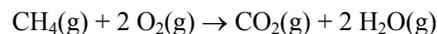


One doesn't discover new lands
without consenting to lose sight
of the shore for a very long time.
--André Gide

Bond Breaking and the Heat of Reaction

All chemical reactions take place with either an absorption or release of energy. Generally this energy is in the form of heat, but in some processes it may take the form of mainly light, or a mixture of forms including some mechanical energy such as sound. Whatever the case, the conclusion we could draw from this aspect of chemical change is that energy is somehow stored in the chemicals and during a transformation there is sometimes excess energy (in which case it will be released) or sometimes not enough energy (in which case it will be absorbed from the surroundings).

The change in energy is due mainly to bond rearrangement during a reaction. Whether there is a net absorption or release of energy depends on the number of bonds broken and formed as well as the strength of those bonds. For example, in the combustion of methane:



we could imagine the reaction taking place by all of the reactant bonds breaking to make individual atoms and then these separated atoms later recombining to form the products. While it is unlikely that the actual chemical process happens in this way, theory and experiment show that the *net* energy difference between reactants and products is the same regardless of the pathway. Therefore, using bond energy values from your text book (p. 291) we would have:

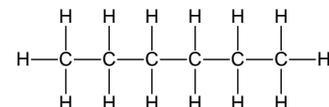
$$4(\text{C-H}) + 2(\text{O=O}) = 4(414 \text{ kJ}) + 2(499 \text{ kJ}) = \text{energy to break bonds (+)}$$

and

$$2(\text{C=O}) + 4(\text{H-O}) = 2(799 \text{ kJ}) + 4(460 \text{ kJ}) = \text{energy to make bonds (-)}$$

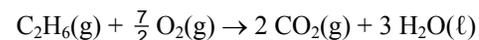
The sum of these two values is -784 kJ--in other words, 784 kJ is *released* when one mole of methane is burned. The experimental heat of combustion is -803 kJ. So it is possible to *estimate* the energy change using a table of experimentally determined bond energies, but such estimates are limited by a number of factors. The most important limitation is the fact that the bond energies have been measured or calculated for gaseous species. In addition, the energy required to break several similar bonds in a molecule is not the same. For example, the energy needed to break one of the hydrogen-carbon bonds in methane is not the same as the energy needed to break the second, third, or fourth one (although they are similar).

In this experiment you will be looking at a series of hydrocarbons from the *alkane* family. Alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$ where n is an integer. Thus methane (CH_4) is the first member of the family. When you use your bunsen burner in the lab you are burning methane and the heat given off is the heat of combustion (or, more generally, the *heat of reaction*). Quantifying how much methane is burned in a given amount of time is difficult. However, as the number of carbon atoms in alkanes increases, the compounds eventually become liquids at room temperature and the mass of a compound burned is more easily measured. Three liquid alkanes will be used in this experiment. They are hexane (C_6H_{14}), heptane (C_7H_{16}), and octane (C_8H_{18}). A *structural* formula for hexane is shown below:



Heptane and octane are similar with longer carbon chains (the Greek prefixes contained in their names gives the number of carbons in the molecule).

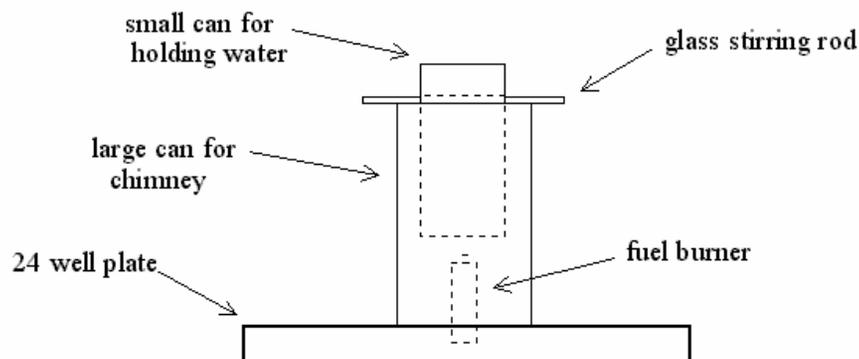
The combustion reactions for the alkanes are all similar. Carbon dioxide and water are products, as the example for ethane below shows:



While bond energy calculations give an estimate of heats of reaction it is also possible to *measure* the energy change during a reaction in the laboratory. Such measurements are generally done in an insulated container (a calorimeter) that is otherwise open to the atmosphere so that the pressure remains constant during the reaction. The heat that is absorbed or released under such conditions is known as q_p . When this number is scaled to a molar quantity it is called the **enthalpy change** of the reaction, ΔH_{rxn} .

Reactions between liquids and solids are easily carried out in such a device or a reaction may be carried out externally (as in this experiment) and the heat conducted to the calorimeter which is filled with water. A thermometer can be used to follow heat flow during the reaction. If the temperature is observed to rise, this means that heat is flowing from the system into the thermometer (and other surroundings). Such a reaction is described as *exothermic* and the enthalpy change is given a negative (-) sign. If the temperature falls, this means that heat is being absorbed from the surroundings into the system, indicating an *endothermic* reaction and making ΔH_{rxn} positive (+).

In this experiment you will use a very simple constant pressure calorimeter which consists of a metal can suspended over a small fuel burner. The can is surrounded by a larger can that helps to hold in some of the heat from the fuel combustion and also limits drafts. Water is held in the smaller can and its temperature change during the burning of the fuel (a combustion reaction) is used to determine the heat of reaction.



While this basic set-up is not insulated, it is possible to obtain good results from it if the experiment is conducted in a consistent manner and if you know something about the heat loss characteristics of the arrangement. The systematic error can be reduced by estimating the "calorimeter constant" or the heat capacity of the calorimeter (i.e., the number of joules required to raise the temperature of the calorimeter by 1°C.). Actually, your measurement will also include a factor for the heat that is lost from the calorimeter during the experiment. To determine the calorimeter constant you will burn a fuel with a known heat of reaction (or heat of combustion in this case) and use the known value to estimate the calorimeter constant. The following example illustrates this.

When 1.0 g of benzoic acid is burned in a calorimeter containing 2,950 g water, the temperature rises from 24.3 to 26.3°C. The heat of combustion for benzoic acid is -3,223 kJ/mol. What is the calorimeter constant (or the heat capacity of the calorimeter)?

$$1) \text{ heat} = \text{mass} \times \Delta t \times \text{specific heat} + \text{heat capacity of calorimeter} \times \Delta t$$

2) the heat is -3223 kJ/mol; in this case; we don't need the sign but we need to scale this value for only one *gram* instead of one mole:

$$\frac{1 \text{ g}}{122.1 \text{ g/mol}} \times \frac{3223 \text{ kJ}}{\text{mol}} = 26 \text{ kJ}$$

we also need to change to joules to match the specific heat of water (4.184 J/g°C), so heat (or q) = 26000 J

$$3) 26000 \text{ J} = 2950 \text{ g} \times 2.0^\circ\text{C} \times 4.184 \text{ J/g}^\circ\text{C} + \text{HC} \times 2.0^\circ\text{C}$$

$$4) \text{HC} = 660 \text{ J}^\circ\text{C}$$

In this experiment you will use the heat of reaction for the combustion of hexane (C₆H₁₄) as your reference to determine the calorimeter constant. The measured value is -4.1 x 10³ kJ/mol. Once you have used this value to determine a calorimeter constant for the experimental set-up, you should be able to determine the heats of combustion for heptane and octane. Converting the data you collect into molar heats of reaction (ΔH_{rxn}) is illustrated in the example below.

2.00 g of liquid pentane (C₅H₁₂) is burned and the heat produced is applied to a calorimeter containing 100.0 g water originally at 10.0°C. The final temperature of the water after reaction is 55.9°C. Assuming that the specific heat of water 4.184 J/g°C, what is the heat of reaction *per mole of pentane*? (the calorimeter constant or heat capacity is 1700 J/°C)

First we need to find out how much heat the reaction produces for the amount of pentane burned:

heat = heat gained by water + heat gained/lost by calorimeter

$$\text{heat} = (\text{mass} \times \text{specific heat} \times \Delta t) + (\text{heat capacity} \times \Delta t)$$

$$q_p = m s \Delta t + C \Delta t$$

$$\text{heat} = [100.0 \text{ g} \times 4.184 \text{ J/g}^\circ\text{C} \times (55.9 - 10.0^\circ\text{C})] + [1700 \text{ J/}^\circ\text{C} \times (55.9 - 10.0^\circ\text{C})]$$

$$\text{heat} = 9.72 \times 10^4 \text{ J}$$

But this is for 2.00 g of C₅H₁₂. To determine the heat of reaction *per mole* of pentane, a simple proportion will suffice:

$$\frac{97.2 \text{ kJ}}{2.00 \text{ g}} = \frac{x \text{ kJ}}{72.0 \text{ g}}$$

or x = -3.5 x 10³ kJ/mole pentane. [negative sign added]

Once you have determined the heats of combustion for heptane and octane then you can see if there is any relationship between the number of carbon bonds and the energy released during combustion.

Preparing to experiment

You will be provided with the following materials:

1. a calorimeter set-up
2. a thermometer probe
3. three labeled fuel burners
4. hexane, heptane, octane
5. a 24-well plate
6. matches
7. a supply of water at approx. 10°C (use about 100 mL each time)
8. a 100 mL graduated cylinder

Design an experiment to determine the heat released by burning hexane, heptane and octane to raise the temperature of a water sample by 20°C. [see **Technique**]

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Technique

1. Using the temperature probe

Using an electronic temperature probe is not quite the same as using an ordinary thermometer. The response time is somewhat slower. For this first time here are some hints to help you get the most out of the instrument.

- a. Set up the CBL unit to read temperature *continuously* (i.e. every 0 seconds)
- b. Stir the water while heating so that the probe is not resting directly on the bottom of the can
- c. Continue to stir a little after extinguishing the flame to be sure the water temperature is the same throughout.

2. Using the calorimeter set-up

The calorimeters have been made so that the inner can will sit at the correct height when the fuel burner is held in a 24-well plate. Be sure to use them that way. This will minimize heat escape. We also use one other trick to help control heat loss. By starting with water below room temperature (which will slowly pick up heat from the

room) and ending with water about the same number of degrees above room temperature (which will slowly lose heat to the room) we can effectively ignore that factor. Of course, not all of the heat from the flame goes into the water, but that's what the determination of the calorimeter constant is all about. Incidentally, although it is better to mass the water in the calorimeter rather than assume a density of 1.0 g/mL (since the graduated cylinder won't deliver every last drop you measure out), in the interest of time, we *will* measure volume and assume the mass is the same. Also, be sure to take a look at the bottom of the can after each heating. It needs to be clean and dry each time.

3. Using the fuel burners

All three alkanes evaporate pretty fast at room temperature. They also attack the plastic burner containers slowly. For that reason, you will find the burners are empty. You can fill them from the bottles of the fuels provided near the balances. They should only be filled about half-way. Be sure to empty them (into the correct beaker!!!!) at the conclusion of the lab. Before lighting the burner, have all your preliminary measurements made and the mass of the burner recorded. Inspect the wick and adjust it so that it is *flush* with the top of the tube and DOES NOT project out of the tube. **THIS IS VERY IMPORTANT. TOO MUCH WICK WILL PRODUCE A DANGEROUSLY LARGE FLAME THAT COULD ENGULF THE ENTIRE BURNER.** After heating, measure the mass of the burner as soon as possible to minimize errors due to evaporation.

Analysis

These questions should be answered in your laboratory notebook following your data and observations.

1. Use your data from the combustion of hexane to determine the calorimeter constant. [note that although the example calculation on a previous page shows 1 g of compound used, you probably did NOT burn 1 g of hexane in this experiment!!!]
2. Calculate the heat or enthalpy of reaction (ΔH_{rxn}) per mole of heptane and per mole of octane burned.
3. The molar heat of combustion for pentane (C_5H_{12}) is -3.5×10^3 kJ/mol. Using this value and the value given for hexane as well as those determined in (2) for heptane and octane, graph the molar heat of combustion vs. the number of C-C bonds in each compound. Does there appear to be a regular relationship? If so, describe it and try to give a brief explanation based on bond energies. [remember, energy is *absorbed* to break bonds and *released* when bonds are formed....hint: try writing balanced equations for the combustions of hexane, heptane and octane, then compare the number of bonds formed in the products for each reaction with the number of C-C bonds in the reactant]

[Don't be fooled!!! -5000 kJ is *more* heat than -4000 kJ]