustration of the combustion of alkanes, consider the combustion of propane:

$$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$$

Propane Oxygen Carbon dioxide Water

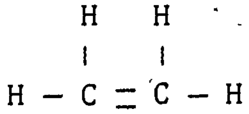
ALKENE SERIES

Members of the alkene series have at least one double bond. This series is also known as the olefins, or the ethylene series, after the first member of the group. The general formula for the series is C_nH_{2n}. The first three compounds in the series are gases, whereas the higher members are liquids and solids. Ethylene is used in artifical ripening of fruits since it destroys the green chlorophyll, changing the fruit from green to yellow. Its major uses are as follows: for production of ethylene glycol, for use as antifreeze, and for synthesis of plastics.

The IUPAC rules for naming alkenes are the same as for alkanes — except for the following rules:

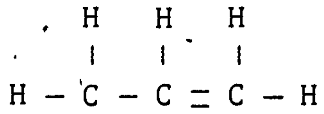
1. The longest chain containing the double bond is numbered.
2. The -ane is changed to -ene for alkenes.
3. The numbering begins from the end of the chain which allows the double bond to be located on the smallest numbered carbon as possible. The double bond is located by the number given to the first carbon of the bond.
4. The prefixes di, tri-, and so on, are used when more than one double bond is present, and they appear within the name just before the -ene.

The preceding rules are illustrated with the following examples:



$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H$$

Ethene
(ethylene)

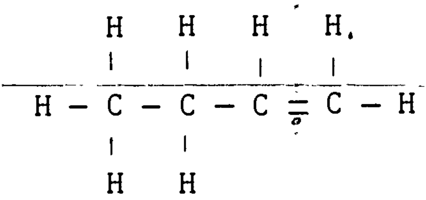


$$H-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H$$

Propene
(propylene)

The first two members of the series, ethene and propene, are shown above. It is not necessary for numbers to be used to locate the double bond since there are no other possibilities for the location. In ethene, the bond must be between the two carbons, and, in propene, the bond can be between either pair of carbons. However, the positions are equivalent. Remember that the molecule is free to rotate. If the bond is on the right pair, a rotation of 180° places the bond on the left, and the molecule is the same one. Common names for these compounds are ethylene and propylene.

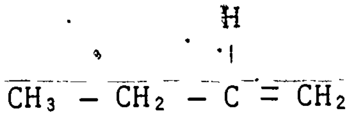
There are two possible compounds of molecular formula C_4H_8: 1-butene and 2-butene. These compounds are shown below:



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H$$

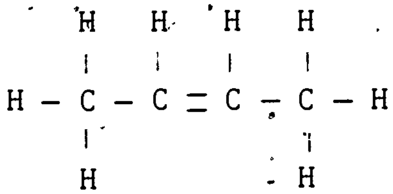
1-Butene

or



$$CH_3-CH_2-\overset{H}{C}=CH_2$$

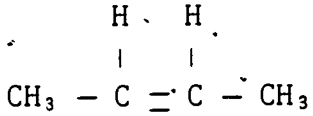
1-Butene



$$H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-H$$

2-Butene

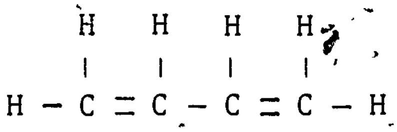
or



$$CH_3-\overset{H}{C}=\overset{H}{C}-CH_3$$

2-Butene

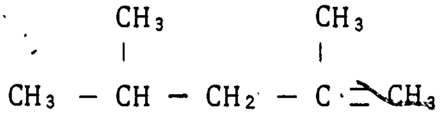
According to the IUPAC rules, the number starts from the side which will place the smallest number next to the carbon-carbon double bond. Thus, the correct name for the first structure is 1-butene (not 3-butene). Note that this is an example of another type of isomer.



$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & = & C & - & C & = & C & - & H \end{array}$$

1,3-Butadiene

This compound has four carbons; therefore the basic name is butane. Since there are double bonds present, the name is butene. The two double bonds are located adjacent to the numbers 1 and 3 carbons. The prefix di- is inserted before the -ene to reinforce the fact that there are two double bonds in the compound.



$$\begin{array}{ccccccc} & & CH_3 & & & & CH_3 \\ & & | & & & & | \\ CH_3 & - & CH & - & CH_2 & - & C = CH_3 \end{array}$$

2,4-Dimethyl-1-pentene

The basic name of this compound is pentane, since it has five carbon atoms in the longest chain containing the double bond. However, the name is pentene because of the double bond. Two methyl groups are present — one on carbon number 2 and one on carbon number 4. Thus, 2,4-dimethyl is part of the name. The double bond is adjacent to the carbon numbered 1. This is indicated in the name by the 1 appearing just before the pentene. Note that this is not 4, since the double bond is located by the smallest number possible. Therefore, the numbering of the carbon atoms begins on the right rather than on the left. Note that in all cases the carbon atom has four bonds.

ALKYNE SERIES

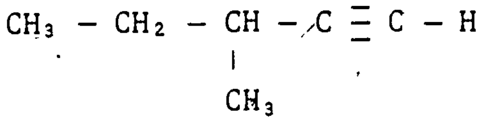
The <u>alkynes</u>, or acetylenes, are unsaturated hydrocarbons that contain a triple bond, or three pairs of shared electrons between adjacent carbon atoms. The general formula for alkynes containing one triple bond is C_nH_{2n-2}. The first member of the series is ethylene, commonly called acetylene:

$H - C \equiv C - H$ Ethylyne (acetylene)

The alkynes are named by using the same rules as those for the ethylene series, exept that -yne is used to replace -ane of the basic name. Examples of members of this series are given below:

$CH_3 - C \equiv C - H$ Propyne (methylacetylene)

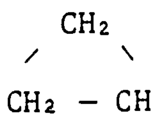
$CH_3 - C \equiv C - CH_3$ 2-Butyne



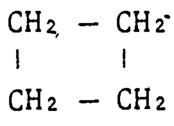
$CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - C \equiv C - H$ 3-Methyl-1-pentyne

CYCLOALKANES

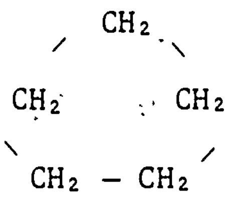
Cycloalkanes are saturated hydrocarbons that have ring structures. The first three members of this series are shown below:



Cyclopropane



Cyclobutane



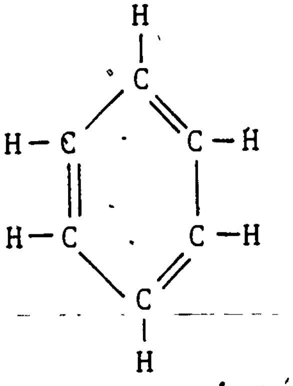
Cyclopentane

These rings are under considerable strain and, therefore, the cycloalkanes, in general, are rather reactive.

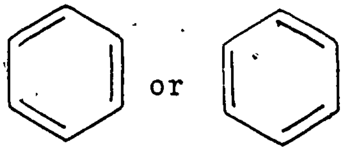
AROMATIC HYDROCARBONS

The aromatic hydrocarbons are ring hydrocarbons that contain the benzene structure. These hydrocarbons are obtained from the destructive distillation of coal, which produces the coal tar containing the aromatics. As the demand for the aromatic compounds has grown, additional supplies have been obtained from petroleum. Many of the aromatic compounds have a rather pleasant odor — hence the name "aromatic." Benzene is a clear, colorless liquid having a fairly pleasant odor. Excessive inhalation of benzene and most aromatics should be avoided because of their toxicity. Benzene freezes at 5.5°C, boils at 80.1°C, is insoluble in water, and is an excellent solvent for fats, waxes, and resins. Benzene and other aromatics have a high antiknock value; therefore, they are used in gasoline to raise the octane number. Larger amounts of the aromatics must be used in no-lead gasoline than in leaded gasoline — which causes the cost of no-lead gasoline to be higher than the leaded.

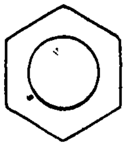
The molecular formula for benzene is C_6H_6. Three commonly used structures for benzene are given on the following page.



(1)



(2)

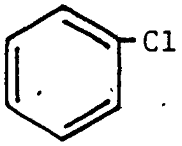


(3)

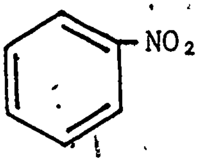
Structure number (1) indicates that the six carbons have alternating single and double bonds – which would indicate that benzene should be fairly reactive since it possesses the double bonds. However, this is not the case; benzene is rather stable. The bonds are equivalent to each other.

NOMENCLATURE OF AROMATIC COMPOUNDS

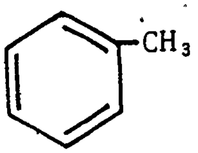
An element or radical may replace one or more of the hydrogen atoms of benzene to give compounds such as the following:



Chlorobenzene

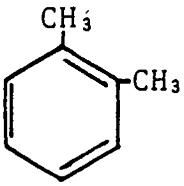


Nitrobenzene

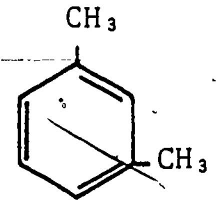


Methylbenzene
(toluene)

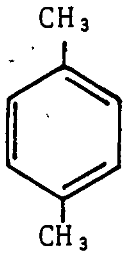
These compounds are named as substituted benzene. The group C_6H_5 (benzene minus one of its hydrogens) is known as the phenyl radical; therefore, the first compound can also be called phenyl chloride. Names of this type are encountered occasionally. When two or more substituents appear on the ring, their relative positions must be designated. This can be done by using the prefixes, ortho- (o), meta- (m), ~~or~~ para- (p); or it can be done by locating the substituents on the ring by numbers. The six carbon atoms are numbered so that the smallest possible numbers are used. Suppose that there are two methyl groups attached to benzene. These are three isometric forms of these dimethylbenzenes, or xylenes:



o-Xylene
(1,2-Dimethylbenzene)



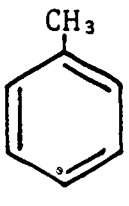
m-Xylene
(1,3-Dimethylbenzene)



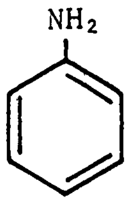
p-Xylene
(1,4-Dimethylbenzene)

In the ortho position, the two substituents are adjacent to each other (on the numbers 1 and 2 carbons). In the meta position, the two substituents are separated by one carbon (on the number 1 and 3 carbons). In the para position, the two substituents are opposite each other (on the numbers 1 and 4 carbons).

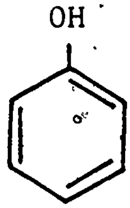
Toluene, aniline, and phenol are three common names given to important derivaties of benzene. Their structures are as follows:



Toluene
(methylbenzene)

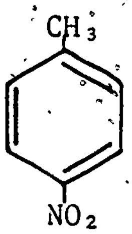


Aniline

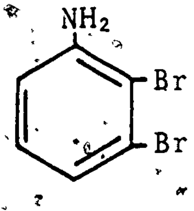


Phenol
(hydroxybenzene)

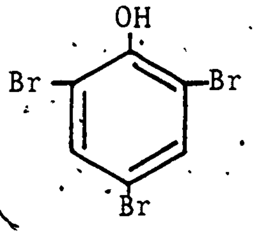
Derivatives of these compounds are named by considering the number 1 carbon to the be one with the group that gives the compound its name (that is, the carbon containing the CH_3, NH_2, or OH group). Examples of these substituted compounds are given below:



4-Nitrotoluene
(p-nitrotoluene)

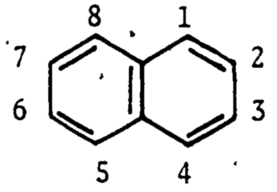


2,3-Dibromoaniline

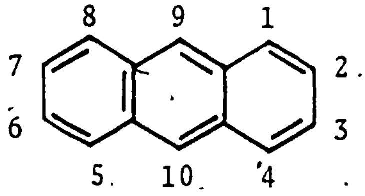


2,4,6-Tribromophenol

The order of naming a compound is alphabetical when three different substituents occupy positions on the ring. Aromatic compounds can contain more than one benzene ring. Examples include naphthalene, with two condensed benzene rings, and anthracene, with three condensed benzene rings:

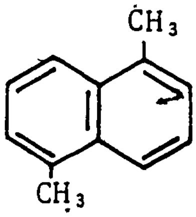


Naphthalene



Anthracene

The numbering system indicated on the structures is used to name substituted naphthalenes and anthracenes. Consider the following substituted naphthalenes:



1,5-Dimethylnaphthalene

SUBSTITUTED HYDROCARBONS

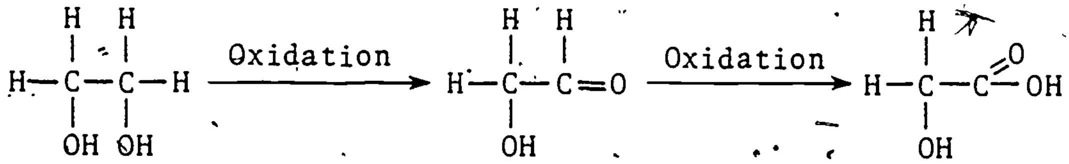
Substituted hydrocarbons are hydrocarbons in which at least one hydrogen atom has been replaced by a functional group. Some of the major substituted hydrocarbon classes and functional groups are identified in Table 6.

The substituted hydrocarbons containing fluorine are an important group of compounds, especially those containing more than one fluorine atom. These polyfluorinated hydrocarbons, which commonly exist as gases, are extremely inert, nontoxic, and noncorrosive. In the liquid state they have a low boiling point. These properties make the polyfluorinated hydrocarbons useful as refrigerants. They are commonly known by their trade name, Freon.

TABLE 6. CLASSES OF SUBSTITUTED HYDROCARBONS AND THEIR FUNCTIONAL GROUPS.

Class	Functional Group	General Formula	Structure	Name
Alcohols	$-O-H$	$R-O-H$	C_2H_5OH	Ethyl alcohol
Phenols	$-O-H$	$R-O-H$	C_6H_5OH	Phenol (carbolic acid)
Ethers	$-C-O-C-$	$R-O-R$	CH_3-O-CH_3	Dimethyl ether
Aldehydes	$-C\begin{smallmatrix}= O\\ \diagdown H\end{smallmatrix}$	$R-C\begin{smallmatrix}= O\\ \diagdown H\end{smallmatrix}$	$CH_3-C\begin{smallmatrix}= O\\ \diagdown H\end{smallmatrix}$	Acetaldehyde
Ketones	$\begin{smallmatrix}\diagdown\\ \diagup\end{smallmatrix}C=O$	$\begin{smallmatrix}R\diagdown\\ R\diagup\end{smallmatrix}C=O$	$CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$	Acetone
Acids	$-C\begin{smallmatrix}= O\\ \diagdown OH\end{smallmatrix}$	$R-C\begin{smallmatrix}= O\\ \diagdown OH\end{smallmatrix}$	$CH_3-C\begin{smallmatrix}= O\\ \diagdown OH\end{smallmatrix}$	Acetic acid
Esters	$-C\begin{smallmatrix}= O\\ \diagdown O-R\end{smallmatrix}$	$R-C\begin{smallmatrix}= O\\ \diagdown O-R\end{smallmatrix}$	$CH_3-C\begin{smallmatrix}= O\\ \diagdown O-CH_3\end{smallmatrix}$	Methyl acetate
Amines	$-NH_2$	$R-NH_2$	$CH_3CH_2-NH_2$	Ethyl amine
Halogens	F, Cl, Br, or I	$R-X$ (where X is a halogen)	CH_3Cl	Methyl chloride

The alcohols, aldehydes, ketones, and acids are interrelated. Upon oxidation, alcohols can produce aldehydes or ketones, depending upon the alcohol. Further oxidation will convert the aldehyde to an acid. For example, upon partial oxidation, ethylene glycol produces glycolic aldehyde — which can be further oxidized to produce glycolic acid, as shown in the following equation:



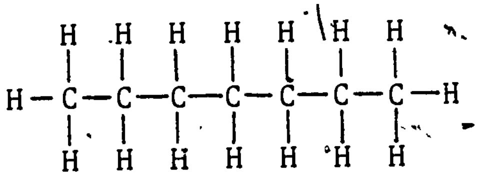
Ethylene glycol Glyoclic aldehyde Glycolic acid

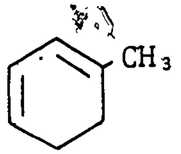
Ethylene glycol is widely used as the heat transfer medium in solar energy panels. If the ethylene glycol is exposed to air (oxygen), it will undergo the undesirable reaction indicated above and produce glycolic acid. The glycolic acid is corrosive and produces damage to pumps and other components of the solar system.

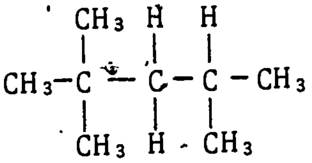
GASOLINE PRODUCTION

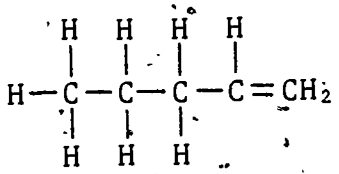
Now that organic chemistry has been briefly considered, gasoline production can be studied. The supply of gasoline from the fractional distillation of petroleum, called straight-run gasoline, is inadequate in quantity and quality for supplying current needs. About 40% of all petroleum is converted to high grade gasoline. A variety of techniques are used to supplement straight-run gasoline.

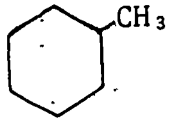
Gasoline is composed of a mixture of hydrocarbons, which includes alkanes, alkenes, cyclic compounds, and aromatics. Examples of these hydrocarbons are as follows:


n-Heptane (alkane)


Toluene (aromatic)


Iso-octane (branched alkane)


1-Pentene (alkene)


Methylcyclohexane

Straight-chain hydrocarbons, such as heptane, are obtained in straight-run gasoline. In general, they burn too fast for smooth combustion. They can ignite prematurely in the engine, causing knocking. This can result in engine damage and loss of power. On the other hand, branched alkanes, cycloalkanes, alkenes, and aromatics burn more evenly – and without knocking. The octane number is a rating used to indicate a gasoline's tendency to knock. On the octane scale, n-heptane is assigned a value of zero, whereas iso-octane is assigned a value of 100. A gasoline with an octane rating of 90 would have the same tendency to knock as would a mixture of 90% iso-octane and 10% n-heptane. Octane tests are conducted in testing internal combustion engines. Blends of n-heptane and iso-octane are compared (in performance) to the gasoline being tested. It is possible to have octane ratings of over 100 — that is, the gasoline will knock even less than iso-octane. Aviation grade fuels generally have octane numbers over 100. Octane ratings can be improved by the use of additives. Tetraethyl lead (TEL) is commonly used to reduce the knocking of a fuel, thereby increasing its octane rating. Table 7 contains a listing of octane numbers of some hydrocarbons with and without tetraethyl lead.

TABLE 7. OCTANE RATINGS.

Hydrocarbon	Formula	ml TEL/gallon	
		0	3
n-Pentane	C_5H_{12}	61.7	88.7
n-Hexane	C_6H_{14}	24.8	65.3
n-Heptane	C_7H_{16}	0.0	43.5
Toluene	C_7H_8	103.2	111.8
n-Octane	C_8H_{18}	-19.0	25.0
Iso-octane	C_8H_{18}	100.0	115.5
Isopropylbenzene	C_9H_{12}	113.0	116.7

Note the marked increase in octane ratings with the addition of TEL, especially for the straight-chain (normal) hydrocarbons. In addition, the effect of branching in the alkanes can be seen by comparing the octane ratings of n-octane and iso-octane. These compounds differ in octane ratings (without TEL) by 119. In order to carry away the lead and prevent unwanted deposits of lead in the engine, ethylene dibromide is added to leaded gasoline. The lead reacts with ethylene dibromide to form $PbBr_2$, which is exhausted into the atmosphere. In an effort to eliminate the environmental hazard of emitting thousands of tons of lead into the atmosphere yearly, later model automobiles use unleaded gasoline. The elimination of lead compounds from gasoline requires that the automobile have a lower compression ratio so that the lower octane gasolines may be used. The lower compression ratio results in decreased power of the automobile. To compensate somewhat for the loss in octane rating by the elimination of lead compounds, the more costly aromatic hydrocarbons must be included in gasoline blends, accounting for the greater cost of unleaded gasoline as compared to leaded. Previously, the aromatic compounds were removed from gasoline during the refining process, so they could be used to produce a variety of products. This increased competition for aromatics has driven their price up, and this increase is reflected in products made from aromatic hydrocarbons.

Normal centane, $C_{16}H_{34}$, is used as the standard for rating diesel fuels. High octane numbers are not desirable for diesel fuels that come from the gas oil fraction during the fractional distillation of petroleum.

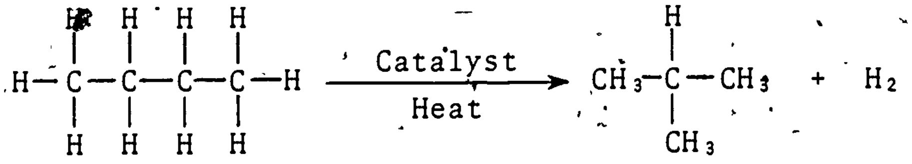
A number of methods are used to increase the yield of gasoline from petroleum and to increase the octane number. In the fractional distillation of petroleum, relatively large quantities of the longer-chain hydrocarbons are obtained. These long-chain hydrocarbons can be broken down into two or more smaller molecules in a process called catalytic cracking. Pressures as high as 1200 pounds per square inch and temperatures up to 1000°F, along with a suitable catalyst, are used in the cracking operation. A variety of products are available from the cracking process. For example, $C_{15}H_{32}$ can be cracked to produce compounds containing six, seven, eight, or nine carbons. The straight-chain compounds can be reformed or rearranged into cyclic or branched compounds to have a gasoline of higher octane number. In the cracking operation, a molecule of centane, $C_{16}H_{34}$, can be split into a molecule of octane and a molecule of unsaturated octene:

$$C_{16}H_{34} \xrightarrow[\text{Heat, press}]{\text{Catalyst}} C_8H_{18} + C_8H_{16}$$

Centane   n-Octane   Octene

Catalytic cracking is the most important technique of increasing the yield of gasoline from petroleum.

Another method of increasing the yield of gasoline is <u>reforming</u>. In reforming, a straight-chain hydrocarbon is converted into a branched hydrocarbon. Consider the reforming of n-butane into isobutane when heated with a suitable catalyst:

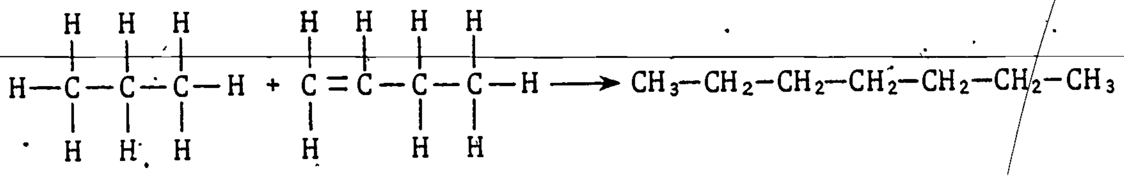


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H} \xrightarrow[\text{Heat}]{\text{Catalyst}} \mathrm{CH_3{-}\overset{H}{\underset{CH_3}{C}}{-}CH_3} + H_2$$

n-Butane   Isobutane   Hydrogen

<u>Polymerization</u> is used in the refining process to combine small-chain hydrocarbons into longer-chain compounds. It is essentially the opposite of cracking. The initial

fractional distillation of petroleum yields propane, butane, and other short-chain compounds that are not useful as gasoline. They may be polymerized, however, into longer-chain compounds. For example, n-propane can combine with 1-butene to produce n-heptane:

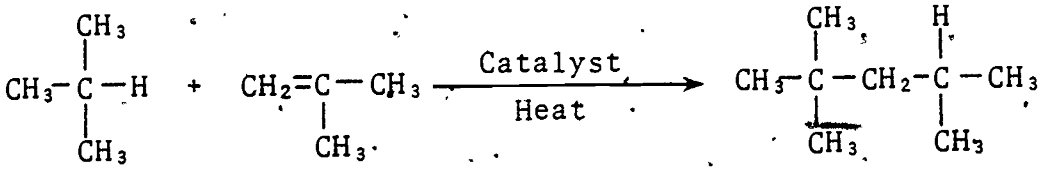


$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H + \underset{H}{\overset{H}{C}}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H \longrightarrow CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

n-Butane 1-Butene n-Heptane

Still another method of increasing the yield of gasoline is dehydrogenation; this involves removing hydrogen from saturated hydrocarbons, such as propane and butane, to form unsaturated hydrocarbons (compounds with double bonds), such as propene and butene. The unsaturated hydrocarbons can then be used in polymerization, as illustrated previously with 1-butene.

Alkylation is similar to polymerization in that smaller molecules are combined to produce larger hydrocarbons. In alkylation, branched alkanes are combined with branched alkenes to form longer-chain compounds. Alkylation is illustrated by the combination of isobutane and isobutene to form 2,2,4-trimethylpentane:



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}H + CH_2{=}\underset{CH_3}{C}{-}CH_3 \xrightarrow[\text{Heat}]{\text{Catalyst}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{H}{C}}{-}CH_3}$$

Isobutane Isobutene 2,2,4-Trimethylpentane

In summary, the fractional distillation of petroleum does not produce the desired distribution of compounds; specifically, much more gasoline is required. To increase the yield of gasoline, a number of methods are used, including catalytic cracking, reforming, polymerization, dehydration, and alkylation.

As indicated earlier, the liquification of coal to form petroleum-like products will be required in the future. Because of the absence of petroleum deposits, Germany — during World War II — developed several processes for the production of liquid fuels from coal. In one of these, coke and steam are used to produce carbon monoxide and hydrogen. The carbon monoxide is then reacted with an excess of hydrogen to produce hydrocarbons that can be used as liquid fuels. The reaction is as follows:

$$\underset{\text{Carbon monoxide}}{8\ CO} \;+\; \underset{\text{Hydrogen}}{17\ H_2} \xrightarrow[\text{Heat}]{\text{Catalyst}} \underset{\text{Octane}}{C_8H_{18}} \;+\; \underset{\text{Water}}{8\ H_2O}$$

The catalyst used is thorium oxide, ThO_2, and the temperature is 250°C. This reaction is known as the Fischer-Tropsch process.

Another method for the liquification of coal, known as the Bergius process, combines hydrogen and carbon directly under high pressures and temperatures:

$$8\ C + 9\ H_2 \xrightarrow[\substack{\text{700 atmospheres} \\ 400^\circ C}]{Fe_2O,\ MoO_2} C_8H_{18}$$

Carbon Hydrogen Octane

The Bergius process can be used to produce diesel fuel, jet fuel, and gasoline. The cost of gasoline, when produced from coal, is not now competitive with that produced from petroleum.

ALTERNATE ENERGY SOURCES

As already indicated, the near exclusive dependence upon fossil fuels and the accelerating utilization of these fuels have resulted in an energy crisis. The availability of natural gas and petroleum is nearing its peak; in the future, less of these fuels will be available. Therefore, considerable research and development is being conducted on alternate, or unconventional, energy sources. Certainly coal gasification and coal liquification (which were discussed previously) can be considered to be unconventional energy sources. Additional alternate energy sources include methanol, ethanol, hydrogen, biomass, solar, nuclear, wind, tidal power, hydroelectric, and geothermal. Nuclear fission and fusion as sources of energy will be considered in a later module.

METHANOL

Methanol (methyl alcohol) has been used as a fuel for over a century. It is a liquid fuel that could be used in internal combustion engines to power automobiles without major modification of the engine. Methanol (also called wood alcohol) can be made from wood, coal, other fossil fuels, farm wastes, and municipal wastes. It burns with a clean, blue flame, with no emission of sulfur oxides or particulates. Although it is being considered primarily as a replacement for gasoline, methanol could also be used for space heating and electric power generation. Methanol, when used as a gasoline additive in present engines without modification, increases engine power and economy while decreasing engine emissions. Methanol is a liquid at room temperature and can be transported and handled in much the same manner as gasoline. A gasoline-methanol mixture containing 15% methanol appears to be the optimum mixture. With this mixture (in an unmodified engine) carbon monoxide emissions decrease by as much as 70%, fuel economy improves by 10%, and acceleration improves by 7%, as compared to gasoline. Methanol has an octane number over 100; therefore it can be used to replace tetraethyl lead as an antiknock agent. Its use as a mixture could stretch gasoline reserves. Methanol's low energy content (approximately half that of gasoline) increases its relative distribution costs. However, a disadvantage of methanol is its corrosive tendency. The two primary limitations to its use are price and availability. As the price of gasoline continues to increase, methanol will become attractive as a fuel (assuming the price of methanol does not increase as rapidly). By using municipal wastes to produce it, methanol would become much more available and less expensive. It is estimated that, if all the municipal wastes in the United States were used to produce methanol, enough would be available to supply nearly 8% of the fuel required/yearly for transportation. Another source of methanol could come from wood, which would be produced on energy plantations. These commercial forests would, in effect, be solar converters that could transform solar energy into wood and then into methanol. The city of Seattle, Washington, is conducting a study of the production of methanol from the city's solid waste. The volume of waste needing to be disposed of is greatly reduced, while, at the same time, 100,000 tons of methanol could be produced.

ETHANOL

Another alcohol with a potential for use as a fuel is ethanol (also called grain alcohol, or ethyl alcohol). Ethanol can be produced by the fermentation of grain. Any grain can be used, but the most economical is milo. The first step in the production of ethanol from grain is the conversion of starch in the grain to sugar:

$$\underset{\text{Starch}}{2\ C_6H_{10}O_5} + H_2O \xrightarrow[\text{in malt}]{\text{Diastase}} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

The enzyme diastase converts the starch to the sugar maltose. In the second step, the maltose is converted to glucose with the aid of the enzyme maltase:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2\ C_6H_{12}O_6$$

Maltose Glucose

Finally, the glucose is converted to ethanol with the aid of the enzyme zymase:

$$C_2H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ C_2H_5OH + 2\ CO_2$$

Glucose Ethanol

The by-product of the fermentation, carbon dioxide, is sold as "dry ice" in the solid form or in tanks as compressed gas. The fermentation process produces ethanol of approximately 10% concentration. The ethanol is separated from the fermentation mixture by fractional distillation.

In addition to being made in the fermentation process, ethanol is also currently made from ethylene. The cost of ethanol made from ethylene is approximately half the cost of ethanol made from grains. A present, it is uneconomical to make ethanol from grain in comparison to the ethylene process. However, no real advantage is obtained in using ethanol made from ethylene as a fuel, since ethylene is a hydrocarbon just as gasoline is. To move from dependence on petroleum, the ethanol used as a fuel must be made from fermentation of grain. A blend of gasoline-ethanol containing 10% ethanol (called <u>gasohol</u>) is being fleet tested. A blend of this composition would raise the price of a gallon of gasoline by three cents a gallon. No advantage of using ethanol is seen in terms of drivability or reduced emissions. Solubility problems associated with gasoline, alcohol, and water would present problems of handling, since storage facilities would require some way to prevent water contamination because of the hygroscopic (water-attracting) nature of ethanol. Cold weather separation has been a problem, as well as slow vehicle warm-up. Ethanol has an octane value of 106; therefore it can be used to replace at least a portion of the tetraethyl lead in gasoline. As with methanol, corrosion problems are associated with the introduction of ethanol into the internal combustion engine. In summary, there are no important technical advantages to the use of ethanol as an automotive fuel, and until the cost and availability of gasoline become significant factors, the use of ethanol will be limited.

HYDROGEN

The term "hydrogen economy" refers to the concept in which conventional fuels would be replaced by hydrogen. This concept has appeal because, potentially, it can solve the pollution problem. When hydrogen burns, the product is water; therefore, unlimited amounts of hydrogen could be burned without polluting the atmosphere. The reaction is simple:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + \text{Heat}$$

Hydrogen could be transported in the pipelines currently used for natural gas. In heating applications, it would require little venting since carbon dioxide and particulates would not be emitted — only water. Hydrogen can be burned in jet engines and, with modification, in the automobile engine. Most of the hydrogen produced today is made from methane.

If hydrogen were to become a useful fuel, it could no longer be made from methane, since there would be no advantage of converting the fossil fuel methane to hydrogen. The best source for hydrogen is from the electrolysis of water. In electrolysis, an electric current is passed through water, and the water molecules are broken down into hydrogen and oxygen gases. The major problem of the hydrogen economy is that electricity must be used to produce the hydrogen. The advantages of the hydrogen economy can be realized only if an inexpensive method of producing electricity is devised, such as by solar energy or nuclear energy. Even if all fossil fuels were depleted, modern society could exist in much the same manner as it is now by utilizing hydrogen – that is, if adequate electrical energy were available.

BIOMASS

Municipal wastes, including garbage, trash, and sewage, have traditionally been discarded. The volume of waste grows each year, making disposal difficult. This waste can be used to produce valuable products. The decay of organic matter by bacteria – in the absence of air – results in methane gas. In the presence of oxygen, methanol can be produced. A certain part of the municipal waste can be incinerated to produce steam for generating electricity. As fuel costs and waste disposal costs rise, more cities will likely start producing fuels from their wastes.

One means of achieving a long-term, perpetual methane economy is to convert a continuously renewable nonfossil carbon to synthetic gas. The renewable carbon could come from plants commonly referred to as <u>biomass</u>. Sources of biomass include trees, plants, grasses, algae, or water plants which are produced from sunlight by photosynthesis. Tremendous quantities of these plants would be required to produce energy at the level of current consumption. The technology for biomass production and gasification is currently available and should be competitive with gas derived from coal. Table 8 lists some examples of fuel gas production from biomass.

TABLE 8. EXAMPLES OF FUEL GAS PRODUCTION FROM BIOMASS.

Biomass	Conversion Reaction	Conditions	Fuel Products
Pine bark	Pyrolysis	900°C	Low Btu gas, char, oil
Rice straw	Pyrolysis	200–700°C	Low Btu gas, char, oil
Wood	Digestion	30°C, 30 days	Intermediate Btu gas
Water hyacinth	Digestion	48°C, 28 days	Intermediate Btu gas
Seaweed algae	Digestion	33°C, 20 days	Intermediate Btu gas

Water hyacinth and algae are high producers of organic materials. Algae production is 73 tons/acre/year (under ideal conditions), whereas water hyacinth production in Mississippi approaches 15 tons/acre/year. Commercial conversion of biomass is expected by 1985.

GEOTHERMAL

Geothermal energy has the potential of providing a much greater amount of energy than is now available from this source. Fifteen countries have operating electrical generating plants or are constructing plants utilizing geothermal steam. At many geothermal sites, steam is led directly to the turbines for electricity production. Much of the western United States has underlying hot-rock formations. It may be possible to drill a well into the thermal region, pump water into the well, and remove steam from another well. The ultimate potential power generation available from geothermal energy is unknown, but this source may provide a significant amount of energy in the future.

SOLAR ENERGY

Solar energy has been described as a virtually infinite source of energy that is free. However, the applications of solar energy have been hampered by the fact that sunlight is diffuse and intermittent. A large land area is required for solar collectors, and means must be provided for energy storage in periods when solar energy is not available. Solar energy is being used in two major areas: for space heating and cooling and for generation of electricity. The necessary research and development for using solar energy for space heating and cooling is well advanced. However, some additional work is required before there can be widespread use of solar energy for generating electricity. It has been estimated that solar energy has the potential of supplying one-half of the world's energy needs.

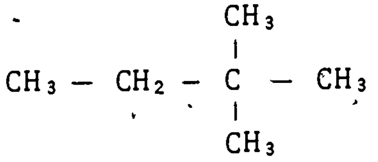
SUMMARY

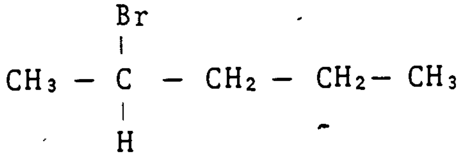
The major solid fuel is coal, but since there are environmental problems associated with burning large quantities of coal, conversion projects to convert coal to usable gases or liquids are being investigated. Coal is the major fossil fuel resource in the United States. It has been estimated that a 500-year supply of coal is available. Natural gas is almost a perfect fuel; it burns cleanly, has a high energy content-per-unit weight, and can be transported easily. Unfortunately, the supply of methane is decreasing. Coal gas, natural gas, bottled gas, and acetylene are important gaseous fuels. Petroleum is the major liquid fuel, supplying gas, gasoline, oil, diesel and jet fuels, as well as being the starting material for the synthesis of numerous organic compounds. The major role of the refinery is to separate the fractions of petroleum and to increase the yield of gasoline for use in transportation. The yield of gasoline is improved by catalytic cracking, reforming, polymerization, dehydrogenation, and alkylation. Alternate energy sources are being developed in order to move away from the dependence upon the fossil fuels that eventually will be depleted. These alternate sources of energy include methanol, ethanol, hydrogen, biomass, solar, nuclear, wind, tidal power, hydroelectric, and geothermal. Currently, these sources of energy cannot compete with the fossil fuels; therefore, their development has been slow. However, as prices of fossil fuels increase, it is expected that most of these alternate sources of energy will be utilized to some extent in supplying the world's energy needs.

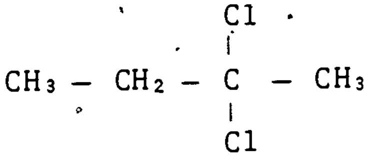
While energy production is important, perhaps as much stress should be placed upon energy conservation. Energy conserved is energy that does not have to be produced. The days of inexpensive energy are gone, and energy consciousness must be instilled in everyone. A number of studies have indicated that a 30% reduction in energy consumption could be achieved without undue hardship on anyone. Designs of equipment, appliances, and dwellings — everything that consumes energy — should be developed with an effort to reduce energy consumption.

EXERCISES

1. Name the following compounds:

a.  $CH_3 - CH_2 - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$ ____________________

b.  $CH_3 - \overset{Br}{\underset{H}{C}} - CH_2 - CH_2 - CH_3$ ____________________

c.  $CH_3 - CH_2 - \overset{Cl}{\underset{Cl}{C}} - CH_3$ ____________________

2. Draw the structural formulas of the following compounds:

a. 2,2,3-Trimethylpentane.

b. 1,3-Dibromopropane.

c. 1-Bromo,3-methylbutane.

d. 2-Chloropropane.

LABORATORY MATERIALS

Laboratory 1
50 ml round-bottom
    distilling flask
Water condenser
Adapter
Thermometer
Clamp
Burner
50 ml Erlenmeyer flask
Rubber tubing
Boileezers
Long stem funnel
25 ml graduated cylinder
Fractionating column
Refractometer

Laboratory 2
Test tubes
Glass tubing
Ring stand
Clamp
Burner
Wood (splinters or excelsior)
Soft coal
Litmus paper

LABORATORY PROCEDURES

LABORATORY 1. FRACTIONAL DISTILLATION.

Distillation is widely used in laboratories and the chemical process industry to separate liquids that are soluble in each other. Consider a mixture of ethanol and water which are totally miscible. Ethanol boils at approximately 78.5°C; water boils at 100°C. When placed in a distillation flask and heated to the boiling point (which would be a point somewhere between 78.5°C and 100°C, depending upon the composition of the mixture), the first portion of vapor coming off and being condensed would be richer in ethanol than in water. If the first distillate were then redistilled, the initial vapor would be even more rich in ethanol. And, if this process were repeated often enough, pure ethanol would ultimately be produced. However, rather than conducting the distillation by this rather laborious process, a fractionating column is used. A fractionating column is a glass column that is packed with some inert material – such as glass beads, glass helices, or clay chips – that provides a large surface upon which the vapor can condense. The hot vapor rises through the packed column until it reaches a cool enough portion of the column to condense. The liquid then flows downward until it becomes hot enough to be reconverted to vapor. Each time the condensate vaporizes, the vapor is richer in the ethanol (or lower boiling point liquid). In this process, called fractional distillation, the components, or fractions, of the original mixture are separated. In this experiment, a mixture of ethanol and water is separated by fractional distillation. All data should be recorded in the Data Table.

A synthetic mixture of ethanol and water may be distilled, or beer may be distilled. Alternately, a mixture of methanol and water may be distilled.

PROCEDURE

1. Set up the apparatus for distillation as illustrated in Figure 1. The distillation vessel is a round-bottom distillation flask that is fitted with an adaptor containing a thermometer. The tip of the thermometer should be near the point where the vapor leaves the side arm of the distillation flask. A water-cooled condenser is fitted to the side arm of the distillation

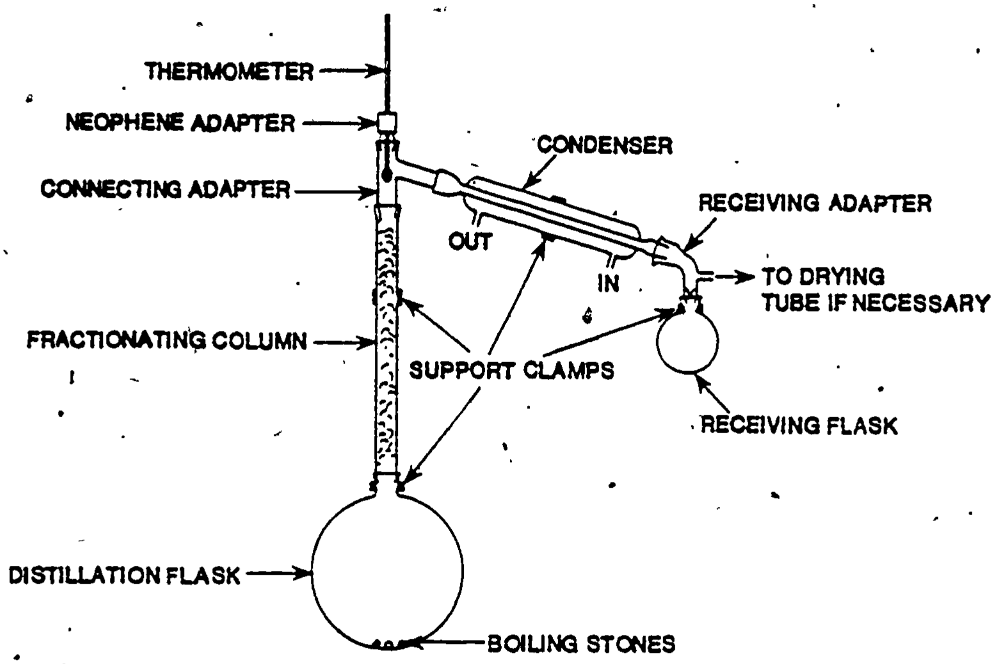


Figure 1. Basic Apparatus for Fractional Distillation.

flask. A condenser adapter leads the condensate into a receiving flask. The apparatus is positioned so that the distillation flask can readily be heated. With extremely flammable liquids, an open flame from the burner must not be used; instead, a heating mantle should be utilized in these cases. The lower end of the water condenser is connected to the water line, and the upper end is connected to the drain.

2. Mix 15 ml of water with 15 ml of ethanol and place the 30 ml of mixture in the distilling flask.
3. Add several Boileezers and insert the cork containing the thermometer.
4. Use a 24 ml graduated cylinder to collect the distillate.

5. Heat the mixture until it boils and record the temperature at which the first drop of distillate appears in the graduated cylinder.
6. Adjust the heating rate so that the distillate drops slowly into the graduated cylinder.
7. Record the temperature every 2 ml as the distillation proceeds.
8. Continue the distillation until the temperature reaches 99°-100°C. (If the distillation resulted in a complete separation, this point would be after 15 ml of ethanol was collected, leaving 15 ml of water. This ideal separation can almost be achieved by using a packed fractionating column.) Record the volume of residual liquid in the distilling flask and the volume collected. Plot the distillation curve (that is, plot temperature versus milliliters of distillate).

   NOTE: A refractometer is often used to determine the composition of the components of a distillation. The refractive index of ethanol is 1.36048 at 20°C, whereas the refractive index of water is 1.33299 at 20°C.

LABORATORY 2. DESTRUCTIVE DISTILLATION OF WOOD AND COAL.

Destructive distillation is used industrially to produce gaseous fuels and aromatic hydrocarbons from wood and coal. These distillation processes will be illustrated in the experiment.

DESTRUCTIVE DISTILLATION OF WOOD

1. Arrange the apparatus as shown in Figure 2. The short exit tube should be glass tubing that has been drawn out into a capillary and cut off. The lower end of the delivery tube should be half an inch from the bottom of the condensing tube.

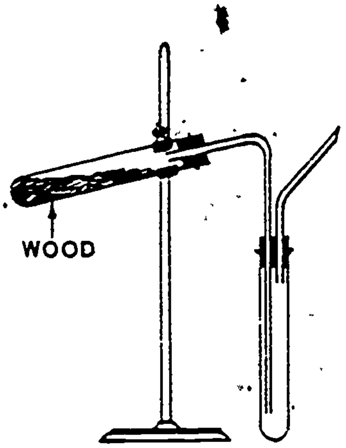


Figure 2. Apparatus for Destructive Distillation.

2. Fill the top test tube with wood splinters or excelsior, and connect the test tube.
3. Gently heat the wood at first; then heat it strongly until no further change is observed. Describe the appearance of the volatile matter coming from the wood.

4. While heating, bring the flame to the end of the capillary tube. Does the gas being emitted burn?

5. Allow the apparatus to cool a[illegible] examine the residue in the test tube. What is the substance in the test tube?

6. Describe the appearance of the substance in the condensing tube. Can distinct layers be seen?

7. Test the liquid in the condensing tube with litmus paper. Is the substance acidic or basic?

This substance is a complex mixture containing wood alcohol (methyl alcohol), acetic acid, acetone, and other organic substances, including aromatic compounds. The destructive distillation of wood produces charcoal, methane gas, and liquid organic chemicals.

DESTRUCTIVE DISTILLATION OF COAL

1. Fill a test tube half full with finely crushed soft coal. Replace the condenser (used above) with a clean one.
2. Heat the test tube containing the coal — gently at first and then strongly. Describe the volatile material. Is it the same as obtained from wood?

3. Bring a flame to the end of the capillary tube. Is the gas combustible?

____

4. Heat the coal until gas is no longer given off.
5. Allow the test tube to cool, and examine the residue. Describe the residue. How does it compare to the original cost? (The residue is called coke.)

____

____

____

6. Examine the condensing tube and describe its contents.

____

____

~~7. Name three products~~ of the destructive distillation of coal.

a. ____________________

b. ____________________

c. ____________________

DATA TABLE. FRACTIONAL DISTILLATION.

Distillation of Water-Ethanol Mixture

Volume Collected	Temperature °C
First drop	________
2 ml	________
4 ml	________
6 ml	________
8 ml	________
10 ml	________
12 ml	________
14 ml	________
16 ml	________

Volume collected: ________ ml

Residual volume: ________ ml

REFERENCES

Fieser, L.F. and Fieser, M. Introduction to Organic Chemistry. Boston: D. C. Heath and Co., 1957.

Griffin, Jr., Rodger W. Modern Organic Chemistry. New York: McGraw-Hill Book Co., 1969.

Morrison, R.T. and Boyd, R.N. Organic Chemistry. Boston: Allyn and Bacon, Inc., 1966.

Nelson, T.W. "The Origin of Petroleum." Journal of Chemical Education 31, 399 (1954).

Rossini, F.D. "Hydrocarbons in Petroleum." Journal of Chemical Education 37, 554 (1960).

Smith, L.O., Jr., and Criston, S.J. Organic Chemistry. New York: Reinhold Publishing Co., 1966.

Wertheim, E. Organic Chemistry. New York: McGraw-Hill Book Co., 1951.

Yohe, G.R. "Coal." Chemistry 40 (January 1967).

Zimmerman, Henry and Zimmerman, Isaak. Element of Organic Chemistry. Encino, CA: Glencoe Press, 1977.

GLOSSARY

Aliphatic compounds: Straight-chain compounds.

Alkanes: A series of hydrocarbons containing single bonds.

Alkenes: A series of hydrocarbons containing double bonds.

Alkylation: Combination of branched alkanes to form longer-chain compounds.

Aromatic compounds: Compounds containing the six-member carbon ring.

Biomass: A renewable carbon source from plants such as trees, grasses, or water plants.

Catalytic cracking: A process in which long-chain hydrocarbons are broken down into two or more smaller molecules.

Cycloalkanes: A series of ring compounds.

Dehydrogenation: The removal of hydrogen from saturated hydrocarbons to form unsaturated hydrocarbons.

Freon: The trade name of polyfluorinated hydrocarbons used as refrigerants.

Fractional distillation: A process consisting of heating a mixture to vaporize and separate it into fractions according to boiling points.

Fuel: Any combustible substance that is burned to produce useful heat.

Gasohol: A blend of gasoline-ethanol containing 10% ethanol.

Hydrogen economy: The concept in which conventional fuels would be replaced by hydrogen.

Isomers: Compounds having the same composition and molecular weight, but different atomic arrangements.

Octane number: A rating used to indicate a gasoline's tendency to knock in an engine.

Organic chemistry: The study of carbon-containing compounds.

Polymerization: The combination of small-chain hydrocarbons into longer-chain compounds.

Reforming: A process in which a straight-chain hydrocarbon is converted into a branched hydrocarbon.

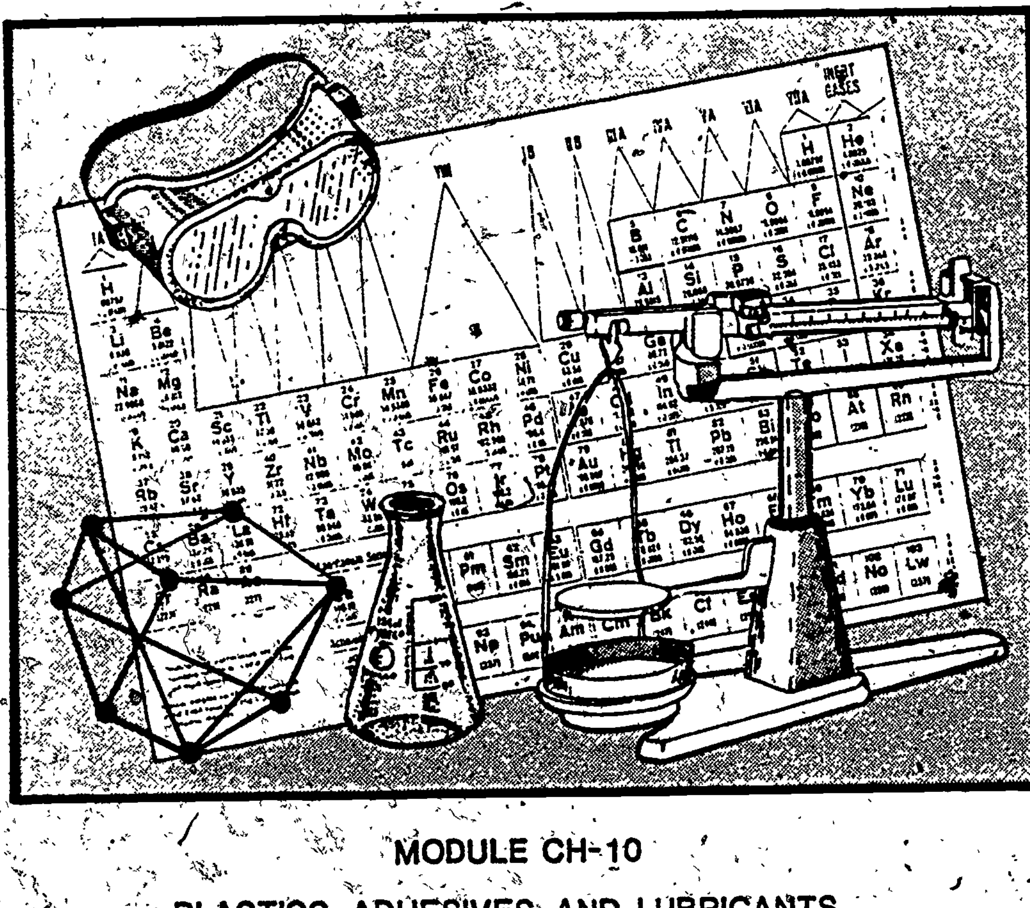
Straight-run gasoline: Gasoline obtained from the fractional distillation of petroleum.

Substituted hydrocarbons: Hydrocarbons in which at least one hydrogen atom has been replaced by a functional group.

ENERGY TECHNOLOGY

CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-10

PLASTICS, ADHESIVES, AND LUBRICANTS

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

Plastics, lubricants, and adhesives are important materials used in the energy field and in everyday life. Knowing the properties of these materials can assist the energy technician in making wise choices as to their utilization as they are encountered on the job.

Plastics are synthetic materials that consist of giant molecules. Several types of plastics are available, each made from different chemical starting materials. It is almost impossible to go through a day without using objects made from plastics since they are used in applications such as packaging, transportation, electronics, construction, furniture, clothing, and appliances. Examples include paints made from plastics (polymers), flooring materials, synthetic fibers for suits, plastic pipes and fittings, automobile steering wheels, telephones, dishes, combs, and seat covers. Plastics are frequently used because of their excellent insulation properties (heat and electrical), resistance to corrosion and chemicals, lightness of weight, strength, range of color, and ease of processing. One of the major disadvantages of plastics is that they deteriorate at high temperatures or in the presence of sunlight.

The plastics industry is a multibillion-dollar business. It produces many articles not dreamed of several years ago. For example, the shoes made for walking on the moon are made from flexible plastic silicone because it provides good thermal insulation that withstands extremely cold and hot temperatures without melting or becoming brittle. The use of plastics in the automobile industry has also increased in the last few years. However, plastics are made from chemicals derived from petroleum, a fact that somewhat places the future of plastics in doubt.

Adhesives, which consist of large, synthetic molecules that are similar to – and sometimes identical to – plastics, are used for joining many types of materials. They are widely used in the automobile, aircraft, electrical, aerospace, and building industries.

Lubricants are used to reduce the friction that wastes energy and that tends to destroy rubbing surfaces. Primarily, lubricants are made from petroleum – although synthetic lubricants are becoming more popular. Several factors important in the practice of lubrication are considered in this module.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of Chemistry for Energy Technology I and Modules CH-06 through CH-09 of Chemistry for Energy Technology II.

OBJECTIVES

Upon completion of this module, the student should be able to:

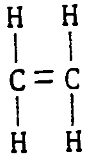
1. Define the following terms:
    a. Monomer.
    b. Polymer.
    c. Copolymer.
    d. Thermoplastic.
    e. Thermosetting plastic.
    f. Engineering plastics.
    g. Adhesive.

h. Lubricant.
i. Friction.
j. Stabilizer.
k. Plasticizer.
l. Glass transition.

2. Identify a common use of the following polymers:
   a. Polyethylene.
   b. Polyvinyl chloride.
   c. Polystyrene.
   d. Teflon.
   e. Polymethyl methacrylate.
3. List three advantages of plastics as compared to metals.
4. List three limitations of plastics.
5. List four methods of processing plastics.
6. List three advantages of joining materials with adhesives as compared to using mechanical methods.
7. List three environmental conditions that play an important role in the practice of lubrication.

PLASTICS

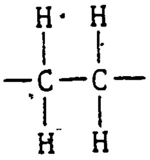
The starting material for all plastics is the monomer. The term "monomer" is derived from "mono," (meaning one) and "mer," (meaning unit, or part). Monomer, therefore, means one unit or part. In producing plastics, or polymers (meaning many units), the small monomer molecules are linked through chemical reaction to form long-chain compounds. One of the more simple monomers is ethylene, C_2H_4:



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

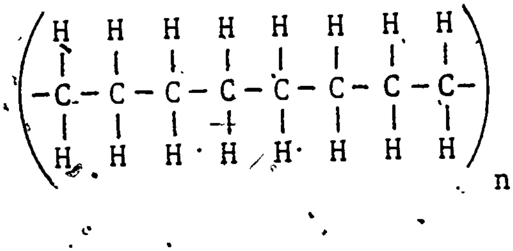
Ethylene monomer

The double bond in ethylene can be rearranged as follows:



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & H & & H & \end{array}$$

The free bonds on the end of ethylene can then combine with other ethylene units to form a long chain, as follows:



$$\left(\begin{array}{ccccccccccccccccc} & H & & H & & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & & H & & H & & H & \end{array}\right)_n$$

The "n" in the lower right-hand corner represents a large number, such as 1000. It is common for polymers to have molecular weights from 10,000 to 100,000. Ethylene, a gas, combines in the ploymerization process to form the solid polymer called polyethylene.

If a pure monomer A, such as ethylene, is polymerized, the polymer obtained is called a homopolymer (meaning alike throughout):

– A – A – A – A – A – A – A – A – A – A – A –

Likewise, the pure monomer B can be polymerized to form a homopolymer:

– B – B – B – B – B – B – B – B – B –

But if both monomers, A and B, are added to each other, and the mixture is polymerized, a polymer called a copolymer is formed:

– A – B – B – B – A – A – B – B – A – A – A –
– B – B – A – A – A – B – A – B – B – B – A –
– A – A – A – B – A – A – A – B – A – A – B –

In many copolymers, the order of the units is random (as indicated in the three preceding structures), and the properties of the copolymer are determined by the ratio of the amount of A to the amount of B in the copolymer. The properties of a copolymer are different from those of the pure polymers, and copolymers can be tailor-made to have properties that are superior to those of pure polymers.

POLYMER ADDITIVES

Most plastics used today undergo some type of modification through the addition of additives. Plasticizers are added to plastics to make them more flexible. For example, polyethylene and polypropylene are too stiff for most applications. However, with the addition of suitable plasticizers, these plastics become flexible enough to be useful. For plastics that will be exposed to sunlight, the addition of a stabilizer will prevent the bonds from being broken by ultraviolet rays of the sun. The addition of approximately 0.1% (by weight) is enough to protect most plastics from decay due to sunlight. A variety of fillers is added during the processing of plastics to give the plastic various physical properties, one of which is to increase the plastic's resistance to heat. Accelerators or inhibitors are added to control the rate of cure of plastics. In addition, pigment or dyes can be added to polymers to give the finished product a desirable color.

Plastics have several desirable characteristics, including the following:

- Chemical resistance – Some plastics are resistant to strong acids, alkalis, and solvents.
- Corrosion and weather resistance – Plastics do not oxidize readily and, therefore, maintain their usefulness in a variety of environments that are detrimental to metals.
- Color – Plastics can be produced in many colors. The color is a permanent part of the plastic, not just a surface coating.

- Shape – Plastics can be economically formed into many shapes through molding, machining, or extrusion.
- Insulation – Plastics are good insulators for heat and electricity.
- Lightness – Plastics weigh about one-half the weight of aluminum and one-sixth the weight of steel.
- Strength, hardness, flexibility – Plastics offer a number of mechanical advantages over other materials, especially in regard to their strength-to-weight ratio.

Plastics can be divided into two groups on the basis of how they react when exposed to heat: thermoplastics and thermosetting plastics. Thermoplastics will soften and flow when heated; when cooled, they harden. However, this process is reversible, and the material can be melted and solidified a number of times without change. In contrast, thermosetting plastics do not soften when heated. They form a set of interlocking bonds between the polymer chains. Under extensive heating, thermosetting plastics will char and degrade rather than soften.

PROCESSING OF PLASTICS

Many different processes are used in changing plastic granules, powders, and liquids into final products. Thermoplastic materials are suitable for certain processes, whereas, in most cases, thermosetting materials will require other methods of forming. Thermoplastics are usually melted and reshaped before they are cooled into the final shape. Thermosets are usually polymerized by heat, pressure, or a catalyst during the processing step. Several of the more common processing techniques will be considered in the following paragraphs.

In injection molding of thermoplastics, the material in pellet or powder form is heated until it reaches a molten state. Then, under hydraulic pressure, the material is pushed through a nozzle to fill a mold cavity. The material is then cooled in the mold where it takes its final shape.

Blow molding is used to mold hollow thermoplastic parts, such as plastic milk bottles. Air, under pressure, is fed into the center of the mold, inflating the material and forcing it against the mold cavity walls. In principle, the process is similar to glassblowing.

In extrusion, the molten plastic is forced through a die that is shaped to the desired form. This method is used to make rods, film, tubes, and pipes. The final form is cooled by air or water and is then cut to length.

Calendering is a process used to produce sheets or films. The heated plastic passes through a series of heated rollers to obtain a uniform thickness. The material then passes between chilled rollers to take its final set.

Casting is primarily used for thermoset materials. No pressure is used in this process. As a liquid, the material is poured into a mold cavity. After the mold is filled, the material is cured into its final hard form by using room temperature or by using heat.

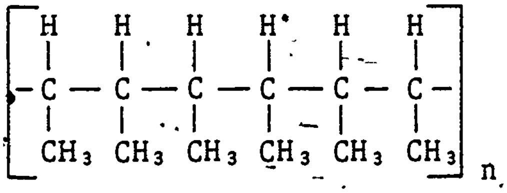
Sheets of cloth, glass, or paper can be impregnated with plastic resin by the manufacturer and then laid on top of each other to form a desired thickness. These "laminates" are then cured under pressure to form a strong material. Circuit boards for electrical devices are constructed in a similar manner, as well as many other products such as table tops, wallboards, and rods. Glass fibers are effective in strengthening polyesters or epoxies to form fiberglass. Boats are an example of the structural uses of fiberglass.

PROPERTIES OF MAJOR PLASTICS

The following paragraphs contain descriptions of several physical and chemical properties of major plastics.

A major family of polymers is known as the <u>polyolefins</u>. An olefin is a compound in the ethylene family; that is, it contains double bonds. Polyethylene is the major member of this family. Polyethylene is made in two ranges of density: low density and high density. Low density polyethylene has a relatively short-chain molecular structure; whereas high density polyethylene has a much longer chain structure. Low density polyethylene is used where flexibility is a primary consideration, whereas high density polyethylene is used in applications requiring more strength, such as bleach bottles. Polyethylene is used for containers, toys, freezer bags, houseware items, detergent bottles, and wire and cable insulation.

Another member of the polyolefin family, polypropylene, is made from propylene gas, which is obtained from the petroleum industry. The structure of polypropylene is given by the following:

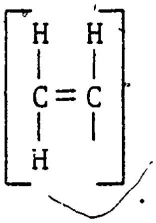


$$\left[\begin{array}{cccccc} H & H & H & H & H & H \\ | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | \\ CH_3 & CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \end{array}\right]_n$$

Polypropylene

Although polypropylene is more costly than polyethylene, it has better rigidity, temperature stability, crack resistance, and tensile strength. Polypropylene is used in pump housings, electronic parts, industrial packaging, luggage, and housewares. In addition, it is widely used in the construction of hospital equipment because of its resistance to chemicals, its transparency, and its ability to be sterilized.

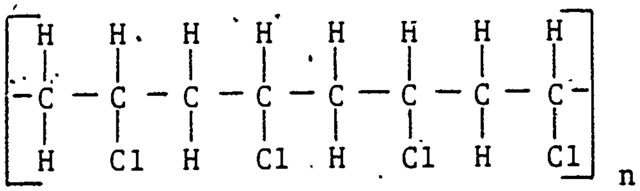
Vinyl resins cover a broad family of plastics, which range from hard, rigid materials to soft, flexible products. They all have the vinyl radical in their structure:



$$\left[\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & \end{array}\right]$$

Vinyl radical

Various side groups can be added to give polymers of varying properties. The most common vinyl resin is polyvinyl chloride (PVC). Its structure is shown below:

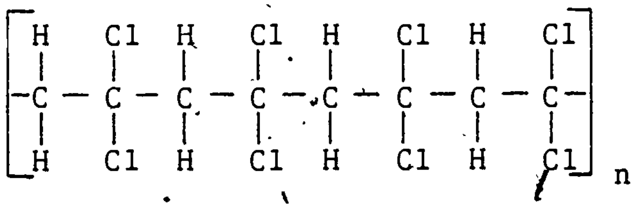


$$\left[\begin{array}{ccccccccccccccc} H & & H & & H & & H & & H & & H & & H & & H \\ | & & | & & | & & | & & | & & | & & | & & | \\ -C & - & C & - & C & - & C & - & C & - & C & - & C & - & C- \\ | & & | & & | & & | & & | & & | & & | & & | \\ H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl \end{array}\right]_n$$

Polyvinyl chloride

As shown, chlorine (Cl) is the atom that is attached to the vinyl radical. Vinyl chloride is polymerized by the breaking of the double bond and the recombination of the molecules to form a long chain. The vinyls have good strength, excellent water and chemical resistance, and many color possibilities.

A unique characteristic of PVC is its self-extinguishing property. Flexible PVC is used for tubing, wire coating, gaskets, and sheeting. Rigid PVC is used for pipe, siding, chemical storage tanks, and gutters. Sheet PVC is used for shower curtains, raincoats, and automobile seat covers. Another member of the vinyl family of resins, polyvinyl acetate, is used primarily as an adhesive for wood, paper, cloth, and leather. Polyvinylidene chloride is similar to polyvinyl chloride, except that it has two chlorine atoms on the carbon atom instead of one, as in PVC:

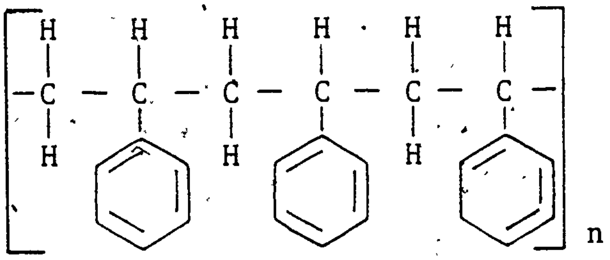


$$\left[-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\right]_n$$

Polyvinylidene chloride

With characteristics such as being odorless, tasteless, tough, and having low water transmission, polyvinylidene is extensively used as a food wrapping material. It has the trade name of Saran. Since it is resistant to moisture and weathering and is sufficient in strength, polyvinylidene chloride is frequently used as webbing material for outdoor furniture.

Styrene resins are usually considered as a separate family of resins because they are quite different from the vinyl resins. However, as can be seen from their structure, they are actually vinyl resins, with a benzene ring being the group attached to the vinyl radical:



Polystyrene

Polystyrene products are found almost everywhere because of the low cost and ease of processing the plastic. Polystyrene is used for many disposable products, such as picnic utensils and food containers. Other uses include the following: picnic coolers; model airplane and car kits; housewares; appliance housings (such as for radios, television, mixers, and refrigerators); and interior automobile parts. Perhaps the most commonly known application is the white plastic coffee cup.

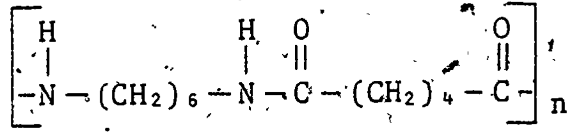
Three monomers — acrylonitrile, butadiene, and styrene — can be combined to produce the plastic ABS. ABS is hard and tough, a combination that is uncommon in thermoplastics. ABS polymers are used in housings of various types where rigidity, strength, and a glossy surface are important. ABS plastics can be electroplated to give the finished product a metallic appearance. Electroplated ABS is used in automotive, appliance, hardware, and houseware applications. ABS is also used in golf club heads, illustrating the strength of this styrene polymer. Styrene-butadiene polymer, a related polymer, is the primary synthetic rubber in use today.

Most of ~~the~~ members of the polyester family are thermosetting plastics. However, polycarbonate resins are thermoplastics. This polyester contains the ester group with benzene rings attached. Polycarbonate resins are in a group of plastics called engineering plastics, a term used to indicate that the plastic has outstanding mechanical, electrical, and chemical characteristics. The dimensional stability of polycarbonates allows them to be used in precision-engineered components where close tolerances are required. Applications of polycarbonates include sunglass lenses, shoe heels, coffee pots, football helmets, pump impellers, cooling fans, and structural housings for power tools.

There are five main cellulosic polymers: cellulose acetate, cellulose nitrate, cellulose propionate, cellulose acetate butyrate, and ethyl cellulose. These cellulose plastics are made from cellulose, which is obtained from wood pulp or cotton linters. The natural cellulose is chemically modified to produce the plastics. Cellulose nitrate was the first commercially produced plastic – in the year 1868. It was widely used in producing film for the movie industry. Unfortunately, the flammability of cellulose nitrate was ~~the~~ cause of many fires in movie theaters. Cellulose's limited applications include the following: industrial products, shoe heels, and housewares. Naturally, its use is curtailed because of its high flammability. Cellulose acetate has good mechanical and electrical (insulating) properties. It is used in making toys, safety goggles, tool handles, combs, cutlery handles, knobs, and housings for small electrical appliances. Because of its ease of processing, its hardness, and its stiffness, cellulose propionate is used in toothbrush handles, pen and pencil barrels, steering wheels, screwdriver handles, eyeglass frames, and telephone housings. Ethyl cellulose is used in flashlight cases, furniture, luggage, and tubing. Applications of cellulose acetate butyrate include safety glasses, outdoor advertising signs, and structural panels in buildings.

Acrylics are methyl methacrylate polymers. The outstanding properties of acrylic plastics are exceptional clarity and light transmission, colorability, and weather resistance. Acrylics are sold under the trade names of Lucite and Plexiglas. Acrylic sheets are used as windows, instrument panels, illuminated signs, lighting fixtures, and so forth — wherever a glass-like material is needed. In the form of fibers, the acrylics are used in carpets.

The two main classes of polyamides — that is, compounds that contain NH or NH_2 groups — include the following: nylons and versamids. Versamids are primarily used as "hot melt" adhesives in applications such as bonding shoe soles to the upper shoe. These adhesives are moisture resistant and flexible, making them ideal for footware applications. A number of nylons are produced — the most common being Nylon 6,6:



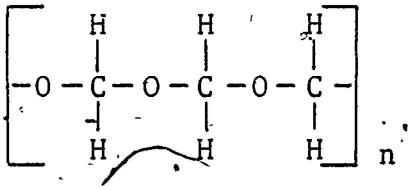
$$\left[-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\right]_n$$

Nylon 6,6

Characteristics that make nylons valuable include high heat, chemical resistance, outstanding toughness, and flexural strength. Nylon is used in gears, windshield wipers, fabrics, hinges, combs, fishing lines, bearings, and rollers. More small industrial parts are made of nylon than of any other plastic. Long-wearing gears made of nylon are quiet running and never require lubrication.

Polyphenylene oxide (PPO), developed by General Electric, is a fairly new plastic. It is increasingly being used as an engineering plastic because of its excellent electrical properties. Polyphenylene oxide is used in battery cases, electrical housings, switches, capacitors, and printed circuits. Because it can withstand prolonged exposure to hot water, it is also used for plumbing parts and food processing equipment that must be sterilized.

Acetal resins are made by the polymerization of formaldehyde to form a structure with alternating carbon and oxygen bonds:



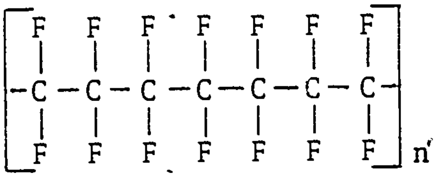
$$\left[-O-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-\right]_n$$

Acetal resin

Acetal resins are rigid thermoplastics that can be used to make parts that are substitutes for metal articles. The resins have excellent abrasion resistance, and, many times, they outlast comparable metal parts. Acetal plastics can be electroplated to form metal-like products. Acetal is used in carburetor parts, bushings, gears, and fan blades. Fan blades, such as those used for cooling movie projectors, are almost exclusively made from acetal resins.

Polyurethanes (also called isocyanates) are used as foams, coatings, and rubber substitutes. The major use of polyurethanes is in the production of flexible and rigid foams. The two components of polyurethane foam are mixed just prior to foam formation in molds, or they are foamed-in-place (usually for insulation applications). The foam is used for flotation in cavity filling of boats, pontoons, and life jackets. Urethanes are gaining popularity in energy-efficient home and building construction as a barrier to outside air along baseplates, windows, and electrical entrances to the structure.

Tetrafluoroethylene resins (TFE) are extremely temperature-stable. As shown in the structure below, the carbon chain is completely protected by fluorine atoms, thus accounting for the temperature stability of these compounds:



$$\left[-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{C}}- \right]_n$$

Tetrafluoroethylene

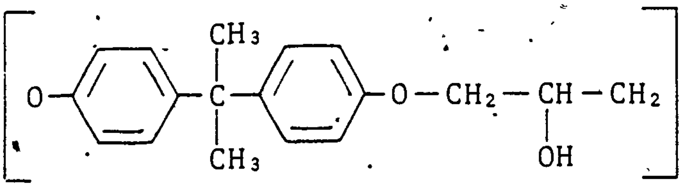
The trade name for these fluorocarbon polymers is Teflon. Teflon is the most chemically inert of all plastics, resisting attack by chemicals even at elevated temperatures. Teflon's coefficient of friction is the lowest for any known solid material; therefore, Teflon is used as a solid lubricant in bearings and bushings of industrial machinery. One common application of these plastics is in the manufacture of non-stick cookware. Teflon can be used in the range of -450°F to 550°F. Because of its excellent insulating properties, Teflon is used to coat electrical wires.

The most common thermosetting plastics in use are the phenol formaldehyde resins called phenolics. Characteristics of phenolics that make them so valuable include the following: relatively low cost, excellent insulating properties, inertness to most solvents, heat resistance to 500°F, and dimensional stability. Large quantities of phenolic adhesive are used in bonding plywood. To impart special characteristics, fillers are often used in phenolics. Fillers that are commonly used include graphite, asbestos, wood flour, and glass fiber.

Polyester resins are combined with glass mat or chopped glass fibers to form the product known as fiberglass. These resins are used to produce boat hulls, automobile body components, aircraft body components, hammer handles, automotive gears, and distributor caps. Polyesters have good weathering characteristics and are strong and tough.

Melamine formaldehyde plastics are thermosetting compounds that are hard, scratch-resistant, and almost unbreakable. Because melamine retains bright colors and resists oils, fats, and detergents, it is used to make dinnerware, coffee makers, kitchen counters, and tabletops.

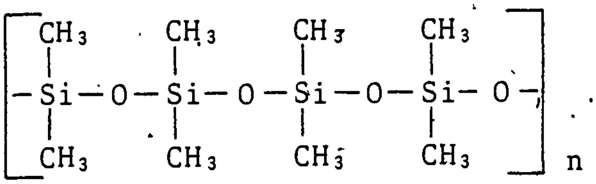
Inasmuch as epoxy resins are versatile, they are used for coatings, adhesives, laminates, molding parts, and encapsulation by potting. The structure of the epoxy polymer is shown as follows:



Epoxy resin

Epoxy adhesives are strong and can be used to bond metals, glass, ceramics, and dissimilar materials, although the bonds tend to be somewhat brittle. Epoxies are used in sealers, aircraft skins, boat bodies, printed circuit boards, insulators, and laminated sheet materials.

The silicone materials are produced as resins, fluids, and elastomers. The chemical structure of silicones is as follows:



$$\left[-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O- \right]_n$$

Silicone

As can be seen from the structure, the backbone of silicones is a silicon-oxygen-silicon repeating structure. Silicon dioxide (SiO_2) is sand, an inert, temperature-stable substance. Therefore, silicones are shown to exhibit a remarkable temperature stability. By replacing the methyl groups with other radicals and by altering the chain length, a variety of materials can be made, ranging from low viscosity fluids to semirigid solids. The solid molding compounds are used for transfer and compression molding, whereas the semiliquids are used for coatings and sealants. Silicone rubber is used where temperature stability is required. It can stretch up to 800% and has excellent tensile strength – although its strength is not comparable to carbon-based rubber. Silicones, which can be used at a temperature range of -150°F to 600°F, are resistant to radiation, water, chemicals, oils, and oxidation. In addition, silicones are odorless, tasteless, and nontoxic. RTV (room temperature vulcanizing) silicones are available in "squeeze" tubes for use in sealing and adhesive bonding. Silicone liquid is used as a mold release, or a parting compound, to allow finished parts to be readily removed from molds.

ANALYSIS AND TESTING OF PLASTICS

Testing and analysis of plastics can be a complex operation that requires sophisticated equipment. Positive identification is often accomplished by using infrared spectroscopy. However, rather simple tests are often sufficient to identify plastics—the most common being the burning test, or flame test. The first step in the identification of a plastic is to determine if the plastic is a thermoplastic or a thermoset. A small piece of the plastic is placed in a test tube and is heated. If the plastic melts, it is a thermoplastic; if the plastic chars and decomposes, it is a thermoset. Next, a strip of the plastic is burned. The flammability, color of the flame, presence or absence of smoke, and odor are observed. Very often the plastic can be identified by comparing the observed properties with those listed in a plastics flame-test chart. It is also helpful to have a series of known plastics to compare to the unknown substances.

Plastics and articles made from these plastics are often subjected to a number of tests. Standard tests for plastics have been developed by groups such as the American Society for Testing Materials (ASTM). The properties tested include physical, electrical, thermal, chemical, and optical.

Physical or mechanical tests include tensile strength, elongation, compressive strength, flexural strength, and cold flow. Most of these tests can be made under ambient conditions or under conditions of high moisture, low temperature, or high temperature. The conditions to which the finished article will be exposed should be simulated to the greatest extent possible.

Tensile strength can be defined as "the resistance of a material to being pulled apart." The test is performed by clamping a standard test specimen – usually 0.125 inch x 0.5 inch x 8 inch – at both ends in the jaws of a tensile tester. The sample is pulled until it breaks, and the maximum load that it carried is observed on a dial or recorder. The psi (pounds per square inch) rating of the plastic is determined by dividing the maximum load by the cross-sectional area of the test specimen. The method for tensile testing of plastics is illustrated in Figure 1. Elongation is determined at the same time that tensile strength is obtained. Elongation is the distance that the specimen has stretched at the break point.

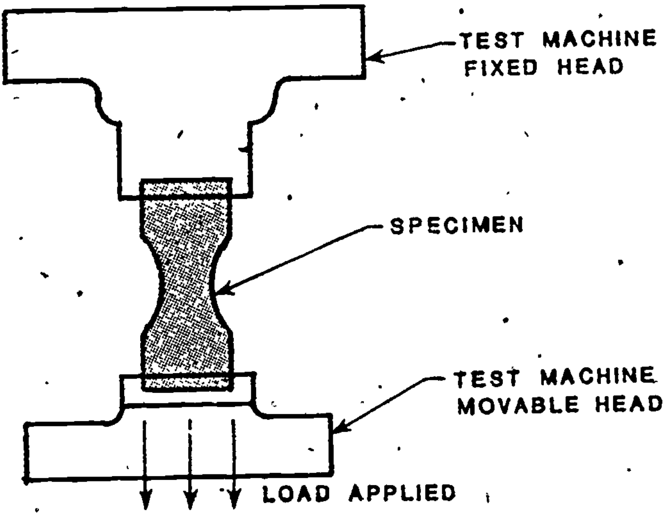


Figure 1: Tensile Test Method.

Compressive strength is the opposite of tensile strength. It is defined as "a measure of the ability of a material to withstand being crushed under a load." The ASTM test specimen for compressive strength is 0.5 inch x 0.5 inch x 1 inch.

Flexural strength is defined as "a measure of the ability of a material to bend or flex." The ASTM test method calls for a 0.5 inch x 0.5 inch x .5 inch test specimen to be supported on two knife edges which are four inches apart. A third knife edge is placed centrally on the opposite side, and pressure is applied. Then, the flexural strength is measured at the break point. The method for determining the flexural strength of plastics is shown in Figure 2.

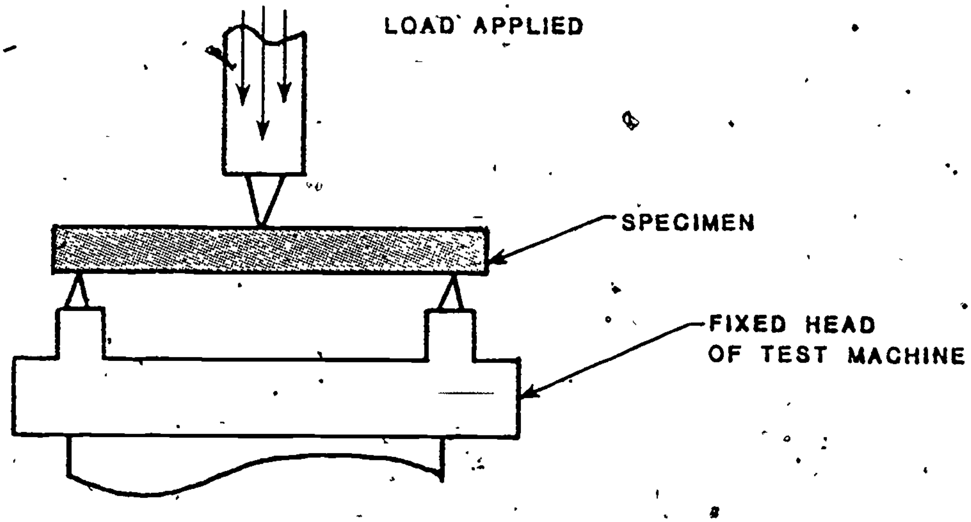


Figure 2. Flexural Test Method.

One major disadvantage of many plastics is their cold flow; therefore, the measurement of cold flow is a common test. Cold flow is the difference between the original dimensions and final dimensions after a specimen has been loaded for a period of time and then removed. Cold flow is important when plastic parts are mechanically fastened (for example, with bolts and screws).

Dielectric strength is one of several common electrical tests. It is a measure of the insulating capability of the plastic. Dielectric strength can be defined as "the voltage at which electrical break-down occurs."

An important property of plastics is their glass-transition temperature. At low temperatures, polymers exist in the glassy state; that is, polymers have the properties of glass — they are hard and brittle. As the temperature of the plastic is raised, its properties undergo a change known as the "glass-transition." Above the glass-transition temperature, the polymer becomes rubbery, soft, elastic, and more flexible. This temperature is not sharp, like the melting point of crystal; rather, the transition occurs over a range of temperatures.

There are three chemical tests normally performed on plastics: acid, alkali, and solvent. Both concentrated and dilute solutions are used in the tests. The plastic is exposed to those substances that could be encountered by the finished product. The plastic is then checked visually for decomposition, crazing, or discoloration. Often the test specimen for tensile, flexural, and compression tests are subjected to chemical exposure prior to testing to determine the effect of the exposure upon mechanical strength.

ADHESIVES

There are many methods of joining materials, including nailing, screwing, riveting, bolting, soldering, brazing, welding, and ashesive bonding. Bonding of materials with plastic adhesives has several advantages over mechanical methods. The following are examples:

1. Certain materials could not effectively be joined by any other means. Examples include the gluing of ceramic materials and the fastening of paper labels to cans or bottles.
2. There is a more uniform transfer of stress from one material to another with the use of adhesives. For example, localized stress is minimized by using adhesives to join aircraft components. Problems associated with stress concentration and fatigue cracking are common when components are joined by riveting.
3. Corrosion of joints between dissimilar metals is reduced by using adhesives since the adhesive joint does not transfer electrons.
4. Adhesives not only bond materials together but also provide an effective seal to keep water out of components.
5. Adhesive bonding is relatively simple, fast, and economical.
6. Often, considerable weight reductions are achieved by using adhesives to join materials.

Disadvantages of adhesives include the following:

1. The materials for joining must be cleaned and prepared for bonding.
2. Heating is sometimes required to form the bond.
3. There is no universal adhesive; that is, each application must be considered independently.
4. Strengths are often directional.
5. Full strength is not developed immediately.

Adhesives are widely used in the automobile, aircraft, electrical, aerospace, and building industries. The adhesives can be classified as to use, chemical composition, method of application, and hardening or setting method. There are three categories based upon chemical composition: thermosetting, thermoplastic, and elastomeric.

Thermosetting adhesives are converted by chemical reaction into a permanently hard, rigid bond. Epoxies, phenolics, polyesters, and acrylics are all thermosetting adhesives that find widespread use. The more common thermoplastic resins include polystyrenes, polyamides, cellulosics, and polyvinyls. Elastomeric resins are used primarily to modify thermosetting adhesives to make them more flexible. Neoprenes, nitriles, polysulfides, and butyls are the elastomeric resins commonly used.

Many adhesives are dissolved in a solvent — either water or an organic solvent. The adhesive bond forms when the solvent evaporates from the bonded joint. The thermosetting adhesives are normally two-part formulations. When the parts are mixed, the chemical reaction begins and the bond starts to form between the materials being joined. Other adhesives, such as the hot-melt adhesives, must be heated or melted. When they cool, the bond is formed to join materials.

Some of the common adhesives are listed in Table 1 well as the types of materials that are joined by the adhesives.

TABLE 1. ADHESIVES AND MATERIALS THEY JOIN.

Group	Chemical Type (or source)	Materials Joined
Animal glues	Animal bones or hides	Paper, wood, fabrics
Vegetable glues	Starch	Paper and fabrics
Natural resins	Asphalts	Floor tiles to concrete
	Gum arabic	Paper, fabrics
Inorganic cements	Cement (Portland)	Bricks, rocks
Thermosetting resins	Epoxies	Metals, glass, many plastics
	Silicones	Silicone rubbers, metals (sealer)
	Urea, formaldehydes	Plywoods
	Polyurethanes	Paper, fabrics
Thermoplastic resins	Polyamides	Paper, leather (hot-melt)
	Acrylics	Glass, acrylics
	Cellulose	Glass, wood, paper
	Vinyls	Wood

LUBRICATION

The practice of lubrication began shortly after the invention of the wheel and axle. When two bodies move or rub relative to one another there is a force that tends to interfere with the motion. This force is called friction, and substances that are used to reduce friction are called lubricants. Lubrication is important since friction wastes energy and tends to destroy the rubbing surfaces.

Speed, load, and temperature are important considerations in lubrication practice. High speed increases the lubrication difficulties. Modern aircraft and power plant turbines operate at fast speeds, and some grinding and textile spindles operate at speeds up to 100,000 revolutions per minute. The load on a bearing surface is distributed over the area of the interface. These loads are expressed in pounds per square inch (psi). Loads in aerospace applications are as high as 50,000 psi. As speed ~~and~~ load increase, the operating temperature increases. High temperatures cause a decrease in viscosity and make it difficult to maintain a film of lubricant.

Design engineers use three basic types of frictional components to support mechanical motion: bearings, gears, and cylinders. The lubrication of these components is important since they are used in transportation systems, manufacturing plants, mines, power generating plants, and processing plants.

In addition to speed, load, and temperature, other environmental conditions are often important and, therefore, must be considered in lubrication practice. For example, in nuclear power plants, radiation destroys many hydrocarbon and synthetic lubricants, and, in space vehicles, the problem of vacuum and temperature extremes is encountered.

Lubricants may be gaseous, liquid, plastic, or solid. Table 2 is a classification of lubricants by state.

TABLE 2. LUBRICANTS.

State	Lubricant
Gaseous	Air, helium, carbon dioxide
Liquid	
Mineral oils	Straight oils compounded with additives
Fixed oils	Tallow, lard, castor oil, palm oil
Synthetic fluids	Silicones, polyglycols, esters
Plastic	Petroleum greases, silicone greases
Solid	Graphite, metal films, polymer films, molybdenum disulfide, other sulfides, wax, borax, mica, talc, fluoride plastic

A variety of additives are used in petroleum lubricants. Inhibitors are added to prevent rust and corrosion. Other additives depress the pour point, retard deterioration of the lubricant, clean the metal surface (detergents), keep solid wear particles dispersed and suspended in oil, and prevent foaming of the oil. Polymethacrylate esters and other acrylates are added to oil to improve their viscosity index. They make the viscosity of oils less temperature responsive.

At high loading, petroleum oils and greases are squeezed out of the bearing surface, leaving the metal surfaces in direct contact. To prevent wear and galling in such cases, a solid lubricant is used. Silver or silver alloys may be electroplated on steel; they act as high load-carrying lubricant. Teflon resin, in combination with a glass fiber matrix, has a low coefficient of friction, an almost complete chemical inertness, and is usable over a wide temperature range — from minus 450°F to plus 500°F.

LABORATORY MATERIALS

Laboratory 1

Castor oil
Glycerol
Stannous octoate
Silicone oil (Dow-Corning 202)
4-methyl-m-phenylene diisocyanate (tolylene-2,4-diisocyanate)
Paper cups or milk carton
Sebacoyl chloride (5% in carbon tetrachloride)
Hexamethylene diamine (5% in water)
Dropper
Glass rod
Small vial (such as a litmus paper vial)
Ring stand
Clamp
Beaker, 600 ml
Test tube

Laboratory 2

Glycerol
Phthalic anhydride, powder
Beaker, 50 ml
Glass stirring rod
Watch glass
Electric hot plate
Mortar
40% formaldehyde solution (Formalin)
Test tube
Saturated aqueous solution of aniline hydrochloride

Lucite or Plexiglas pellets or chips
100 ml distilling flask
Condenser
Heating mantle
Thermometer
Expendable glass jar
Benzoyl peroxide
Aluminum foil
Hot water bath

Laboratory 3

Beaker, 150 ml
Beaker, 400 ml
Erlenmeyer flask, 125 ml and 250 ml
Dropper
Separatory funnel
Ring and ring stand
Litmus paper
Dimethyldichlorosilane
Ether
$NaHCO_3$, saturated solution
Boric oxide
Na_2SO_4, anhydrous
Oil bath
Hot plate

LABORATORY 1. POLYMERIZATION, PART I.

Polymers are giant chemical compounds formed by a process, called "polymerization," in which small compounds, called monomers, combine with each other. The molecular weights of polymers can be in excess of 10,000 amu. In the first part of this experiment, a polyurethane foam is prepared from castor oil and glycerol. Although polyurethanes are not commercially made from these starting materials, the experiment illustrates the methods used. Polyurethanes can be prepared as a rigid molding material or as a flexible, rubbery material. Most polyurethane goes into the production of foamed plastics, which can be either rigid or flexible. These foams are good sound and energy absorbers, providing good cushioning properties. These materials are used in refrigerator insulation, sponges, automobile and furniture cushioning, and mattresses.

In the second part of this experiment, Nylon 6-10 will be prepared from sebacoyl chloride and hexamethylenediamine by a procedure called the Nylon Rope Trick. The experiment is often used to illustrate polymerization reactions. Nylon was first introduced as a fiber to weave hosiery as a replacement for silk. Because of its high strength and ease of processing, nylon has become one of the leading polymers of the plastics industry. A few of its many applications include combs, drawer slides and rollers, fishing lines, electric tool housings, bearings, and gears.

Polyurethane

1. Weigh out 35 g of castor oil and 10 g of glycerol into a wax-lined paper cup, using a top-loading balance.
2. Mix and add 0.5 ml (5 drops) of stannous octoate, 10 drops of silicone oil (Dow-Corning 202), and 10 drops of water.
3. Using a glass stirring rod, mix these ingredients thoroughly until a creamy, viscous product is formed.
4. In a separate container, weigh out 30 g of 4-methyl-m-phenylene diisocyanate (tolyl diisocyanate). CAUTION: AVOID CONTACT WITH SKIN, EYES, OR CLOTHING SINCE THE MATERIAL CAN CAUSE SKIN IRRITATION.
5. Rapidly add all of the 4-methyl-m-phenylene diisocyanate to the mixture in Step 3. Mix rapidly and thoroughly to form a smooth, homogeneous mixture.
6. When the container becomes warm to the touch, stop stirring and place the container on a piece of newspaper in a fume hood, allowing the reaction to proceed.
7. After the foaming has stopped, allow the polymer to cool and "set" for several hours; then remove the foam from the cup. The foam should be of the compressible type.

Nylon

CAUTION: AVOID BREATHING THE VAPOR FROM ANY OF THE REAGENTS USED IN THIS EXPERIMENT. DO NOT ALLOW ANY OF THE REAGENTS TO CONTACT THE SKIN; IF THEY DO, WASH OFF IMMEDIATELY.

1. Pour 25 ml of the hexamethylenediamine solution into a beaker.
2. Into a clean 150 ml beaker, add 50 ml of sebacyl chloride solution.
3. Tip the 150 ml beaker slightly and slowly add the aqueous hexamethylenediamine solution. Try to avoid mixing the two liquids by pouring the aqueous hexamethylene solution slowly so that this layer remains on top.
4. Note the film that forms at the interface between the two solutions. This is the nylon polymer.
5. Reach through the upper layer and grasp the nylon interface with a hooked wire or forceps. Wrap the string around a test tube until approximately two feet have been removed. Do this by rotating the test tube.
6. Wash the nylon thoroughly in a bath of 50% acetone and 50% water; then allow it to dry or dry it between paper towels.
7. Try melting some of the nylon after it is certain that all of the acetone has been removed.
8. Compare the strength of fibers drawn out of the melt, using a wood splint with the original string.

LABORATORY 2. POLYMERIZATION, PART II.

Alkyd Resins

The condensation product of polyhydroxyl alcohols and anhydrides is a type of polyester known as alkyd resins. These resins are used in making modern enamels and paints.

1. Into a 50 ml beaker, place 2 g of glycerol and 3 g of powdered phthalic anhydride.
2. Mix with a glass stirring rod.
3. Cover with a watch glass and heat gently over an electric hot plate. (An electric hot plate is preferable to an open flame since the resin is flammable.)
4. Continue heating until large bubbles form and the mixture puffs up.
5. Allow the resin to cool.
6. Grind the resin and try to find a suitable solvent. (Try benzene, chloroform, and 6 N HCl.)
7. If a suitable solvent is found, pour some of the solution onto a piece of metal or wood. Does the resin have any of the desirable characteristics of a protective paint?

Phenolics

The phenol formaldehyde resins, commonly known as phenolics, are produced from the reaction of phenol (carbolic acid) with formaldehyde in the presence of a catalyst. These resins, called Bakelite plastics, were some of the earliest plastics produced.

1. Into a test tube, add 10 ml of 40% formaldehyde solution (called Formalin).
2. Into another test tube, add 10 ml of a saturated solution of aniline hydrochloride in water.
3. Simultaneously pour the two solutions into a 50 ml beaker.
4. Note whether the reaction gives off heat or absorbs heat.

5. Phenolics are hard, rigid, heat-resistant materials that are brittle. Examine the product and compare its properties with those given previously.

Acrylic Resins

The acrylic resins (methyl methacrylate polymers) have outstanding clarity, light transmission, weather resistance, and colorability. They are marketed in the United States under the trade names Lucite and Plexiglas. The methyl methacrylate polymer is made by adding benzoyl peroxide, as an initiator, to the monomer methyl methacrylate. <u>EXTREME CAUTION</u> MUST BE OBSERVED IN HANDLING BENZOYL PEROXIDE SINCE IT IS VERY EXPLOSIVE AND MAY BE DETONATED IF IMPROPERLY STORED OR HANDLED. To avoid the grinding effect such as that obtained when screwing on a bottle cap, benzoyl peroxide is shipped and stored in a paper container.

1. Place 25 g of Lucite or Plexiglas pellets or chips in a 100 ml distilling flask with ground glass connections.
2. Attach a condenser and distill, using a heating mantle. CAUTION: AVOID INHALING THE VAPORS OF THE MONOMER METHYL METHACRYLATE.
3. At about 300°C the polymer softens and undergoes rapid depolymerization, forming the monomer. Continue the distillation until most of the solid has been converted into liquid.
4. Redistill the liquid and collect the distillate between 100°C and 110°C.
5. The yield of monomer should be about 20 g.

6. To repolymerize the methyl methacrylate, place 10 ml of the liquid in a expendable glass container (such as a baby food jar) and add 0.01 g to 0.02 g of benzoyl peroxide. CAUTION: REREAD THE PRECAUTIONS FOR HANDLING BENZOYL PEROXIDE GIVEN AT THE BEGINNING OF THIS EXPERIMENT. BE CAREFUL TO USE 0.01 g, NOT 0.1 g.
7. Cover the jar with a piece of aluminum foil that is held in place with a rubber band.
8. Place the jar in a hot-water bath that is kept just below the boiling point of water for approximately one-half hour.
9. Allow the polymer to cool; then observe its properties.

LABORATORY 3. PREPARATION OF A POLYMERIC SILICONE.

Silicone resins have many diverse applications, ranging from low viscosity fluids to semirigid solids that resemble rubber. Silicone materials can be used over a wide temperature range – from -140°F to 600°F. In addition to heat, they are resistant to oxidation, chemicals, and water. Silicones are used as protective coatings, in adhesive bonding, and in gaskets that are fuel and solvent resistant. Chemically, silicones have alternating silicon and oxygen atoms in a straight chain, with a variety of side chain groups. Variations in silicone properties are obtained by varying the side chain groups.

In this experiment, a rubber-like silicone polymer, commonly known as Silly Putty, will be made by the hydrolysis (reaction with water) of dimethyldichlorosilane, according to the following reaction:

$$n\,(\mathrm{CH_3})_2\mathrm{SiCl_2} + n\,\mathrm{H_2O} \qquad [(\mathrm{CH_3})_2\mathrm{SiO}]_n + 2n\,\mathrm{HCl}$$

Dimethyldichlorosilane   Silicone Polymer

The polymerization occurs at elevated temperature in the presence of boric acid as a catalyst.

CAUTION: THIS EXPERIMENT MUST BE CONDUCTED IN THE HOOD. THERE MUST BE NO FLAMES IN THE LABORATORY. ETHER IS FLAMMABLE, AND ITS VAPORS CAN BE EXPLOSIVE.

1. Add 40 ml of ether to a 250 ml Erlenmeyer flask.
2. Add 20 ml of dimethyldichlorosilane to the ether, and mix by swirling.
3. Dropwise, slowly add 40 ml of water. (If the water is added too rapidly, the reaction will get hot, and the reaction mixture will bubble out of the flask.)
4. Transfer the mixture to a 125 ml separatory funnel and separate the ether layer from the water layer, keeping the ether layer in the funnel.
5. Cautiously wash the ether layer with a saturated sodium bicarbonate solution, being careful to allow the carbon dioxide that is generated to escape without allowing the solution to bubble out of the separatory funnel. Add 10 ml of the bicarbonate solution at a time, swirling the funnel until the carbon dioxide is no longer formed.
6. The purpose of the sodium bicarbonate solution is to neutralize the hydrochloric acid formed in the polymerization. Test one drop of the solution with litmus paper. Continue washing with sodium bicarbonate until the aqueous phase is no longer acidic.

7. Remove the ether layer and transfer it to a dry 125 ml Erlenmeyer flask which contains 1 g of anhydrous Na_2SO_4.
8. Allow the ether layer to dry for about 15 minutes (by being in contact with the anhydrous Na_2SO_4).
9. Put the ether into a 150 ml beaker and evaporate the ether by placing the 150 ml beaker in a 400 ml beaker of hot water. CATUION: DO NOT USE A FLAME TO HEAT THE WATER.
10. When all of the ether has evaporated, obtain the weight of the silicone oil.
11. Calculate the weight of 5% of the silicone oil and add this amount of boric oxide to the silicone oil while stirring continuously. Continue to stir for several minutes after the addition of the boric oxide.
12. Transfer the mixture to a test tube and heat in an oil bath at 200°C for three to four hours.
13. Remove the test tube and cool it; then examine the contents. This putty differs from the commercial product since it lacks additives that enhance the mechanical strength.

REFERENCES

Arnold, Lionel K. Introduction to Plastics. Ames, IA: Iowa State University Press, 1968.

Bikales, Norbert M., ed. Adhesion and Bonding. New York: John Wiley & Sons, Inc., 1971.

Brewer, Allen F. Effective Lubrication. Huntington, NY: Robert Krieger Publishing Co., 1972.

Cagle, Charles V. Adhesive Bonding Techniques and Applications. New York: McGraw-Hill Book Co., 1968.

Crosby, Edward G. and Kochis, Stephen N. Practical Guide to Plastics Applications. Boston: Cahners Books, 1972.

Gunther, Raymond C. Lubrication. Philadelphia: Chilton Book Co., 1971.

Katz, Irving. Adhesive Materials; Their Properties and Usage. Long Beach, CA: Foster Publishing Co., 1971.

GLOSSARY

Adhesive: A material used to join components.

Copolymer: Combination of two or more polymers.

Engineering plastics: Plastics that have outstanding mechanical, electrical, and chemical characteristics.

Friction: A force that tends to interfere with the motion of two objects that are in contact with each other.

Glass transition temperature: The temperature at which a plastic softens or melts.

Lubricants: A substance used to reduce friction.

Monomer: Starting material for making plastics.

Plasticizer: A chemical added to plastics to help keep them from getting hard and brittle.

Polymer: A long-chain organic chemical — plastic.

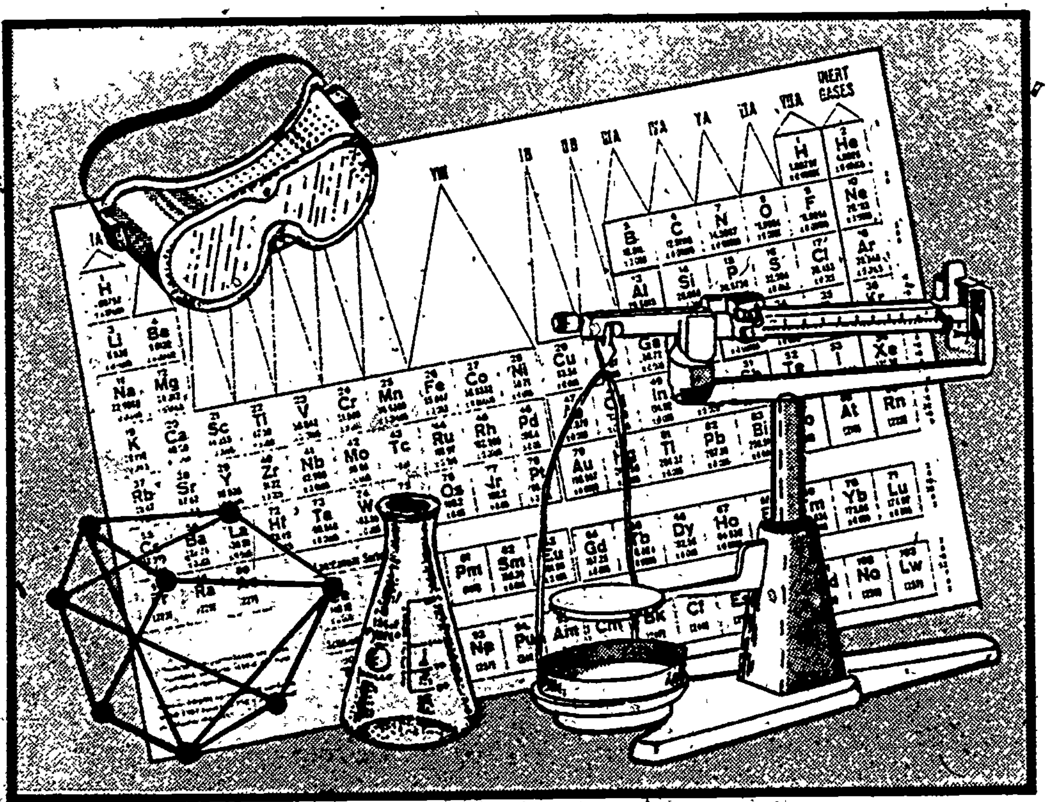
Stabilizer: A chemical added to plastics to retard deterioration due to sunlight.

Thermoplastic: Plastic that will soften when heated.

Thermosetting plastic: A plastic that hardens through chemical reaction and will not soften under heat.

ENERGY TECHNOLOGY
CONSERVATION AND USE

CHEMISTRY FOR ENERGY TECHNOLOGY II



MODULE CH-11
NUCLEAR CHEMISTRY

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

INTRODUCTION

As was learned from an earlier module, chemical reactions involve the interaction of electrons in atoms. These electrons are found in energy shells surrounding a nucleus. In general, chemical reactions involve the gain, loss, or sharing of orbital electrons by atoms. Nuclear chemistry (or nuclear physics), however, deals with what happens to the nucleus of atoms. In ordinary chemical reactions, the atoms taking part retain their identity; in nuclear reactions, new elements are often formed.

Nuclear reactions are accompanied by energy changes that are several orders of magnitude greater than those associated with ordinary chemical reactions. For example, the energy evolved when one gram (g) of radium undergoes radioactive decay is about 500,000 times as great as that given off when an equal amount of radium reacts with chlorine to form radium chloride. Still larger amounts of energy are given off in nuclear fission and nuclear fusion reactions — a fact that insures their importance today. In fact, nuclear energy has the potential of supplying much of the world's energy needs, providing that associated problems can be solved. This module is a study of radioactive isotopes (which are widely used in medicine, industry, and chemistry), as well as fission and fusion processes.

PREREQUISITES

The student should have completed Modules CH-01 through CH-05 of Chemistry for Energy Technology I and Modules CH-06 through CH-10 of Chemistry for Energy Technology II.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    a. Critical mass.
    b. Chain reaction.
    c. Breeder reactor.
    d. Alpha particles.
    e. Beta particles.
    f. Electron capture.
    g. Positron.
    h. Half-life.
    i. Fission.
    j. Fusion.
    k. Gamma rays.
2. Complete and balance nuclear reactions.
3. Use the half-life of a substance to predict the amount of radioisotope present after a period of time.
4. Use Einstein's mass-energy relationship to calculate the energy change, or mass change, of a nuclear reaction.
5. Describe the design of a nuclear power plant and explain the role of control rods, cooling fluid, and fuel elements.
6. Describe fusion and fission nuclear processes.

NUCLEAR CHEMISTRY

Ordinary chemical reactions involve only the electrons in the outer shells of atoms. Nuclear chemistry deals with certain unstable atoms that can emit various particles and rays and, in the process, be transformed from one element into a different element. The property of emitting particles and rays from the nucleus of an atom is called radioactivity. Nuclear reactions in which the action is spontaneous, known as "natural" radioactivity, cannot be speeded up or slowed down by any physical or chemical means. Artificial radioactivity, produced when substances are made radioactive by bombardment with particles such as alpha particles, protons, electrons, and neutrons, is of extreme importance.

Nuclear reactions differ in another important way from ordinary chemical reactions — that is, in the amount of energy released. In nuclear reactions, matter is converted into energy, thereby releasing tremendous amounts of energy. The energy released by nuclear reactions dwarfs the energy produced by chemical reactions.

The nucleus is composed of two types of large particles, protons and neutrons, as well as many smaller particles. The proton is positively charged and has a relative weight of approximately one atomic mass unit (amu). The neutron also has a relative weight of approximately one amu, but it is neutral. The mass number of the atomic nucleus is the number of particles, or nucleons. Therefore, the mass number is equal to the number of protons plus the number of neutrons. Furthermore, the number of protons is equal to the atomic number of the element. From earlier experimentation with the scattering of alpha particles, it was concluded that the nucleus occupies only a very small fraction of the volume of an atom and that it is very compact. Nuclear radii do not exceed 10^{-12} cm, whereas atomic radii are about 10,000 times larger.

NUCLEAR RADIATION

Some nucleii are unstable and spontaneously emit particles and radiation. The discovery of this natural radioactivity is credited to the French scientist, Henri Becquerel, in 1896. Becquerel's research was spurred by the discovery of X rays by W. C. Roentgen earlier that same year. Becquerel discovered that uranium produces a spontaneous radiation that can develop an image on a photographic plate.

An unstable nucleus can be transformed into a stable one by the emission of particles or radiation. The three most common types of radiation emitted by radioactive substances are alpha particles (α), beta particles (β), and gamma rays (γ).

Alpha rays are particles consisting of two protons and two neutrons, having a weight of four amu and a double positive charge. Alpha particles are identical with the helium nucleus; that is, they are helium atoms that have lost their two orbital electrons to form the doubly charged ion, He^{++}. These particles are traveling at a speed of up to 20,000 miles per second as they leave the nucleus. However, in spite of this speed and their mass, they are not especially penetrating. Alpha particles will travel only a few centimeters in air before they are stopped. Items such as paper, aluminum foil, or rubber gloves will stop them. Radioactive decay, through the emission of alpha rays, is shown by the following reaction:

$$^{222}_{86}\mathrm{Rn} \longrightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} \quad \text{Alpha emission}$$

This reaction illustrates the type of equation used to denote nuclear reactions. The symbol $^{222}_{86}\mathrm{Rn}$ denotes the isotope of radon (Rn), which weighs 222. The 86 is the atomic number of radon. Radon disintegrates to form plutonium (with a mass number of 218 and an atomic number of 84) and the alpha particle He (with a mass number of 4 and an atomic number of 2). Note that the subscript and superscript numbers on each side of the equation must balance. For example, the masses of Po and He equal the mass of Rn, as follows:

$$222 = 218 + 4$$

In addition, the atomic number must balance, as follows:

$$86 = 84 + 2$$

Nuclear equations can often be completed through such a balancing process.

Beta rays are streams of electrons traveling at enormous speeds (approaching the speed of light). These electrons coming from the nucleus are not the orbital electrons. How can electrons come from the nucleus, which supposedly is composed only of neutrons and protons? Emission of beta particles can be considered to be the result of the conversion of a neutron into a proton and an electron, as shown below:

$$^{1}_{0}\mathrm{n} \longrightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e}$$

In this process, the neutral neutron (weighing one amu) is converted into the positive proton (weighing one amu) and the negative electron or beta particle (weighing less than one amu). The weight of the electron is 1/1846 that of the proton; therefore its weight is negligible, compared to the weight of the proton or the neutron. This nuclear equation is balanced since the masses on either side of the equation are equal:

$$1 = 1 + 0$$

The charges are also balanced as shown below:

$$0 = 1 + (-1)$$

The protons remain in the nucleus, whereas the beta rays are shot out of the nucleus at high speed. Beta rays are many times more penetrating than alpha rays because the beta rays travel at much faster speeds. An example of beta emission is the sponaneous radioactive decay of thorium 234 to protactinium 234:

$$^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e} \quad \text{Beta emission}$$

Note that, in beta emission, the negative electron leaves the nucleus and that the positive proton formed in the process increases the atomic number by one unit (in this example from 90 to 91). Therefore, a new element is formed through beta emission.

Gamma rays consist of electromagnetic radiation of very short wavelength. Gamma rays have no charge or particle behavior; they act as true waves. Gamma rays can be compared to X rays, except that they have even shorter wavelengths and, therefore, are much more penetrating. These rays present the main danger in working with radioactive materials since they can easily penetrate the body and can cause serious physiological damage. It requires almost a foot of lead or several feet of concrete to shield against gamma rays. Gamma radiation is not generally shown when writing nuclear equations since charge and weight do not change in gamma emission. However gamma emission is usually accompanied by other radioactive emissions.

The effect of an electrical field upon alpha, beta, and gamma emissions is illustrated in Figure 1.

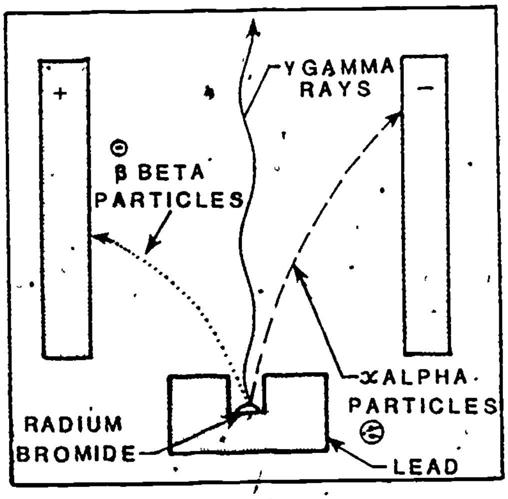


Figure 1. Alpha, Beta and Gamma Rays in an Electrical Field.

In addition to alpha, beta, and gamma radioactivity, there are two other decay processes: positron emission and electron capture. A <u>positron</u> is a particle that has the same mass as an electron but an opposite (positive) charge. The symbol for the positron is ${}_{+1}^{0}e$. Carbon-11 is an example of an isotope that decays by positron emission:

$${}^{11}_{6}C \longrightarrow {}^{11}_{5}B + {}_{+1}^{0}e \qquad \text{Positron emission}$$

Positron emission can be considered to be the conversion of a proton into a neutron and a positron:

$${}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}_{+1}^{0}e \qquad \text{Positron formation}$$

Proton	Neutron	Positron

The energy level, or shell, nearest the nucleus is known as the K-shell. It is possible for the nucleus to capture one of these K-electrons in a process called electron capture. For example, vanadium-49 can capture a K-electron to become titanium-49:

$$\underset{\text{K-electron}}{{}^{49}_{23}\mathrm{V} + {}^{0}_{-1}\mathrm{e}} \longrightarrow {}^{49}_{22}\mathrm{Ti} \quad \text{Electron K-capture}$$

Electron capture may be thought of as converting a proton to a neutron as follows:

$$^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{1}_{0}\mathrm{n}$$

RADIOACTIVE DECAY SERIES

As indicated earlier, unstable nuclei can lose particles or radiation and become stable. Often, this may involve more than one step. For example, Figure 2 shows uranium can decay in a series of steps until, finally, lead-82 is formed. In the first step, uranium-238 decays through alpha emission to form thorium as follows:

$$^{238}_{92}\mathrm{U} \longrightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

Then, the thorium-234 decays by beta emission:

$$^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$

The decay continues through 13 or 14 steps, depending upon the specific route taken (Figure 2), until lead-206 is formed.

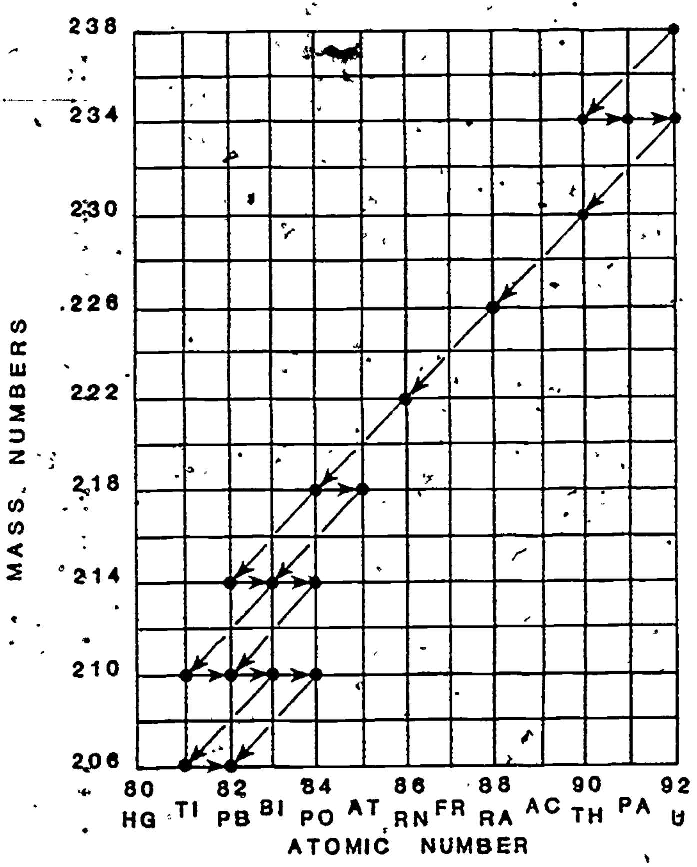


Figure 2. Radioactive Decay Series for Uranium-238.

(In Figure 2, the short, horizontal arrows pointing to the right indicate beta emission, and the long arrows pointing down and to the left correspond to alpha emission.)

HALF-LIFE

Each nuclear decay reaction has a characteristic decay time. This reaction rate is usually expressed as the "half-life." The half-life is the time required for half of a given quantity of a radioactive substance to react. Each isotope has its own characteristics half-life. For example, the half-life of strontium-90 is 28 years. If one started with 100 g of strontium, after 28 years, only 50 g of strontium would remain. The other 50 g of strontium would have been converted to yttrium-90 through beta decay, as shown by the following reaction:

$$^{90}_{38}Sr \longrightarrow {}^{90}_{39}Y + {}^{0}_{-1}e$$

After another half-life period (28 years), only 25 g of the strontium-90 would remain. Half-lives of the radioactive elements vary widely — from as short as millionths of a second to as long as billions of years. The rate of disintegration of a radioactive material cannot be increased; therefore, the material must be stored properly to allow it to become non-radioactive. Unfortunately, it may take millions of years for some radioactive wastes to decay to safe levels. In the meantime, they must be contained so they are not released into the environment.

An interesting application of natural radioactivity has been in its use to determine the age of the earth. In this procedure, the radioactivity of a given isotope is measured and its half-life is used to calculate the time the isotope has been in existence. For example, one g of uranium-238 would produce 0.433 g of lead-206 and 0.067 g of helium, leaving 0.500 g of uranium-238 after one half-life — or 4.5 billion years. By comparing the amount of lead-206 to the amount of uranium-238 in a mineral, the age of the rock can be established. This analysis indicates that the age of the earth's crust is approximately 2.6 billion years.

The half-lives and types of decay processes are given for some artifical and natural radioisotopes in Table 1.

TABLE 1. HALF-LIVES AND DECAY PROCESSES OF SOME RADIOACTIVE ISOTOPES.

	Isotope	Half-life	Decay Process
Artificial Radioisotopes	Plutonium-239	24,000 yr	Alpha
	Cesium-137	30 yr	Beta
	Strontium-90	28 yr	Beta
	Iodine-131	8 days	Beta
Natural Radioisotopes	Thorium-232	1.4×10^{10} yr	Alpha
	Uranium-238	4.5×10^{9} yr	Alpha
	Potassium-40	1.3×10^{9} yr	Alpha
	Carbon-14	5,700 yr	Beta

DETECTION OF RADIOACTIVITY

Alpha, beta, and gamma rays all interact with the atoms of matter by dislodging orbital electrons, thus forming ions. The amount of radiation, therefore, can be determined by the amount of ionization produced by the radiation. Not all interactions between radiation and matter cause ion formation. In some cases, electrons can be raised to higher energy levels (shells). When these electrons return to their normal energy level, X rays, ultraviolet, or visible light may be emitted, depending on the energy levels. In addition, some of the energy of the particles of radiation may appear as heat.

Although one cannot see, hear, feel, taste, or smell radiation, there are a number of methods used to detect it.

1. Photographic plates and film have been used to detect radiation for many years. The radiation affects photographic film in much the same way as ordinary light. The darkening of film can give a quantitative measure of the amount of radiation to which the film has been exposed. It is common practice for people who work with radioactive substances to wear film badges to record the amount of radiation to which they have been exposed.
2. Historically, cloud chambers have been used to detect radiation. In the cloud chamber, the ions produced by ionizing radiation pass through a supersaturated vapor. The ions from the radiation become nuclei for the production of liquid droplets, which form a cloud-like track. The cloud chamber can be placed in a magnetic or electrical field to assist in determining the type of radiation present.
3. The Geiger-Mueller counter (or, simply, the Geiger counter) is the most common device for detecting and measuring radiation. The Geiger counter consists of a cylindrical cathode with a wire anode running along its axis. The anode and cathode are sealed in a gas-filled glass tube. An electrical potential difference is maintained between the anode and the cathode. This potential is just slightly below that required to produce an electric discharge in the gas. When ionizing radiation enters the tube, it causes the formation of ions which, in turn, causes an electrical breakdown of the gas, sending a pulse of electrical current to a counter. A schematic representation of a Geiger counter is shown in Figure 3.

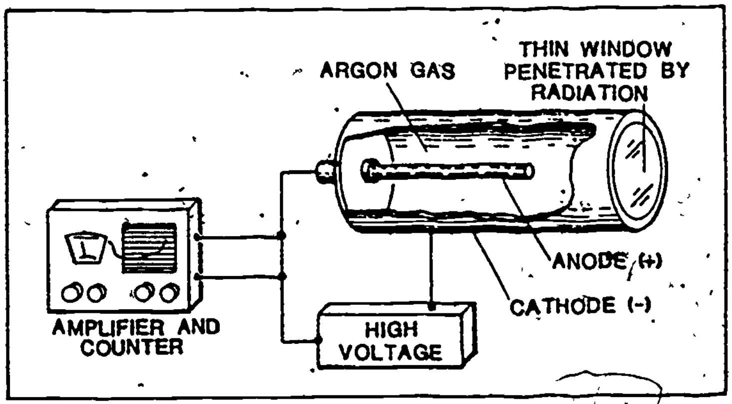


Figure 3. Geiger Counter.

4. In the scintillation counter method of radiation detection, dials of luminous watches are painted with a mixture of zinc sulfide (ZnS) and radium sulfate ($RaSO_4$). The zinc sulfide fluoresces, forming visible light when struck by the radioactive emissions from the radium. The visible light may be focused upon a photomultiplier, enabling the radiation to be measured.

People are constantly exposed to natural radioactivity. This "background" radiation comes from cosmic rays, ultraviolet light, and radioactive elements such as uranium in minerals. The level of this radiation varies with the amount of exposure to the sun and other light sources and with the elevation above seal level. Concern has been expressed because of the increased exposure to radiation from artificial radioactivity. The interactions of radiation with living matter are the same as with other molecules: ionization, molecule excitation, and heat generation. It is known that large amounts of radiation kill organisms, but the safe level of radiation above background level is not well established. Even slight exposures (including background radiation) can cause changes in cell chromosomes and, thus, cause birth defects, leukemia, bone cancer, and other forms of cancer. The benefits to be derived from certain radiation exposures, such as dental and other medical X rays, must be weighed against possible risks of such exposure. Because of the uncertain effect of prolonged radiation, it seems prudent that extreme care be exercised in the use of radioactive materials.

NUCLEAR REACTIONS

In nuclear reactions, mass is converted to energy. Einstein, in his theory of relativity, related energy and mass by means of the following equation:

$$E = mc^2 \qquad \text{Equation 1}$$

where:

E = Energy, in a unit called ergs.
m = Mass, in grams.
c = Velocity of light, in cm per second.

The fact that the velocity of light is high (3×10^{10} cm/sec) and the term is squared in Einstein's equation makes it evident that a tremendous quantity of energy results from the destruction of a small quantity of matter. Consider the amount of energy associated with the alpha decay of uranium-238. The nuclear reaction for the decay may be shown as follows:

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He + \text{Energy}$$

The masses of the atoms are as follows:

$^{238}_{92}U = 238.0508$ $^{234}_{90}Th = 234.0437$ $^{4}_{2}He = 4.0026$

Now, 234.0437 + 4.0026 = 238.0463. The 238.0463 is 0.0045 amu less than 238.0508. Therefore, 0.0045 amu was lost during the decay process and converted to energy. This kinetic energy is carried away by the alpha particle. Using Einstein's equation and using the conversion of amu to grams, one obtains the following:

$$E = 0.0045 \text{ amu} \times 1.661 \times 10^{-24} \text{ g/amu} \times (3 \times 10^{10})^2 \text{ cm}^2/\text{sec}^2 = 6.7 \times 10^{-6} \text{ erg.}$$

Converting the erg value to million electron volts (MeV) gives the following:

$$= 6.7 \times 10^{-6} \text{ erg} \times 1 \text{ MeV}/1.602 \times 10^{-6} \text{ erg} = 4.2 \text{ MeV.}$$

This calculation and similar calculations indicate the tremendous energy involved in nuclear reactions. For example, the energy released through the nuclear reaction of one pound of uranium is equivalent to that released by combustion of 1500 tons of coal.

NUCLEAR FISSION

When certain heavy elements, such as uranium-235, uranium-233, or plutonium-239, are struck by slow-moving neutrons, the nucleus is split into two large particles and, on the average, 2.4 neutrons. Three possible reactions are indicated as follows:

$$
{}^{1}_{0}n + {}^{235}_{92}U
\begin{array}{l}
\nearrow {}^{142}_{92}Ba + {}^{91}_{36}Kr + 3\,{}^{1}_{0}n \\
\rightarrow {}^{72}_{30}Zn + {}^{160}_{62}Sm + 4\,{}^{1}_{0}n \\
\searrow {}^{90}_{37}Rb + {}^{144}_{55}Cs + 2\,{}^{1}_{0}n
\end{array}
$$

Figure 4 illustrates the first reaction above in which a thermal or slow-moving neutron strikes a uranium-235 atom, causing it to split into barium-142, krypton-91, and three more neutrons. This process – in which a large atom is split into smaller fragments – is known as nuclear fission. It is the basic reaction that occurs in the atomic bomb and nuclear reactors for generating electricity.

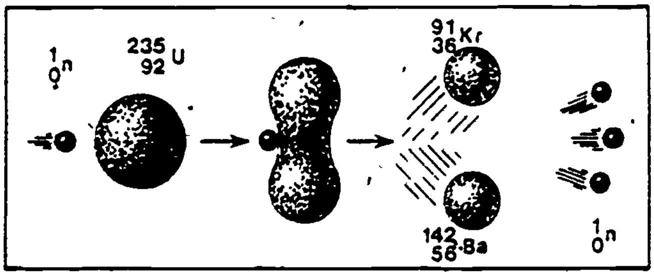


Figure 4. Fission of Uranium-235.

More than 200 different isotopes of 35 different elements have been found among the fission products of uranium-235.

On the average, 2.4 neutrons are produced by every fission of uranium-235. If one fission produces two neutrons, these two neutrons can cause two additional fissions, releasing four neturons. The four neutrons can then produce four more fissions – and so forth, as illustrated in Figure 5.

The number of fissions and their associated energies quickly escalate and, if left unchecked, can result in an explosion. This process is called a chain reaction. A certain mass of fissionable material must be available for the reaction to be self-sustaining. This mass, called the critical mass, is required so that the emitted neutrons have the opportunity to strike other atoms before they escape from the sample. In the atomic bomb, two sub-critical masses are brought together by a chemical explosive to form a critical mass. Only 6000 g of plutonium-239 are required to form a critical mass. The small size of this critical mass needed to form an atomic bomb has caused fear that enough material to build a bomb could easily be stolen.

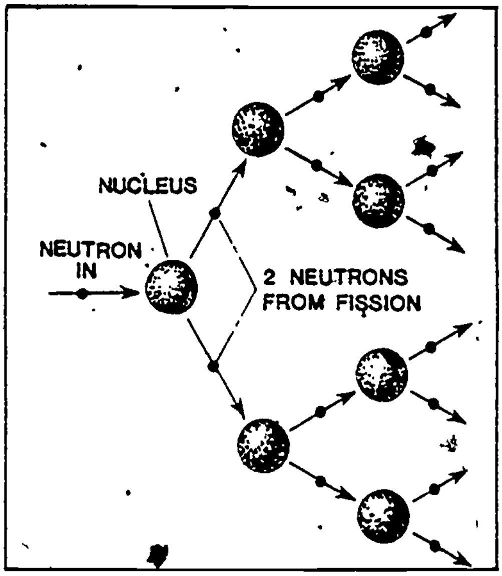


Figure 5.
Chain Reaction.

NUCLEAR FUSION

Light atoms can combine under certain conditions to form heavier atoms, with a release of tremendous amounts of energy. This process is called nuclear fusion. Nuclear fusion occurs in the sun and in the hydrogen bomb. If the fusion reaction can be controlled, it can produce an almost unlimited amount of energy. One of the most important fusion reactions is the following:

$${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + \text{Energy}$$

The $^{2}_{1}H$ atom is called heavy hydrogen, or deuterium. About one atom out of every 7000 natural hydrogen atoms is deuterium. Deuterium has one proton and one neutron, whereas normal hydrogen has only a proton and no neutrons. Deuterium is obtained by the electrolysis of water. Water molecules, which contain deuterium rather than normal hydrogen, are slightly more difficult to decompose with a current than regular water. Therefore, when water is broken down into oxygen and hydrogen by electrolysis, the last small fraction of water that remains undecomposed will be rich in water containing deuterium. Then, by electrolyzing this remaining water, nearly pure heavy hydrogen can be obtained. The second atom in the preceding reaction, $^{3}_{1}H$, is called tritium. Tritium is an extremely rare isotope of hydrogen that contains one proton and two neutrons in the nucleus. The combination of deuterium and tritium forms helium, a neutron, and tremendous quantities of energy.

The fusion reaction is an appealing source of energy since the light isotopes are readily available and the fusion products are generally not radioactive. Since deuterium comprises about one in every 7000 hydrogen atoms, the oceans can supply an almost limitless amount of nuclear fuel. The tritium for the hydrogen fusion reaction can be obtained from liquid lithium, which can serve for both a heat transfer medium and a tritium source. The tritium can be obtained through the following reaction:

$$^{7}_{3}Li + ^{1}_{0}n \longrightarrow ^{4}_{2}He + ^{3}_{1}H + ^{1}_{0}n$$

It is estimated that there is sufficient lithium on the earth to provide a source of tritium for energy production for about one million years.

Although the fusion reaction holds much promise for providing unlimited quantities of energy, there are many technological problems that must be overcome before the potential of fusion reactions is realized. Extremely high temperatures are required to trigger the fusion reaction. Temperatures in excess of 40,000,000°C must be reached to permit the fusion reaction to occur. Currently, the only known means to achieve these temperatures is through a fission bomb. In the hydrogen bomb, these high temperatures are attained by exploding an atomic bomb, which then triggers the fusion reaction. There is no known container material that can be used to contain a substance at these fantastically high temperatures. Therefore, a method must be devised to confine the materials out of contact with other materials and still maintain a high enough density to permit the fusion reaction to occur. Two methods are under investigation: confinement in a magnetic field and heating a frozen deuterium-tritium pellet with a laser beam. Although there is reason for a limited amount of optimism, it is impossible to know at this time if fusion reaction will ever become a practical source of energy.

NUCLEAR REACTORS

Nuclear reactors convert the heat that is produced by the fission of uranium-235 into steam which can then be used to generate electricity. Figure 6 is a schematic of a nuclear reactor of the pressurized water type.

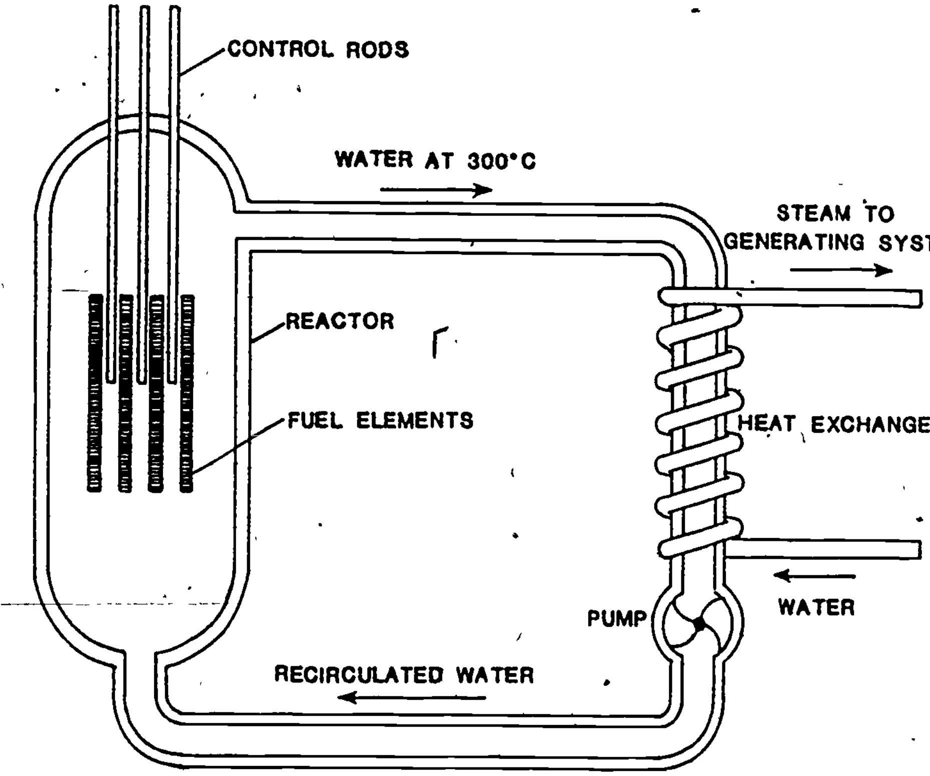


Figure 6. Nuclear Reactor.

This type of reactor is the most common type used in the United States. At a pressure of 2000 psi, water is passed through the reactor to absorb the heat given off by the fission process. The water, coming out of the reactor core at a temperature of 300°C, is circulated through a closed loop that contains a heat exchanger. A second stream of water – at a lower pressure – passes through the heat exchanger and is converted to steam at 270°C. This steam is then used to drive a turbine to produce electrical energy. Nuclear power plants have several advantages over conventional coal- or oil-fired power plants. One major advantage is the relatively low fuel cost compared to conventional fuels.

The uranium used in a nuclear power plant accounts for only about 20% of the cost of electricity produced, whereas fuel costs in other types of power plants account for about 40% of the cost of electricity produced. Another advantage attributed to a nuclear power plant is the low amount of emissions it discharges into the atmosphere, as compared to a fossil fuel plant, which can discharge several hundred thousand tons of sulfur dioxide, nitrogen oxides, and ash particles into the atmosphere each year. The most serious problem associated with nuclear reactors is the hazard from the radioactive products of the fission process. Large amounts of these products are obtained, and safe, long-term storage of these wastes is a serious problem. In addition, there is always the possibility that an accident at a nuclear power plant could occur, releasing dangerous amounts of radioactive materials.

As indicated in Figure 6, the nuclear reaction is controlled by rods that can be lowered into the fuel elements. These control rods are made of cadmium, which absorbs neutrons very effectively. During start-up of the power plant, the control rods are gradually raised, allowing the fission reaction to start. By careful manipulation of the rods, a steady state is reached whereby the heat that is generated is balanced by the heat that is carried off to the heat exchanger. Thus, the reaction proceeds safely with no danger that the reactor will explode.

BREEDER REACTORS

It has been estimated that in less than 50 years all of the uranium-235 in the United States will be depleted.

Only 0.7% of all uranium is uranium-235; the remaining 99.3% is uranium-238. In conventional nuclear reactors, uranium-235 can be split rather easily with slow-moving neutrons; but uranium-238 will not undergo splitting with slow neutrons. However, it may be possible for the neutrons given off by the 235 isotope to cause fission of the 238 isotope, according to the following reaction:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2\ {}^{0}_{-1}\mathrm{e}$$

The plutonium-239 that is formed can readily undergo fission, according to the following reaction:

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{90}_{38}\mathrm{Sr} + {}^{147}_{56}\mathrm{Ba} + 3\ {}^{1}_{0}\mathrm{n}$$

Theoretically, it is possible that a reactor utilizing these reactions could produce more fuel than it consumes. Thus, these reactors are called breeder reactors. Breeder reactors are currently under development, but they pose many technical problems. For instance, these reactors use liquid sodium as the cooling medium. Sodium is extremely reactive and causes severe corrosion problems. In addition, the plutonium is an extremely dangerous radioactive material. Because of its long half-life (24,000 years), any accident involving plutonium could leave an affected area almost permanently contaminated.

RADIOISOTOPES

Radioisotopes are widely used in medicine and industry. Cobalt-60 is used in the treatment of cancer to destroy or slow the growth of malignant tissue. The basis for such treatment is the fact that, although gamma radiation tends to destroy all cells, cancerous cells are more easily destroyed than normal ones. Trace amounts of radioactive materials can be injected into the blood stream, and any build-up of radiation can pinpoint problems such as circulatory disorders. Industrially, radioactive isotopes are used to measure frictional wear and corrosion rates. The thickness of very thin sheets of metal, paper, or plastic can be measured by placing them between a radioactive source and a detector such as the Geiger counter. The amount of radiation passing through the material is a measure of its thickness. This method can be used to nondestructively test for flaws in many materials. Neutron activation analysis is an important analytical technique. In this procedure, the sample is bombarded with neutrons, and the element of ~~interest~~ is converted into a radioisotope. A measurement of the radioactivity of the isotope can then be used to calculate the amount of the element in the sample. This method of analysis is especially attractive for two reasons: it can be used to determine trace amounts of an element and it is nondestructive.

EXERCISES

1. Complete the following nuclear reactions:

   a. ${}^{59}_{27}\text{Co} + ? \longrightarrow {}^{56}_{25}\text{Mn} + {}^{4}_{2}\text{He}$

   b. ${}^{235}_{92}\text{U} \longrightarrow {}^{4}_{2}\text{He} + ?$

   c. ${}^{24}_{12}\text{Mg} + {}^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{H} + ?$

2. The half-life of hydrogen-3 is 12.3 years. How much of a 50 mg sample will remain after 24.6 years?

3. Given the following atomic masses –

   ${}^{6}_{3}\text{Li} = 6.01513$
   ${}^{4}_{2}\text{He} = 4.00260$
   ${}^{3}_{1}\text{H} = 3.01604$
   ${}^{1}_{0}\text{n} = 1.008665$

   calculate the amount of energy – in million electron volts (MeV) – given off in the following nuclear reaction:

   $${}^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \longrightarrow {}^{4}_{2}\text{He} + {}^{3}_{1}\text{H}$$

4. Write an equation for each of the following radioactive decay processes:

   a. K-capture of ${}^{51}_{24}\text{Cr}$

   b. Beta decay of ${}^{40}_{19}\text{K}$

   c. Alpha emission of ${}^{225}_{89}\text{Ac}$

5. Radium has a half-life of 1690 years. Starting with 20 g of radium, how much radium would be left after . . .

   a. 845 years?
   b. 1690 years?
   c. 3380 years?

LABORATORY MATERIALS

Laboratory 1	Laboratory 2
Geiger counter	Geiger counter
Radium dial watch	Watch glass
Meter stick	Separatory funnel
Cardboard	Pipette
Radioactive ores	Pipette bulb
Aluminum foil	Potassium iodide
Lead foil	Radioactive potassium iodide
Gamma source	Carbon tetrachloride
	Bromine water
	Sodium hydroxide, 0.2 M

LABORATORY PROCEDURES

LABORATORY 1. RADIOACTIVITY.

The radioactive samples of ore used in this experiment are available from chemical supply houses. They present no particular hazard; however, it is good to develop and use the same techniques and precautions that must be used with other, more dangerous radioactive materials. Precautions and disposal suggestions should be found in the literature available with the samples. The radioactive samples will give off beta and gamma rays. In this experiment, the shielding effects of cardboard, aluminum, and lead will be examined, using a Geiger counter. A graph of radioactivity versus distance from source will then be constructed.

PROCEDURE

1. If the Geiger counter is of the 110-volt type, plug it into the power source.
2. When the counter has warmed up (immediately, if it is battery powered), hold the probe toward the ceiling. The clicks that will be heard are from natural background radioactivity.
3. Place one of the radioactive samples on the laboratory bench and position the probe three feet (ft) from the sample.
4. Count the clicks (or flashes) heard for one minute (min). Record the number of clicks.

   ________ (1 min at 3 ft)
5. Position the probe one foot from the source and count the clicks for one minute.

   ________ (1 min at 1 ft)
6. How does distance relate to the number of clicks?

   ____
7. Place a radium-dial watch one foot from the probe and observe the radioactivity, as indicated by the counter. Compare the intensity of radiation of the ore sample with the intensity of the radiation from the watch.

   ____
8. Place a piece of cardboard between the probe and the ore sample. Count the number of clicks for one minute, at one foot and three feet.

   ________ (1 min at 3 ft, with cardboard)

   ________ (1 min at 1 ft, with cardboard)

9. Place a piece of aluminum foil between the probe and the ore sample. Count the number of clicks for one minute at one foot and three feet.

_____________ (1 min at 3 ft, with aluminum foil)

_____________ (1 min at 1 ft, with aluminum foil)

10. Place a piece of lead sheet between the probe and the ore sample. Count the number of clicks for one minute at one foot and three feet.

_____________ (1 min at 3 ft, with lead sheet)

_____________ (1 min at 1 ft, with lead sheet)

11. Compare the intensity of radiation striking the unshielded probe to that striking the probe when shielded by the materials in Steps 8, 9, and 10.

____

____

12. Close the shield covering the probe to prepare the counter for use with the gamma source.

13. Place the gamma source 5 cm from the probe and remove the shield. Count the number of clicks for one minute, for a second minute, and for a third minute, recording the data below. Average the three values and record the average. Repeat these measurements after moving the gamma source further away — 1 cm at a time until the source is 20 cm from the probe.

Distance from Probe (cm)	Clicks/ Minute	Clicks/ Minute	Clicks/ Minute	Average
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				

14. On a sheet of graph paper, plot a curve of activity versus distance of source to the probe. Plot the number of clicks (activity) on the y-axis, and the distance (in cm) on the x-axis. Note that the curve is not a simple inverse proportion. The curve illustrates the law of inverse squares for radioactivity.

LABORATORY 2. ISOTOPIC PROPERTIES (Demonstration).

This experiment illustrates that the chemical properties of radioactive isotopes are identical to the chemical properties of non-radioactive isotopes.

PROCEDURE

1. Dilute a small amount of the radioactive potassium iodide solution (less than one microcurie) with five drops of the sodium hydroxide solution.
2. Add a small crystal of non-radioactive potassium iodide and stir until it dissolves.
3. Position the Geiger counter probe 5 cm from the radioactive mixture and note the activity.
4. Pour 10 ml of the solution into the separatory funnel and add a few drops of bromine water. (The bromine should react with the iodide ion, converting it into free iodine.)
5. Add 10 ml of carbon tetrachloride. Shake the mixture and let it stand. (The lower layer of liquid in the funnel should indicate the characteristic iodine color.)
6. Draw off the bottom liquid into a small beaker and test its activity with the counter.
7. Answer the following questions:
    a. Does the bottom colored layer contain radioactivity?
    b. Do radioactive and non-radioactive compounds mix in solution?
    c. Did the isotopic forms of iodine accompany each other through the extraction?
    d. Do radioactive and non-radioactive isotopes have the same chemical properties? Do they have the same physical properties?
    e. Describe the difference betweeen radioactive and non-radioactive isotopes.

REFERENCES

Aryes, E. and Scarlett, C.A. Energy Sources - The Wealth of the World. New York: McGraw-Hill Book Co., Inc., 1952.

"Breeder Reactors Hold Key to Energy Needs." Chemical Engineering News (December 1962) p. 21.

"Energy." A special issue of Science 180, 4134 (1974).

Gregory, Dereck P. "The Hydrogen Economy." Scientific American 228, 1 (1973) p. 13.

Leachman, R.B. "Nuclear Fission." Scientific American (August 1965).

Linnenbom, V.J. "Radioactivity and the Age of the Earth." Journal Chemical Education 32, 58 (1955).

GLOSSARY

Alpha rays: Particles consisting of two protons and two neutrons.

Beta rays: Streams of electrons traveling at enormous speeds.

Breeder reactor: A nuclear reactor that produces more fuel than it consumes.

Critical mass: The mass of fissionable material that must be available for a reaction to be self-sustaining.

Deuterium: An isotope of hydrogen, containing one neutron.

Electron capture: A nuclear reaction in which an electron is captured by the nucleus.

Gamma rays: Electromagnetic radiation of very short wavelength.

Geiger counter: A device for measuring radiation.

Half-life: The time required for half of a given quantity of radioactive substance to decay.

Neutron: Neutral particle found in the nucleus of an atom.

Nuclear chemistry: The branch of chemistry dealing with atoms that contain unstable nuclei.

Nuclear fission: A process in which a large atom is split into smaller fragments.

Nuclear fusion: The process in which light atoms combine to form heavier atoms, with a release of tremendous amounts of energy.

Nucleus: The inner core of an atom.

Positron: A particle that has the same mass of an electron, but a positive charge.

Proton: Positively charged particle found in the nucleus of an atom.

Radioisotopes: Radioactive substances widely used in medicine and industry.

Tritium: An isotope of hydrogen, containing two neutrons.