

Measurements of Heat Transfer in Physical and Chemical Processes Using Computer-Interfaced Calorimetry

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INTRODUCTION

This unit is designed for students taking first year high school chemistry, but it also intends to improve students' knowledge in physics and mathematics. It utilizes laboratory techniques in conjunction with computer technology.

Prerequisite skills: knowledge of Physical Science I and Algebra I.

OBJECTIVES

Students will be able to know and perform the following:

- Know how heat of fusion, heat of vaporization, specific heat of a metal, heat of dissolution, and heat of a chemical reaction can be measured using a calorimeter;
- Answer questions on calorimetry and solve calorimetric problems using class notes and reference chemistry texts;
- Perform calorimetric experiments by classic laboratory methods and by use of a computer.

The instructor may use the following teaching techniques and teaching tools.

Teaching Techniques: Use of lectures, discussions, questions and answers, diagrams, formulas, equations, charts, graphs, computer graphics, defining, describing, demonstrations, experimentation, data collections, calculations, logical reasoning, the Internet site Yahoo!, and encouragement.

Teaching Tools: chalk board, overhead projector, calculators, slide, video presentation, computer monitor and probe (thermistor), power point, hyper studio, laser disc, laboratory equipment and supplies.

WHY IS THE STUDY OF HEAT ENERGY IMPORTANT?

Of all the factors responsible for our present high economic standards, the use of energy is the most important one. Nations that have developed the ability to control and convert available forms of energy into useful forms have the highest standards of living and exert the greatest influence in the world today.

Three primary sources of available energy are: nuclear fusion reactions taking place on the surface of the Sun releasing heat energy, nuclear fission reactions occurring when the nuclei of atoms split, and chemical energy in matter which is recoverable through the rearrangement of atoms during a chemical reaction.

At present, steam power plants represent the most important method of converting available energy into useful energy. In these plants, the internal energy of coal, oil, or natural gas is released as heat by burning. The heat is converted into mechanical energy when the steam produced by heating water is used to turn a turbine. The turbine is coupled to a generator, which converts mechanical energy to useful electric energy.

BACKGROUND

Thermodynamics is a study of the principles involved in the utilization of energy in thermal systems. Thus energy, defined as the ability to accomplish an effect, is the primary concern of the thermodynamicist and of the engineer who proposes to apply energy relationships to such seemingly diverse equipment as steam or gas turbines, air or refrigeration compressors, internal combustion engines, turbojets, ramjets, and rockets. Fortunately, the diversity in thermodynamic equipment is due largely to differences in the field of application rather than to differences in underlying theory.

Since the mid-nineteenth century tremendous changes have occurred in applied thermodynamics, but the principles have remained almost unaltered. Although such new equipment as internal combustion turbines, thermojets, and reversed cycle heating systems have been developed as a result of metallurgical and mechanical advances, they utilize thermal processes and cycles which have long been known. It is paradoxical that one of the most modern important devices, the gas turbine, operates on a cycle which many engineers considered obsolete. Similarly, the air refrigeration system used in some modern transport planes utilizes a cycle that had been abandoned because of excess weight and volume. Thermodynamic space heating has become commercially important only since 1945, yet recognition and analysis of the possibility of its development were presented by William Thompson (later 1st Baron Kelvin) in 1852. Even in the field of nuclear power there is every reason to believe that the energy released through atomic fission and fusion will be utilized by the application of essentially the same thermodynamic relationships that apply to all existing machines.

Thermodynamics is in part a science and in part an art. The science is concerned with the investigation and analysis of thermal paths leading from an energy source (usually some form of fuel) to useful work. The art relates to the development of actual equipment that will operate over thermal paths closely analogous to those devised from theory. Although there is a necessarily close relationship between the science and the art, it is nonetheless advantageous to separate them partially for purpose of study. Such separation does not insulate theory from practice, but rather permits a more powerful application of the theoretical relationships to the problems of practical design. This is true because theory undergoes obsolescence much more slowly than equipment, and a thorough knowledge of thermodynamics is therefore applicable equally to the equipment of the past, the present, and the future. From general thermodynamic theory special relationships can be derived as readily for a uranium pile as for a steam boiler, as readily for a space rocket of 1960 as for a kerosene engine of 1900. The reverse holds true to a much lesser degree, since special knowledge concerning the "art" of the kerosene engine

could hardly be extrapolated to assist in developing the space rocket.

The rational study of thermodynamics begins with the raw material, the various sources of energy, and then proceeds along one of many thermal paths leading eventually to the desired product—electricity or mechanical work. Many steps are usually required to achieve overall conversion, but each of them has as its purpose the liberation, storage, transfer, transportation, transformation, or utilization of energy. One step may combine more than one of these basic purposes, but in no case will any thermodynamic path contain elements other than these six fundamental ones. In practice, liberation of energy usually occurs either through nuclear fission (nuclear fusion in the case of the sun and in a hydrogen bomb) or through the more widely used process of combustion ($q.v.$). Whether in a microscopic system of molecules or in a macroscopic system made up of tangible matter, energy storage occurs through the agency either of velocity or of position. Energy transfer occurs by only one of two mechanisms: heat or work. Energy transportation occurs through the mass transfer of the working substance in which the energy is stored. Thus the entire field of engineering thermodynamics is concerned with establishing a suitable thermal path from fuel to useful work, the path to consist of a series of transformations among the forms of energy in storage or in transition.

When matter is involved in a chemical or physical process, its total energy content is usually altered. The difference in energy between the initial and final states, ΔE (Δ , the symbol for the Greek letter delta, means "change in"), must be transferred to or from the environment of the system. This energy exchange between the system and its environment is in the form of heat or work, or both. In calorimetry, the energy exchanged as heat is quantitatively evaluated. If a temperature change develops in an open container, the heat measured directly is q_p due to constant pressure exerted on the system by the atmosphere. If a reaction occurs under condition of constant volume, then the measured heat is q_v . In a bomb calorimetry, the volume is considered constant during a reaction. The heat absorbed by the system, q , is related to the work done by the system on its environment, w , and the increase in internal energy of the system, ΔE , by the thermodynamic relationship $q = \Delta E + w$. When calorimetric measurements are performed at constant pressure and only pressure-volume work is involved, q is equal to the increase in heat content or enthalpy, ΔH .

Calorimetry is the science of measuring the quantity of heat, q , absorbed or evolved by matter when it undergoes a change in its chemical or physical state. The apparatus in which the measurement is performed is a calorimeter, and the experimenter is frequently referred to as a calorimetrist.

Many chemists have been curious about the heat effects that accompany chemical reactions. In the early 1780s, the French chemist Lavoisier measured the heat given off by a guinea pig. He kept the animal in an enclosed container so its body heat would melt ice. From the amount of ice melted, he calculated the heat produced by the animal. The apparatus used to contain the guinea pig and measure its body heat was an ice calorimeter.

The process selected for calorimetric study may be a simple change in the physical state of matter, such as a change in temperature of the material, or it may consist of a series of complex chemical reactions such as are encountered in the combustion of many fuels. In fact, nearly any process involving a chemical or physical change in matter might well become a necessary subject for calorimetric investigation.

¹ Calorimetric determinations of energy changes are essential in many theoretical and practical problems. Heat capacity or specific heat data are vital to the design of heat exchange equipment. The thermal properties of steam and certain metals are a major consideration in the design of modern boilers and turbines. The heats of combustion of fuels are essential in rocket, engine and gas turbine design. The heat liberated by chemical reactions must be considered in the development of chemical process equipment. Often the required equilibrium constant of a process is most conveniently obtained by a simple calculation from the free energy change, ΔG . For a great many processes, numerical values of ΔG can be obtained from the change in heat content, ΔH , and the entropies of the participating substances, S , using the thermodynamic relationship, $\Delta G = \Delta H - T\Delta S$ where T is the absolute temperature.

The design and constructional details of calorimeters vary widely because of the diversified nature of the processes suitable for calorimetric study. However, the basic principles are general and their consideration constitutes a common requirement in practically all designs. Suitable devices and procedures for three essential measurements are usually required, but one or two can sometimes be omitted by operating under certain restrictions. The measurements are (1) the temperature of the calorimeter and its contents, (2) the quantity of energy that is added to the calorimeter from an external source, and (3) the quantity of heat that is exchanged between the calorimeter and its environment.

Most calorimetric operations involve a temperature change, since the heat liberated (or absorbed) during the process is stored in the calorimeter and its contents by virtue of their combined heat capacity. Thermocouples, thermopiles and resistance thermometers are commonly used for temperature measurements. The quantity of energy liberated or absorbed in a calorimetric process is evaluated in terms of electrical energy.

Calibration of calorimeters may be done by use of three similar methods. (1) In an exothermic process where heat is liberated, the calorimeter is cooled to the original temperature; the temperature rise is then duplicated using an electrical resistance heater. (2) In an endothermic process, heat absorbed is supplied by an electrical heater at such a rate as to keep the temperature constant. (3) In heat-capacity measurements, the electrical energy is supplied directly by a heater. Electrical energy and temperature can be measured very accurately by modern methods, but the problem of heat transfer between the calorimeter and its environment is more difficult. The minimization of and accurate correction for heat exchange is the major problem to be reckoned with in modern calorimetry.

INSTRUCTIONAL SUB-UNITS

Lesson 1

Energy, Heat, and Temperature

Discussion, Practice Questions and Problems of Appendix

Energy is defined as the capacity to do work or to produce heat. Energy is intangible. Whether it is in storage or in transition, its presence can be recognized only by observation of the effect it has on the material in which it is stored or through which it is passing. Thus all measurements of energy are necessarily indirect. Heat is energy that is transferred from one object to another because of a difference in their *temperatures*. Imagine yourself in dance class where student switch partners on every part of a dance pattern. As new couples hold hands, the heat always flows from a warmer hand to a colder hand. This is the basic principle of the heat transfer.

The transfer of heat can be detected by measuring the resulting temperature change. The temperature of an object is proportional to the average *kinetic energy* of its atoms or molecules. As the temperature of a substance increases, the average velocity of its atoms or molecules increases. Thus the total heat energy of the substance must increase also. Let us assume that hot water in a teakettle and a cup have the same temperature. Now which one contains more heat energy? Of course, the answer is the kettle, simply because there are more water molecules in the kettle, so the sum of all their kinetic energies is greater. Thus, because the water in the kettle has more mass, it has more energy, even though both containers of water have the same temperature.

Working Substance (Medium of Heat Transfer)

Discussion, Practice Questions and Problems of Appendix

Some kind of tangible material must be used to establish the thermodynamic path along which energy conversion takes place. This tangible material is called the working substance. All working substances are merely inert materials that serve as thermodynamic vehicles to convey the energy through the steps from energy source to energy utilization.

Theoretically, there are no limitations on the choice of a working substance, since all materials are capable of receiving, storing, transporting and releasing energy. In practice, however, certain classes of material possess marked advantages, whereas others have evident shortcomings. Solids, for example, are entirely unsuited to continuous circulation. Among fluids, gases and vapors afford a greater degree of flexibility than liquids, since energy in the form of work can be much more readily put into or taken from a material, which undergoes a substantial change in volume as a result of a change in pressure. Liquids, on the other hand, occupy much less space than gases or vapors and so permit the use of a smaller transportation system.

In some cases, combination systems permit the engineer to take advantage of the most desirable characteristics of both vapors and liquids. Thus steam power plants use water, which for part of the circuit is in liquid form and for part is in vapor form. Refrigeration systems likewise use liquefiable vapors as the working substance. Some systems use more than one working substance. Power plants are in operations that use both water and mercury in separate flow systems, and refrigeration systems using two different fluids in series are not uncommon. Proposals for the thermal utilization of atomic piles have included the use of molten lead as the preferable working substance. Water with its high heat capacity is a desirable working substance for calorimetric experiments.

The selection of a working substance must be made based on many considerations other than the fundamental thermodynamic ones. Thermodynamically, a particular fluid might have a large capacity for storing energy and might lend itself readily to the rapid reception or liberation of energy, but it would not be of practical usefulness unless its physical properties remained within limits established by mechanical, metallurgical, and economic considerations.

The first and major requirement of an ideal thermodynamic fluid is that it be homogeneous and a continuum. When such a fluid receives, liberates, or transforms energy, its various physical properties would be expected to change in value, but the change would be assumed to occur uniformly throughout the mass of the fluid.

Measuring Heat Energy

Discussion, Practice Questions and Problems of Appendix

Processes. The series of continuous states followed by a working substance as it liberates, transfers, transforms, or receives energy is defined as a thermodynamic process. There are an infinite number of possible processes. Based on the ways in which energy can be transferred or transformed, or both, a major problem in thermodynamics is to classify the various types of processes and then to select for engineering applications the ones which provide the best combination of theoretical desirability with practicability. Under conditions of constancy there are three measurable properties: (1) an *isothermal process*, one which occurs without change in temperature; (2) an *isopiestic process*, one which takes place at constant pressure; and (3) an *isometric process*, which is a constant volume process. An isothermal process occurs for example, when thermal energy is added to ice and melting takes place; an isopiestic is represented by expansion against atmospheric pressure; and an isometric corresponds to the heating of a material contained within a rigid and nonexpanding container.

The SI unit of energy is called the *joule*. One joule is a very small amount of energy—a heartbeat produces about 1 joule of energy. Chemists typically express energies in kilojoules ($1 \text{ kJ} = 1000 \text{ J}$).

Chemists have often used a non-SI energy unit—the calorie. The calorie is defined as $1 \text{ cal} = 4.184 \text{ J}$. The former metric system definition of the calorie is the amount of

energy needed to increase the temperature of one gram of water one degree Celsius. You are familiar with the nutritional energy unit called the Calorie. This unit of energy is actually one kilocalorie.

Factors determining heat transfer. The amount of heat transferred depends on three factors: the capacity of a substance to absorb heat, its mass, and its change in temperature. In fact, the amount of heat transferred is directly proportional to each of these factors as any one of them increases, so does the amount of heat transferred. Often chemists are interested in comparing the capacity of different substances to absorb heat. In order to make this comparison, equal masses and temperature changes are necessary. The *specific heat* is a measure of this property and is defined as the quantity of heat needed to raise one gram of a substance one degree Celsius. The SI units of specific heat are $\text{J/g}^\circ\text{C}$.

To evaluate the heat transferred to or from a substance, you must know its specific heat, its mass, and the temperature change, ΔT .

Storing energy. A substance with a large value of specific heat has the capacity to store a large amount of energy. For example, water with its high specific heat absorbs great quantities of heat before it could undergo a change in temperature. Water in solar heated homes absorbs the sun's energy during the day, and during the night the energy stored in water is transferred to the air warming the inside of the home.

Lesson 2

Measuring Heat Transfer in a Phase Change

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment A of Appendix

The specific heat of a substance indicates the amount of energy that must be added to or removed from one gram of a substance to change the substance's temperature by one degree Celsius. Changing the temperature of a substance can also cause it to change from one state to another. For example, a gas can be cooled until it condenses to a liquid. Further cooling can cause the liquid to freeze.

During a change of state, a phase change, the energy of a substance changes. The change from the liquid phase to the gas phase is called vaporization. The quantity of heat that must be absorbed to vaporize one gram of a liquid is called the *heat of vaporization*. Likewise, the quantity of heat needed to cause one gram of a solid to melt into its liquid phase is called the *heat of fusion*. Heats of vaporization and fusion are usually measured in joules per gram. (J/g .)

The quantity of heat transferred as a result of a phase change is the product of the mass of the substance and the heat of the phase change.

$$\text{Heat transferred} = (\text{mass}) \times (\text{heat of the phase change})$$

Temperature remains constant during a phase change. No temperature changes occur during melting or vaporization process. The heat is being absorbed to produce a phase change in a substance. Heat of vaporization and heat of fusion of a substance can be measured using a calorimeter. A calorimeter is a well-insulated container that minimizes the amount of heat transferred to the surroundings. The word calorimeter literally means "heat measurer" from calor meaning "heat" and meter meaning measure

Lesson 3

Measuring Specific Heat of a Metal

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment B of Appendix

The specific heat of a metal, such as copper, can be determined by placing the metal into a calorimeter containing water that has a temperature different from that of the metal. Suppose that the copper is initially at a higher temperature than the water. Heat will be transferred from the copper to the water. The water will warm, while the metal will cool. When both reach the same temperature, heat will no longer be transferred.

The calorimeter minimizes any loss of heat to the surroundings. Therefore the heat gained by the water is equal to the heat lost by the copper. Remember that the quantity of heat transferred depends on the mass, the specific heat, and the temperature change. Thus the mass and the initial temperature of both the water in the calorimeter and the piece of copper must first be measured. The copper is placed in boiling water long enough to reach the temperature of the water and then quickly placed in the calorimeter. After the water and copper reach the same temperature, the final temperature of both substances is measured. Since the specific heat of water is $4.18 \text{ J/g } ^\circ\text{C}$, the specific heat of the copper can be calculated from the data.

Lesson 4

Measuring Heat Transfer in Dissolution Process

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment C of Appendix

The ease of the dissolution process depends upon two factors: (1) the change in energy (exothermicity or endothermicity) and (2) the change in the disorder (called entropy change) accompanying the process. The spontaneity of a process is favored by (1) a decrease in the energy of the system, which corresponds to an exothermic process and (2) an increase in the disorder, or randomness of the system. Let us concentrate first on the factors that determine the change in heat content, factor (1) above. This change is called the *heat of solution*, $\Delta H_{\text{solution}}$. In a pure liquid to be used as a solvent, the

intermolecular forces are all between like molecules; when the liquid and a solute are mixed, each molecule then experiences forces from molecules (or ions) unlike it as well as from like molecules. The relative strengths of such interactions help to determine the extent of solubility of the solute in the solvent. The interactions that must be considered to assess the heat of solution for the dissolution of a specific solute in a specific solvent are:

- (1) solute - solute interactions
- (2) solvent-solvent interactions
- (3) solvent-solute interactions

Generally, dissolution is favored when the first two of these interactions are relatively small and the third is relatively large. The intermolecular or interionic attractions among solute particles in the pure solute must be overcome to dissolve the solute. This part of the process requires an *input* of energy. Likewise, separating the solvent molecules from each other to make room for the solute particles also requires the input of energy. However, energy is released as the solute particles and solvent molecules interact in the solution. Thus the dissolving process can be exothermic.

Many solids dissolve in liquids by endothermic processes. The reason such solids are soluble in liquids is that the endothermicity is outweighed by a great increase in disorder of the solute accompanying the dissolving process. The solute particles are very highly ordered in a solid crystal, but are free to move about randomly in liquid solutions. Likewise, the solvent particles increase in their degree of disorder as the solution is formed, since, they are in a more random environment; they are surrounded by a mixture of solvent and solute particles.

Quantitative measurements of the heat liberated (or absorbed) during the solution of a solid or of another liquid by a solvent are performed in solution calorimeters. Heats of solution, dilution and mixing are common determinations of this type. In addition to participating in the process under investigation, the solvent is used as a means of attaining uniform temperature and composition throughout the calorimeter. This feature necessitates stirring, which is usually accomplished with mechanically or magnetically driven stirrers. Sometimes, however, the calorimeter itself is rotated. Regardless of the method used, the quantity of heat introduced by the stirring must be determined either directly or indirectly and a suitable correction must be applied. Another feature characteristic of solution calorimeters is the method of adding the sample. It must either be equilibrated with the solvent in the calorimeter or its heat content relative to the calorimeter temperature must be determined. A common method for solids is immersing a capsule containing the sample in the solvent and breaking it at the desired time.

Lesson 5

Measuring Heat Transfer in an Exothermic Reaction

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment D of Appendix

The measurement of the amount of heat released during a chemical reaction is called calorimetry. It is usually done with the aid of a device called a calorimeter. The reaction to be measured occurs inside a reaction chamber surrounded by a known mass of water. Heat released by the reaction enters the water and raises its temperature. The temperature change is measured with a thermometer. The outside of the calorimeter is well insulated to prevent any significant loss of heat. The quantity of heat transferred to the water in the calorimeter can be calculated by multiplying three factors: (1) the mass of the water in the calorimeter (in grams), (2) the change in the water's temperature (in degree Celsius), and (3) constant, called the specific heat of water.

Lesson 6

Measuring Heat Transfer in a Neutralization Reaction

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment E of Appendix

Strong solutions of acids and bases with the same concentration and mass will neutralize each other to produce a salt and water releasing energy as a side product. The heat evolved from these exothermic processes can be measured by calorimetric method. When dilute (1.0 M to 3.0 M) solutions of strong acids and bases are mixed together in a flask, the heat of reaction can be felt by touching the flask before and after the reaction. The solution is distinctly warmer after mixing. You should use a thermometer to verify that an exothermic reaction has occurred. However, the observation does not prove that the process was a chemical reaction. Changes in temperature can also accompany physical changes, such as when a solution forms, or when a super saturated solution crystallizes.

Lesson 7

Measuring Heat Transfer in a Combustion Reaction

Demonstration, Discussion, Data Collection, Formulas, Calculations, and Experiment F of Appendix

In 1881, Berthelot devised a closed container he called a BOMB, based on the then known fact that many substances, including hydrocarbons, will react easily with oxygen. Today we are using a similar apparatus called a calorimeter that utilizes the bomb concept to contain combustion reactions. The bomb works by allowing high pressure

oxygen to burn in a stainless steel container to keep the volume constant. The heat evolved by the reaction can be measured.

Solid combustible substances and fuels can be ignited in a bomb (combustion) calorimeter and the heat can be measured by a reaction occurring at a constant volume. In this type of calorimeter a strong steel vessel (the bomb) is immersed in a large volume of water. As heat is produced or absorbed by a reaction going on inside the steel vessel the heat is transferred to or from the large volume of water, so only very small temperature changes occur. For all practical purposes, the energy changes associated with the reactions are measured at constant volume and constant pressure. For exothermic reactions, we may write:

$$\text{heat lost by system} = (\text{heat gained by calorimeter bomb}) + (\text{heat gained by water}).$$

In order to simplify calculations, the amount of heat absorbed by the calorimeter is usually expressed as its water equivalent, which refers to the amount of water that would absorb the same amount of heat as the calorimeter per degree temperature change. The water equivalent of a calorimeter is determined by burning a sample of a compound that produces a known amount of heat and measuring the temperature rise of the calorimeter.

The heat of combustion of fuels and similar materials is usually measured by bomb calorimetry. The solid or liquid sample is contained in a bomb (pressure vessel) containing excess oxygen, or other suitable gas under pressure. The bomb is immersed in a calorimeter containing a liquid, usually water. The reaction is initiated by igniting the sample with a measured amount of electrical energy, and the heat evolved is measured in terms of the temperature rise of the calorimeter. Electrical energy is usually used to duplicate the temperature rise and thus evaluate the heat liberated. However, sometimes a standard sample of a substance having a known heat of combustion, such as benzoic acid, is used to calibrate the apparatus. In bomb calorimetry corrections to standard conditions must be applied.

There are many other important types of calorimeters, such as flow calorimeter, microcalorimeters, flame calorimeters, etc. Nearly any process can be studied by the investigator who is ingenious enough to devise the appropriate apparatus and who has the resources and patience to undertake an extensive project. Although calorimetric measurements are, in general, time-consuming and tedious, they are essential for a fundamental and practical understanding of many important chemical and physical processes.

COMPUTER-INTERFACED CALORIMETRY IN GRAPHICAL INTERPRETATION OF DATA

²External Calibration and Programming of the 12 Probe (Used in Colorimetry). You will be calibrating *transmittance* values. For the calibration, you will assign arbitrary values to a "blank" (pure water) and a solution, whose concentration you need to know. Values suggested are "1000" for the blank and "100" to the most concentrated solution. The

transmittance values will be I/I_0 where $I_0 = 10000$. In the main program, use "I2 probe" (and not "12").

Place the blank (cuvet of water) in the colorimeter. From the main menu,
CALIBRATE SENSORS Enter Probe Enter 11 probe Enter Linear Enter
You will be presented with a box asking you to enter the necessary voltage for the DAC.
Enter the DAC voltage needed:

(where the phototransistor is plugged in). You want to supply 1000 millivolts:
1000 Enter

You will be given (the current reading may be anything):

Place your probe in
The calibration substance.
Input current: 144.58 microamperes
Press <ENTER>to continue

Enter

You will then be given the box:

Enter the correct value:

Enter the value of 1000:

1000 Enter

Now replace the cuvet of solution. You will duplicate the previous two steps. You will have the box:

Place your probe in
The calibration substance.
Input current: 8.57 microamperes
Press <ENTER>to continue

Enter

You will then be given the box:

Enter the correct value:

Enter the value of 100:

100 Enter

Sample Program

Here is a sample program used to read phototransistor values, using the 12probe with external calibration.

1. CLEAR WHOLE SCREEN
2. PAUSE
3. SET DAC TO 1000 MILLIVOLTS
4. PRINT INPUT FROM 12PROBE LARGE
5. PAUSE
6. IF INPUT FROM SwX = ON GOTO 8
7. GOTO4
8. STOP

APPENDIX

Calorimetric Experiments

Instructor performs pre-laboratory demonstrations by displaying and describing the use of equipment and supplies used in an experiment. He also would explain how the experiment is to be conducted and will point out the safety precautions to be taken.

Students will perform the following experiments under the instructor's supervision. They will record and analyze the data obtained by using the classic laboratory techniques. If a lab computer is available, students will use thermistor probe connected to the computer monitor to collect data. Students will download the graphs of temperature vs. time for analysis.

Experiment A: Measuring Heat Transfer in a Phase Change

Experiment B: Measuring Specific Heat of a Metal

Experiment C: Measuring Heat Transfer in an Endothermic Dissolution Process.

Experiment D: Measuring Heat Transfer in an Exothermic Reaction

Experiment E: Measuring Heat Transfer in a Neutralization Reaction

Experiment F: Measuring Heat Transfer in a Combustion Reaction

Experiment A: Measuring Heat of Fusion of Ice and Heat of Vaporization of Water

Purpose: To measure the amount of heat required to vaporize 10 grams of ice from temperature of -5°C to 10.0 g of superheated steam at temperature of 105°C .

Heat transfers in physical processes occur when matter goes through a phase change or a temperature change, without being chemically altered

Caution: Ice at -5°C should be handled by a pair of tongs. Steam can produce severe burns. Pairs of goggles and gloves are required.

Apparatus and supplies: Adiabatic vacuum calorimeter or hot plate, a Celsius thermometer, and 250 ml pyrex Erlenmeyer's flask, # 5 two hole rubber stopper, glycerin.

Procedure: Place 10 grams of crushed ice at -5°C in a 250 ml flask. Using a glycerin lubricant, insert a thermometer in one of the holes of the rubber stopper and secure it on the mouth of the flask so that the tip of the thermometer will touch the ice. Place the flask and its contents on a hot plate. Start with the lowest temperature setting and gradually increase the temperature as you take readings on the thermometer during the phase changes taking place.

Sample Calculations for heating 10.0 g of ice from a temperature of -5°C to 10.0 g of superheated steam at temperature of 105°C requires an input of heat energy in the following steps:

³a) From 10.0 g of ice at -5°C to 10.0g of ice at 0°C
 $q = m (C_p)(\Delta T) = (10.0 \text{ g})(2. \text{ J/g} \cdot ^{\circ}\text{C})(5^{\circ}\text{C}) = 100 \text{ J}$

b) From 10.0 g of ice at 0°C to 10g of water at 100°C .
Hf= heat of fusion (melting) Hf (ice) = 334 J/g
 $q = m (\text{Hf}) = (10.0\text{g})(334 \text{ J/g}) = 3340 \text{ J}$

⁴c) From 10.0 g of water at 0°C to 10.0 g of water at 100°C .
 $q = m (C_p)(\Delta T) = (10.0 \text{ g})(4.18 \text{ J/g} \cdot ^{\circ}\text{C})(100^{\circ}\text{C}) = 4180 \text{ J}$

d) From 10.0 g of water 100°C to 10.0 g of steam at 100°C
Hv = heat of vaporization of water = 2259 J/mole
 $q = m(\text{Hv}) = (10.0 \text{ g})(2259 \text{ J/g}) = 22590 \text{ J}$

e) From 10.0 g of steam at 100°C to 10.0g steam at 105°C
 $q = m (C_p)(\Delta T) = (10.0\text{g})(1.7 \text{ J/g} \cdot ^{\circ}\text{C})(5^{\circ}\text{C}) = 85\text{J}$

The total heat energy absorbed by the ice is found by the sum of the heat input in steps a) through e).

⁵
 $q_{\text{total}} = 100\text{J} + 3340\text{J} + 4180\text{J} + 22590\text{J} + 85\text{J} = 30295\text{J} = 30.295\text{kJ} = 30.3\text{kJ}$

Experiment B: Measuring Specific Heat of a Metal

Purpose: To determine the specific heat of copper.

Caution: Goggles and gloves are required. Boiling water can cause burns.

Apparatus and supplies: Simple Constant pressure calorimeter, Bunsen burner, platform balance, iron ring and stand, burette clamp, two 250 ml beaker, 100 ml beaker, 180 mm test tube, 50 grams of copper shots, an 8-ounce Styrofoam cup, Celsius thermometer.

Apparatus: A simple constant pressure calorimeter is used to measure the release or absorption of heat energy during a physical or chemical process in an aqueous solution. It is also called a "coffee" cup calorimeter. This device consists of two concentric polystyrene cups nested inside of a 250 ml beaker with a thermometer and stirrer inserted into the cup through a plastic foam covering the cups. (See Diagram 1 of Appendix.)

Procedure: Measure 50 g of copper shots in 100 ml beaker and transfer it to a standard size test tube. Secure the test tube by a burette clamp in a 250 ml beaker filled with 150 ml of water. Using a Bunsen burner, bring the water to boil and allow it to boil vigorously for 5 minutes. Measure the temperature of boiling water. Secure a coffee cup filled with 100 ml of distilled water inside of a 250 ml beaker. Record the temperature of the water inside of the cup. Remove the test tube containing the copper shots from the boiling water and transfer its content into the cold water in the cup. Measure the temperature of the cup containing the copper shots after 10 seconds, and record all data.

Formula and Calculations

$$\Delta T (\text{water}) = T_f - T_i \quad H (\text{water}) = m (C_p) (\Delta T)$$

$$\text{Heat absorbed by water} = (\text{mass of water})(C_p \text{ of water})(\Delta T \text{ of water})$$

$$\text{Heat absorbed by water} = \text{heat lost by the metal}$$

$$\Delta T (\text{metal}) = T_f - T_i \quad H (\text{metal}) = m (\Delta T) C_p$$

$$C_p \text{ of (metal)} = -H \text{ of water} / (m(\text{mass of metal})(\Delta T \text{ of metal}))$$

If the correct answer for this experiment is 0.38 J / g. C°

$$\text{Percent error} = \frac{|\text{Experimental value} - \text{Accepted value}|}{\text{Accepted value}} \times 100\%$$

Data	Mass of copper shots	_____	g
	Initial temperature of boiling water	_____	°C
	Initial temperature of water in the cup	_____	°C
	Final temperature of the water in the cup	_____	°C
	Specific heat of copper	_____	J/g °C
	Percent Error	_____	%

Experiment C: Measuring Heat Transfer in an Endothermic Dissolution Process

Purpose: This experiment is designed to calculate the heat absorbed by a solvent in dissolving process.

Apparatus and Supplies: Simple constant pressure calorimeter, distilled water, granular Potassium Chloride (KCl), Celsius thermometer, electronic balance.

Procedure: Weigh the inside cup of a calorimeter and add 50 g of water into the cup. Reassemble the calorimeter. Weigh exactly 2.5 g KCl. Determine the temperature of the water in the calorimeter to the nearest 0.5 °C. Add the KCl to the water in the calorimeter and swirl gently. As soon as temperature stays constant for 10 seconds record the temperature of the mixture to the nearest 0.50 °C. Calculate the number of joules absorbed in the dissolving process and the molar heat of solution of KCl.

A thermister connected to a computer monitor may be used instead of a thermometer to measure instantaneous changes taking place during dissolving process. Using 4.0 g, 5.5 g, and 7.0 gram samples of KCl to separate 50 g samples of water in order to obtain sufficient data to determine the mean and standard deviation for the experimental results and to calculate the number of joules absorbed in the solution process.

Formulas and calculations:

Heat absorbed = (mass of water) (specific heat of water)(change in temperature)

Molar heat solution = number of Joules absorbed / number of moles of KCl

If the correct answer for this experiment is 10 kJ/mole, calculate the percent error.

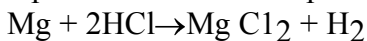
$$\% \text{ Error} = \frac{|\text{Experimental value} - \text{Accepted value}|}{\text{Accepted value}} \times 100\%$$

Data

Mass of water in the calorimeter	_____	g
Mass of KCl added	_____	g
Initial temperature of water	_____	°C
Final temperature of solution	_____	°C
Joules of heat released or absorbed	_____	°C
Moles of KCl added	_____	moles
Molar heat of solution	_____	kJ/ mole
Percent error	_____	%

Experiment D: Measuring Heat Transfer in an Exothermic Reaction

Purpose: This experiment is designed to calculate the heat released from a single replacement reaction represented by the following equation:



Caution: Hydrochloric Acid: Avoid contact with eyes, skin, or clothing. Do not breathe

vapor. Use adequate ventilation and goggles. Vapor or solutions of HCl can cause severe burns.

Apparatus and Supplies: Simple constant pressure calorimeter, magnesium ribbon, 1. M HCl and Celsius thermometer.

Procedure: Measure a piece of magnesium ribbon 22 cm. long which weighs approximately 0.2 g. Weigh the inside cup of a calorimeter and add exactly 150 g. of 1. M HCl. Reassemble the calorimeter and read the temperature of the solution on a Celsius thermometer to the nearest 0.5 °C. Curl the ribbon into a small ball and drop it into the acid solution of the calorimeter. Swirl slowly so that the magnesium doesn't cling to the sides of the calorimeter. Record the temperature of the acid solution 10 seconds after the reaction has stopped. If a computer monitor is available instead of using a thermometer, place the thermometer in the solution to measure the instantaneous changes in temperature. Use 0.4 g, 0.6 g and 0.8 grams of magnesium ribbon in 1. M HCl solution to get sufficient data to determine the mean and standard deviation for the experimental results. The computer will graph temperature in Celsius versus time in seconds.

Assume the specific heat of the acid solution to be the same as water. Calculate the number of joules of heat released by the reaction and the number of joules that would be released by one mole of magnesium = enthalpy change for a reaction.

Formulas and Calculations:

Heat released = (mass of HCl solution) (specific heat of water) (change in temperature)

Molar heat of reaction = number of joules released / moles of magnesium

If the correct answer for this experiment is - 922 k J/mole, calculate percent error.

Percent error = $\frac{\text{Experimental value} - \text{Accepted value}}{\text{Accepted value}} \times 100\%$

$$T = T_f - T_i \quad q = - (m) (C_p) (\Delta T)$$

H reaction = q / Moles Mg

moles Mg = (g Mg) (1 mole Mg) / 24.3 g Mg

Data:

Mass of HCl used	_____ g
Mass of magnesium used	_____ g
Initial temperature of the acid	_____ °C
Final temperature of the solution	_____ °C
Heat released or absorbed	_____ joules
Moles of magnesium used	_____ moles

Molar heat of reaction _____ kJ/mole
 Percent Error _____ %

Experiment E: Measuring Heat Transfer in a Neutralization Reaction

Purpose: To determine the amount of heat released in an acid-based neutralization reaction.

Caution: Solutions of acids and bases can produce burns if they come in contact with bare skin. Goggles and gloves are required.

Apparatus and supplies: A simple constant pressure calorimeter, 250 ml beaker Celsius thermometer, glass rod, 50 g 1.0 M HCl solution, and 50 g 1.0 M NaOH solution. Both acid and base solutions should be at room temperature.

Procedure: Add 50 g of 1.0 M HCl to a 250 ml beaker. Secure a thermometer in the beaker and record the temperature in Celsius. Gradually pour 50 ml of 1.0 M NaOH into the beaker containing the acid. Stir the neutralized solution and record the highest temperature read on the thermometer to the nearest 0.5 °C.

Neutralization equation: $\text{HCl} + \text{Na OH} \rightarrow \text{Na Cl} + \text{H}_2\text{O}$

Formulas and Calculations

Heat released = (mass of neutralized solution)(Cp of water) (ΔT of solution)

$$\Delta T = T_f - T_i \qquad q = - (m) (C_p) (\Delta T)$$

If the correct answer for this experiment is -57.3 kJ/mole, calculate the percent error.

Percent error = $\frac{\text{Experimental value} - \text{Accepted value}}{\text{Accepted value}} \times 100\%$

Experiment F: Measuring Heat Transfer in Combustion Reaction of Solids

Apparatus: An Oxygen Bomb (constant volume) calorimeter with isothermal jacket consists of three main parts: Steel combustion chamber which houses the sample, oxygen gas and ignition wires. Steel bucket which holds measured amount of water, thermometer, and the steel combustion chamber. The outer jacket which is used to thermally insulate the entire apparatus. In an isothermal system the jacket, Temperature remains constant while the bucket temperature rises. The energy changes can be measured by noting the temperature changes in a measured amount of water surrounding the reaction chamber. This apparatus is used for combustion of solid substances in powder form such as carbohydrates, benzoic acid, etc. (See Diagram 2 of Appendix.)

Procedure Summary: Benzoic acid is in a powder form and needs to be compressed into pellets. Weigh out 1.0 g of benzoic acid for each pellet to be made, and press them it into

pellet form. Cut 10 cm long length of Iron ignition wire and wrap two ends around two electrodes and loop around the pellet. Move the pellet into the body of the bomb and screw cover over it. Immerse the bomb into the steel bucket containing 1000 g of water. Slowly let 25 atm of oxygen into the bomb. Lower the thermometer into the calorimeter. Attach the rubber belt to the stirring motor. Push both ignition button and timer button at the *same* time. After 20 seconds take temperature reading. When the run is complete, turn off the stirring motor, lift and move the cover. Next, lift the metal bucket out of the calorimeter, then remove the bomb from the bucket. Dry the bomb gently, and open the gas outlet valve to relieve the inside pressure gently. Check the inside walls of the bomb for beads of water or soot. These are signs of complete combustion. (See Diagram 4 of Appendix.)

Experiment G: Measuring Heat Transfer in Combustion Reaction of Liquids and Gases Apparatus: Flame Calorimeter with adiabatic jacket

In an adiabatic system the jacket temperature is kept the same as that of the bucket temperature. The enthalpy change on combustion of gases, such as natural gas (90% methane), propane, and butane isomers are usually determined in a flame calorimeter. A gas is burnt in a flame with excess oxygen and the heat produced is measured by observing the rate at which the combustion products heat a known quantity of water. The apparatus must be calibrated using electrical heating. This apparatus working at constant pressure gives ΔH directly from the heat evolved on combustion. The result of such an experiment gives -2877 kJ/mole for the standard enthalpy change on combustion of n-butane. (See Diagram 3 of Appendix.)

Equation for combustion: $\text{C}_4\text{H}_{10}(\text{g}) + 6.5 \text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5 \text{H}_2\text{O}(\text{l})$
 $\Delta H = [\text{Hf}(\text{product(s)})] - [\text{Hf}(\text{Reactant(s)})]$

$\Delta H(\text{com})[\text{n-C}_4\text{H}_{10}] = [4(\text{CO}_2)(\text{g}) + 5(\text{H}_2\text{O}(\text{l}))] - [1(\text{C}_4\text{H}_{10}(\text{g}) + 6.5(\text{O}_2)(\text{g}))]$

$\Delta H = [4(-393.5) + 5(-285.8)] - [1(-888.0) + 6.5(0)] = [(-1575) + (-1429)] - [(-888.0) + 0]$

$\Delta H(\text{com}) = -3003 + 888 = -2115 \text{ kJ/mole}$ (an exothermic reaction)

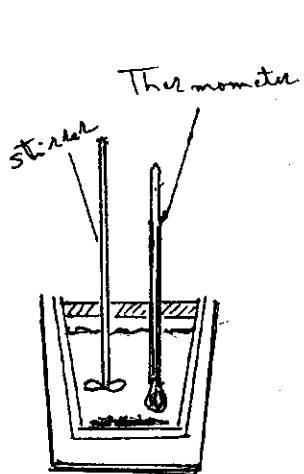
Practice Questions and Problems

1. Sketch a simple calorimeter and label its parts.
2. Sketch a "bomb" calorimeter and label its parts.
3. What is the medium of heat transfer or "working substance"?
4. What are the requirements for a "working substance"?
5. How is absorption or release of heat energy detected in a calorimeter?
6. What are the exothermic and endothermic reactions?
7. List the types of heat transfer measurements that require the use of a calorimeter.
8. Why is the study of heat energy important?
9. Define thermodynamics.
10. Give several examples on application of thermodynamic principles.

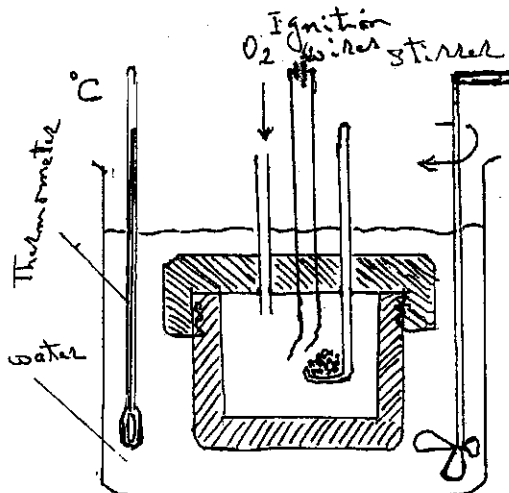
11. Write a thermodynamic equation for Gibb's free energy and label its parts.
12. Define q , ΔE and w in a thermodynamic equation.
13. Define energy, heat, and temperature.
14. Name the units used in the measurement of heat energy.
15. Write a formula for calculating a change in temperature.
16. Define heat of fusion, heat of vaporization.
17. What are the units for heat of fusion, heat of vaporization, and heat capacity?
18. What is calorimetry?
19. List three different types of calorimeters.
20. Explain what determines a dissolution process to be endothermic or exothermic.
21. List three pieces of information necessary to calculate heat absorbed by a calorimeter.
22. Write an equation for calculating heat released by a substance.
23. Write an equation for neutralization reaction of nitric acid and potassium hydroxide.
24. Write a balanced equation for combustion of propane gas in a calorimeter.
25. Explain how graphical data analysis can be done using a lab computer.
26. What are a thermistor and a monitor?
27. How is the minimum energy supplied to a "bomb" calorimeter for combustion?
28. Give specific examples of the following energy conversions: (a) chemical to heat, (b) electrical to heat, and (c) electrical to light.
29. What concept is based on the sensation of "hotness" and "coldness"?
30. What are the individual units of a temperature scale called?
31. What are the two fixed points on which the Celsius temperature scale is based?
32. On the Celsius scale, what is the freezing point of water?
33. How are temperatures below the freezing point of water indicated on the Celsius scale?
34. What is the boiling point of water on the Kelvin scale?
35. How do you convert Celsius temperature to Kelvin temperature?
36. Convert 25° Celsius to Kelvin scale.
37. Describe what happens when two bodies of matter of different temperatures are brought together.
38. How many calories of heat must be added to 250 g of water to raise its temperature from 20°C to 25°C?
39. Calculate the heat required to melt one 5-g of ice cube at 0°C to give water, also at 0°C. [Given: heat of fusion of ice = 334 J/g]
40. How much heat is released when 15 g of steam at 100° C condenses to give 15 g of water at 100°C? [Given: heat of vaporization of water = 2260 J/g]
41. Define enthalpy, entropy, and free energy.
42. Describe the change in (a) enthalpy, ΔH° , and (b) entropy, ΔS , when ice melts spontaneously.
43. Why is it difficult to measure the total energy of a chemical system?
44. A 40.0 g sample of a metal at 90°C is placed in a calorimeter containing 50.0 g of water at 25°C. The temperature stopped changing at 33°C. What is the specific heat of the metal? [Given $C_p(\text{H}_2\text{O}) = 4.18 \text{ J/g}^\circ\text{C}$]
45. A 3000 g mass of water in a calorimeter has its temperature raised by 4.0°C while an exothermic chemical reaction is taking place. How much heat is transferred to the

water by the heat of the reaction?

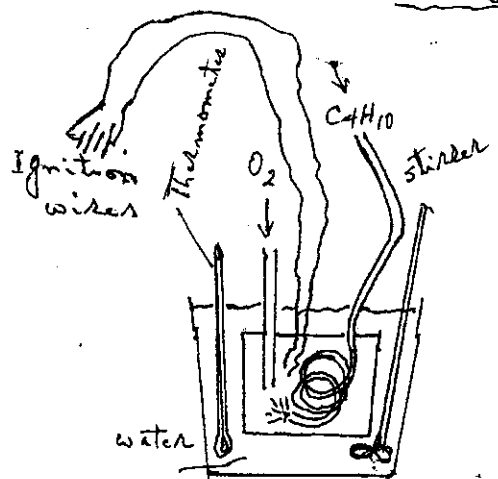
46. Calculate the change in enthalpy (ΔH) for the exothermic reaction
 $3 \text{ CO (g)} + 2 \text{ Fe}_2\text{O}_3 \text{ (s)} \rightarrow \text{Fe (S)} + 3 \text{ CO}_2 \text{ (g)}$. [Given: $\Delta H_f(\text{CO}_2) = -393.5$,
 $\Delta H_f(\text{Fe}_2\text{O}_3) = -184.2$, $\Delta H_f(\text{CO}) = -110.5 \text{ kJ/mole}$]



Constant Pressure
Simple Calorimeter
Diagram 1

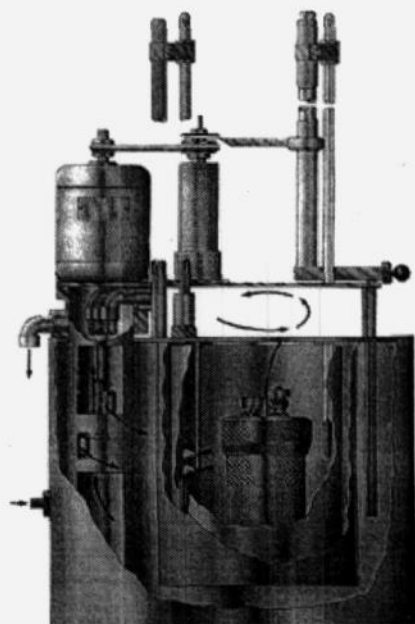


Constant Volume
(Bomb) Calorimeter
Diagram 2

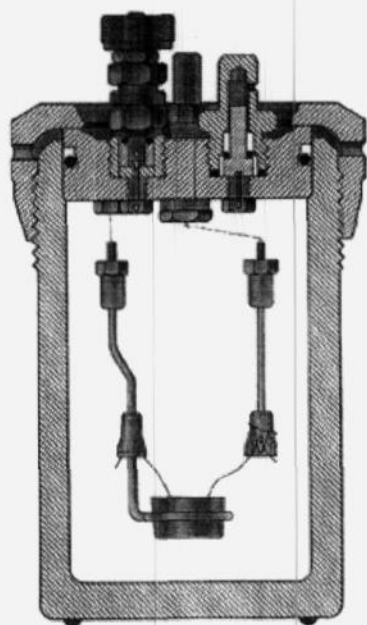


Flame Calorimeter
Diagram 3

Diagrams 1, 2, and 3



**Calorimeter
cross-section**



**Bomb
cross-section**

Diagram 4

NOTES

1. The Background Knowledge section concerning Colorimetry was written by J. E. Kunzler in *The Encyclopedia of Chemistry*, Reinhold Publishing Corporation.
2. External Calibration and Programming of the I2Probe (used in Calorimetry) was obtained from appendix F of 21st Century Laboratory Chemistry from Test Tubes to Computers by J. Marshall and S. Bott.
3. Although specific readings in °C and K of a substance are different, an interval in °C and K are identical, that is $\Delta^{\circ}\text{C} = \Delta\text{K}$.
4. The range is 4.18-4.22 over the liquid state of water 0°-100°C. In the range convenient in the laboratory (20°– 60°), the specific heat is relatively constant at 4.18. In calories (the older units of heat), the specific heat of water is 1 calorie/g °C.
5. Heat of reaction, solution, etc., are customarily given in kJ, not J. However, to avoid confusion we will not convert to kJ until the last step on the data pages.

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Student Reading List

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Herron, Dudley J., David V. Frank, and Jerry L. Sarquis. *Heath Chemistry*. Lexington, MA: Heath, D. C. and Company, 1993.

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Suggested Film List from HISD Media Resource Video Catalog

1. Combustion - An Introduction To Chemical Change	MS	03769
2. Dipole Molecule H ₂ O	S	VC14070
3. Energy in Vaporization & Electrolysis of H ₂ O	S	VC14068
4. It's a Chemical: Phase Changes	MS	14077
5. Lab Safety: Accident At Jefferson High	MS	LD17193
6. Solutions	S	VC13830
7. Using the Bunsen Burner and Working With Glass	MS	VTI3101

Suggested Field Trips

1. Exxon Oil Company Laboratories
2. Houston Water Processing Plant Laboratories
3. Rohm & Haas Company Laboratories
4. Shell Oil Company Laboratories

List of required equipment and laboratory supplies for every two students are mentioned within each experiment.