HEATS OF COMBUSTION OF SOME
CYCLIC HYDROCARBONS

by

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INTRODUCTION

Determinations of heats of combustion are of prime importance in thermochemistry because they offer one of the best experimental methods for acquiring data to calculate heats and free energies of formation, and heats of reaction. In addition, accurate energy data such as those obtainable from heats of combustion are of use in solving many questions concerning molecular structure. Since about 1920 there has been considerable activity directed toward the attempt to discover additive relations between heats of combustion, or values derived from them, and molecular structure (1, 2, 3, 4).

As a basis of correlation the method of bond energies has proven most useful. A value can be calculated from combustion data which gives the total heat of dissociation of a polyatomic substance into atoms, or the sum of the energies of the bonds in the substance. Individual bond energies are not obtained in this manner, except in the case of diatomic molecules, and accordingly, it has become customary to define the mean values obtained as the bond energies. Thus the heat of formation of methane, CH_4, from gaseous atoms at $18^{\circ}C$ is, $\Delta H_{291^{\circ}} = -349.3$ kcal. per mole, from which the value 87.3 kcal. per mole is calculated as

the C-H bond energy, although it is highly unlikely that
equal quantities of energy are required to dissociate each
successive hydrogen atom from methane. Heats of formation
calculated by the bond energy method usually agree within
one or two kilocalories per mole with the experimentally
determined quantities, and in spite of their approximate
nature hold considerable interest for the structural
chemist.

Many cases have been cited in which bond energies
defined in the above manner are not strictly additive (5,
6, 7, 8, 9). In some instances (benzene, for example) it
is not possible to represent the structure of the molecule
by a single classical valence bond formula, and the mole-
cule is more accurately described by a resonance hybrid of
several structures. The difference between the observed
heat of formation and that calculated for one of the hybrid
structures is taken empirically as the value for the reso-
nance energy relative to the structure considered.

It has been suggested (10, 11) that the concept of
constant bond energies be replaced by the assumption that
there is a one-to-one correspondence between bond length and
bond energy of atoms in a molecule. Thus it has been found
that the carbon-carbon, carbon-oxygen, and carbon-nitrogen
single, double, and triple bond energies fall on a smooth

curve when plotted against bond length. This suggests that the heat of formation of a molecule might be directly deducible from its geometry without consideration of bond character or resonance. While the method gives results in fair agreement with experiment in the case of many molecules, it gives rather poor agreement for the class of compounds called cyclic hydrocarbons, particularly those in which the carbon atoms are "strained" from their normal tetrahedral angles. In general the bond lengths are observed to be slightly shorter in strained hydrocarbons, which on the basis of the above theory gives a resultant increase in bond energy. This, however, is in contradiction to experiment. As might be expected in the case of highly strained compounds, such as cyclopropane, cyclobutane, etc., the bond energies are found to be less than the normal values. Consequently in calculating the heat of formation from bond energies it is necessary to make some correction for strain which the molecule possesses by virtue of its geometrical configuration.

A theory proposed by Kilpatrick and Spitzer (12) (see next section for discussion) takes into account the strain involved in calculating the heats of formation of cyclic hydrocarbons, and is shown to be in good agreement with the observed values for the strain energies per CH_2 group

in cyclopropane and cyclobutane. A portion of the work described in this thesis is devoted to determinations of the heats of combustion of spiropentane and methylcyclobutane for purposes of comparison with those predicted by the method of Kilpatrick and Spitzer.

There are two types of apparatus commonly used for measurements of heats of combustion, from which data having an accuracy of a few hundredths of a percent may be obtained. Both types are non-isothermal, although the ordinary method which employs a calorimeter surrounded by a constant temperature jacket (13) is commonly called the "isothermal method". In the other method, properly named adiabatic, the temperature of the jacket is maintained equal to that of the calorimeter (14).

Little can be said to favor one method over the other as far as precision or accuracy are concerned. The work of Gilbert, et al. (15, 16, 17, 18, 19) may be cited as an example of the capabilities of a properly operated adiabatic calorimeter, while the measurements of Huffmann, et al. (20, 21, 22, 23) show those of the "isothermal" type. An erudite and interesting discussion of the relative merits of the adiabatic and ordinary methods of calorimetry is given by White (24).

Since the disadvantages usually attributed to the

ordinary method are easily overcome, or reduced to a minimum, with a reasonable amount of care, and the apparatus and measurements are considerably less complicated than those required for the adiabatic method, the constant temperature jacketed calorimeter was used in these investigations. A large portion of this thesis is devoted to a description of the construction, operation, and calibration of an "isothermal" calorimeter.

THEORY OF NON-TETRAHEDRAL CARBON ATOMS

The theory of non-tetrahedral carbon atoms plays an important part in discussions of cyclic hydrocarbons, such as cyclopropane, △ , cyclobutane, ☐ , and spiropentane, ⋈ , in which one or more of the valence angles of the carbon atom is restricted by the geometry of the molecule. The theory is derived from the method of valence bond orbitals first applied to molecules by Pauling (25) and based on the following postulates. A single bond arises from the interaction of two unpaired electrons of opposite spin derived from different atoms. Bonding occurs in the direction of overlap of the orbital wave functions of two atoms, and the strength of the bond is proportional to the amount of overlap.

In applying these postulates to the carbon atom it is assumed that the orbitals are formed from a combination, or hybridization of s and p orbitals. The hybridization is made in such a way as to give the maximum possible bond strength to the hybrids. The result of such a calculation for the carbon atom is that four equivalent bonds are obtained with directions toward the corners of a regular tetrahedron. The strength of the resulting bonds is two, a value greater than that for either an s or p orbital alone. [The strengths of bonds have been

taken as proportional to the product of the magnitudes of
the angular dependence of the bond orbitals (26), giving
rise to the value 1 for an s orbital, and 1.732 for a p
orbital.]

While hybridization of s and p orbitals in carbon
compounds was originally introduced to provide four sym-
metrical atomic orbitals with strong directional proper-
ties, it being supposed that attached groups were located
along the lines of greatest electron density, there is now
sufficient evidence available from accurate measurements
of molecular dimensions to state with a fair degree of
certainty that the ideal hybrid bonds of quantum mechan-
ics are found only when the symmetry of the bonded system
is identical with that of the hybridized atomic orbitals.
It seems that the presence of any strain in the molecule
causes the angles between the bonds to deviate from the
ideal values which are characteristic of unstrained mole-
cules.

It is interesting to see the results of applying the
theory to a carbon atom in which one of the valence angles
is specified. Duffey (27) has made some calculations for
cyclopropane, cyclobutane, and cyclopentane by construct-
ing s, p hybrids with maxima in the direction of the
required bonds.

As is customary, although probably not justified in

many cases, the radial parts of the wave functions ψ_s, ψ_{p_x}, ψ_{p_y}, ψ_{p_z}, were assumed to be so similar that their differences could be neglected. The angular parts of the wave functions, normalized to 4π by the integral,

$$\int_0^{2\pi} \int_0^{\pi} \psi_i^2 \sin \vartheta \, d\vartheta \, d\varphi$$

are

$$s = 1$$
$$p_x = \sqrt{3} \sin \vartheta \cos \varphi$$
$$p_y = \sqrt{3} \sin \vartheta \sin \varphi$$
$$p_z = \sqrt{3} \cos \vartheta$$

where ϑ and φ are the angles used in spherical polar coordinates.

New functions of the form

$$\psi_i = a_i s + b_i p_x + c_i p_y + d_i p_z$$

were then sought to yield maximum bond strength and normalized to 4π, which requires that

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1$$

The normalization condition together with the orthogonality requirement,

$$a_i a_j + b_i b_j + c_i c_j + d_i d_j = 0, \quad i \neq j$$

are sufficient for determining the coefficients a_i, b_i, c_i, d_i, where $i = 1, 2, 3,$ or 4, corresponds to the bonds of carbon, if it is assumed that bonds 1 and 2 are equivalent and that bonds 3 and 4 are equivalent.

Carrying out the calculations Duffey was led to the rather unreasonable value of 180° for the H-C-H angles in cyclobutane and cyclopropane.

Shortly afterwards, Kilpatrick and Spitzer (12) performed similar calculations which yielded somewhat more reasonable results. They abandoned the stringent requirement of maxima in the direction of the required bonds, and assumed that the bond strength was proportional to the value of the orbital in the desired direction, whether or not the maximum of the orbital lay in that direction. This treatment showed that considerably stronger bonds resulted in the direction of neighboring atoms.

Two of the orbitals available, say ψ_1 and ψ_2, were used in forming the carbon-carbon bonds determined by the geometry of the molecule, and the directions of the other two bonds were taken in the maxima of the other two orbitals, ψ_3 and ψ_4. In order to simplify the equations, the maxima of orbitals ψ_1 and ψ_2 were chosen in the xz plane, equally inclined to the z axis. Accordingly, the orbitals ψ_3 and ψ_4 must be in the yz plane and also be equally inclined to the z axis.

After the requirements of normalization and orthogonality have been met, the functions have the form:

$$\psi_1 = as + bp_z + (1/2)^2 p_x$$
$$\psi_2 = as + bp_z - (1/2)^2 p_x$$
$$\psi_3 = bs - ap_z + (1/2)^2 p_y$$
$$\psi_4 = bs - ap_z - (1/2)^2 p_y$$

where
$$b = + (1/2 - a^2)^{1/2}$$

The values of a and b were determined by setting $\frac{\partial \psi_1}{\partial a} = 0$, so that ψ_1, would have a maximum value in a particular direction, ϑ_o, in the xz plane. Solving, it is found that

$$a = \left(\frac{1}{2 + 6 \cos^2 \vartheta_o} \right)^{1/2}$$

$$b = \left(\frac{3 \cos^2 \vartheta_o}{2 + 6 \cos^2 \vartheta_o} \right)^{1/2}$$

In order to calculate the angle, ϑ_{34}, between the bonds formed by the orbitals, ψ_3, and ψ_4, the expression

$$\tan \vartheta_{34} = \frac{-2 (1 + 3 \cos^2 \vartheta_o)^{1/2}}{3 \cos^2 \vartheta_o}$$

is given.

Table I gives the results of the calculations of Kilpatrick and Spitzer in terms of $2\vartheta_o$., the C-C-C angle, ψ_{o_1}, the bond strength of the "fixed" carbon bond orbital,

TABLE I[*]

Bond Strengths

$2\vartheta_0 = \vartheta_{12}$	Strength of bonds (1) and (2) ψ_{01}	ϑ_{34}	Strength of bonds (3) and (4) ψ_{03}
$0°$	1.414	$126°52'$	1.982
$60°$	1.887	$121°58'$	1.989
$90°$	1.984	$115°23'$	1.995
$108°$	2.000	$109°58'$	2.000
$109°28'$	2.000	$109°28'$	2.000
$120°$	1.996	$105°50'$	1.998
$180°$	1.932	$90°$	1.732

[*] Taken from Kilpatrick and Spitzer, Reference (12)

ϑ_{34}, the H-C-H angle, and ψ_{03}, the bond strength of the "variable" carbon bond orbital.

By assuming that the bond energy is proportional to the square of bond strength, and taking the values (4) 59 and 87 kcal. per mole for the normal carbon-carbon and carbon-hydrogen bond energies, the values 8 and 2 kcal. per mole are obtained for the strain energies per CH_2 group in cyclopropane and cyclobutane. (Kilpatrick and Spitzer (12) calculate 10 kcal. per CH_2 group for cyclopropane. This value seems to be in error.) The experimental values (28) are 10 and 4 (estimated from cyclobutane derivatives) and if one follows the authors' suggestion that "probably about 2 kcal. should be added to the calculated values for torsional strain (29)", the agreement is excellent.

Furthermore it is to be noted that the exterior angle in cyclopropane is given in Table I as $121°58'$ and not $180°$. This value is in fair agreement with the value of $120° \pm 8°$ reported (30) for the H-C-H angle in spiropentane from electron diffraction experiments, and $112° \pm 4°$ found for monochlorocyclopropane and 1, 1-dichlorocyclopropane (31).

As pointed out by Kilpatrick and Spitzer the ideas of s,p hybridization and proportionality of bond energy to square of bond strength are approximations, and the

agreement of the calculations with experiment is per-
haps fortuitous. It will be shown later in the
Discussion of this thesis that the agreement between
the heats of formation of spiropentane and methyl-
cyclobutane calculated from the theory, and those
derived from the combustion data is such as to lend great
support to the theory as a method for estimating thermal
data for cyclic hydrocarbons from molecular structure.

Strain in non-tetrahedral carbon atoms has been
reported recently (32) to have been discussed by Coulson.
Unfortunately the writer has not been able to obtain the
publication and consequently can only present the material
included in the abstract.

By assuming that the bonds to attached atoms do not
necessarily lie along the direction of maximum charge
density of the atomic orbital, a mixing function, λ, is
defined by writing the carbon orbitals as

$$\psi(\lambda) = (s + \lambda p) \div (1 + \lambda^2)^{1/2}.$$

This function, λ, which may also be regarded as a
hybridization ratio, is treated as a variational
parameter and the energy, E, of a molecule is expressed in
terms of λ, and E (λ) minimized. In this way a de-
scription of the molecule in terms of the pure valence

state approximation of perfect pairing is obtained. By
applying the method to cyclopropane a value of 113° is
obtained for the H-C-H angle, and the two orbitals from
any one carbon atom make an angle of about 106° with one
another. It is found that less overlapping of the wave
functions of paired electrons is more than offset by a
decrease in strain energy at the carbon atom, and gives
a gain of about 5 e.v. per CH_2 group over a model (27)
in which the angle is set at 90°.

It is also stated that it is possible to account
qualitatively for the anomalous bond shortening asso-
ciated with strained compounds. The difficulties
arising in the determination of bond energies for strained
cyclic hydrocarbons from conventional bond order - energy
curves was mentioned earlier (p. 3) in this thesis.

THE CALORIMETRIC SYSTEM

General Considerations for an Isothermal Calorimeter (24).

The requirements of an isothermal calorimetric system are a calorimeter, the outer surface of which has all points always at the same temperature as the liquid within, and a closed jacket which has at all times a known constant temperature. The calorimeter should be separated from the jacket by a distance of about one centimeter and the materials in the space between the two should be good heat insulators of small heat capacity. The liquid most commonly and conveniently used in the calorimeter is water which must be kept well stirred so that its temperature is always sensibly uniform throughout. The energy of stirring should be constant and preferably small. The entire surface of the calorimeter should be in contact with the liquid contained within and as little of the liquid surface as possible exposed to prevent evaporation.

Description of the Apparatus.

The calorimetric system used in these investigations was of the isothermal type constructed largely from parts of the adiabatic system used by Gilbert, et al. (15, 16,

17, 18, 19). A schematic representation is shown in Figures 1 and 2. The calorimeter C is supported on three Lucite pegs mounted in brass collars on the floor of the calorimeter jacket, W. The pegs fit into small copper indentures in the bottom of the calorimeter and thus serve to position the vessel in the proper position reproducibly each time the pegs are placed in the recesses. In this manner an air gap of about one centimeter is obtained between the calorimeter and the water jacket, W.

The calorimeter proper: The calorimeter vessel is of the form shown in Figures 2 and 5. It is constructed from copper sheet which is heavily plated with nickel and highly polished. The interior is divided into two unequal sections by means of a thin copper partition (Figure 1, D) which does not extend completely to the top or bottom. The smaller compartment contains the stirrer, S, a two bladed stirrer which directs the water downward under the copper divider and after circulating about the bomb contained in the larger compartment returns over the top of the partition to the stirrer well. The stirrer shaft in addition to having the two blades for stirring, has mounted near the top a well into which oil may be put. An inverted well from the top of the calorimeter fits into the oil pocket (not shown in

Figure 1: Schematic Diagram of Calorimeter System
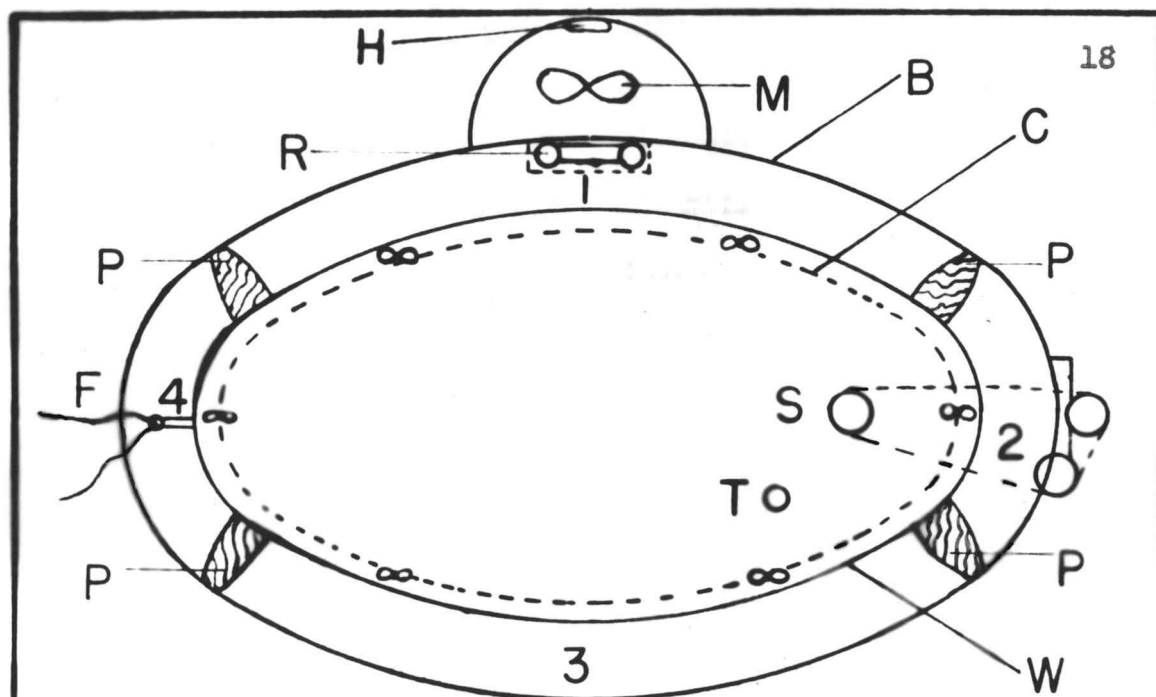
Figure 2: Top View of Calorimeter and Bath
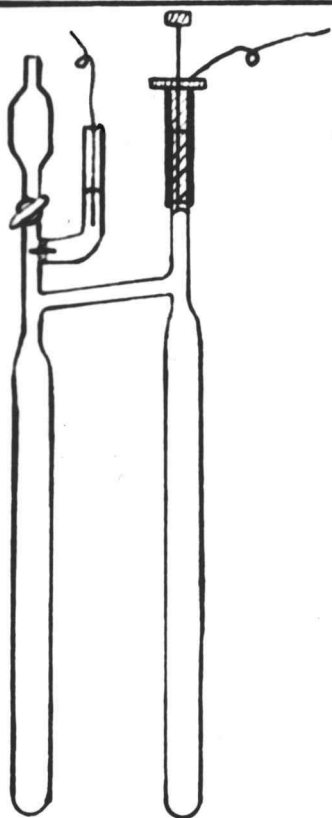
Figure 3: Thermoregulator
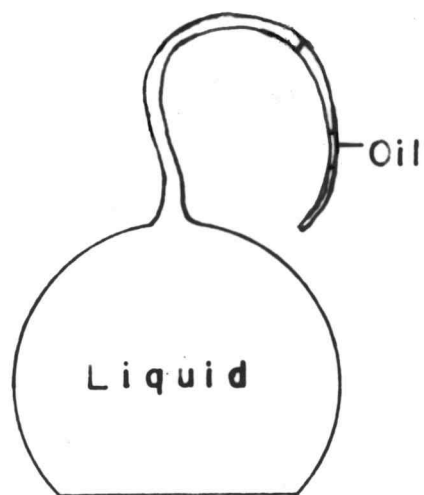
Figure 4: Design for

Unsealed Ampoule

Figure 5: Photograph showing the water bath containing
heater, stirrer, and thermoregulator, calorimeter jacket and
lid, calorimeter, bomb, calorimeter stirrer, and platinum
resistance thermometer.
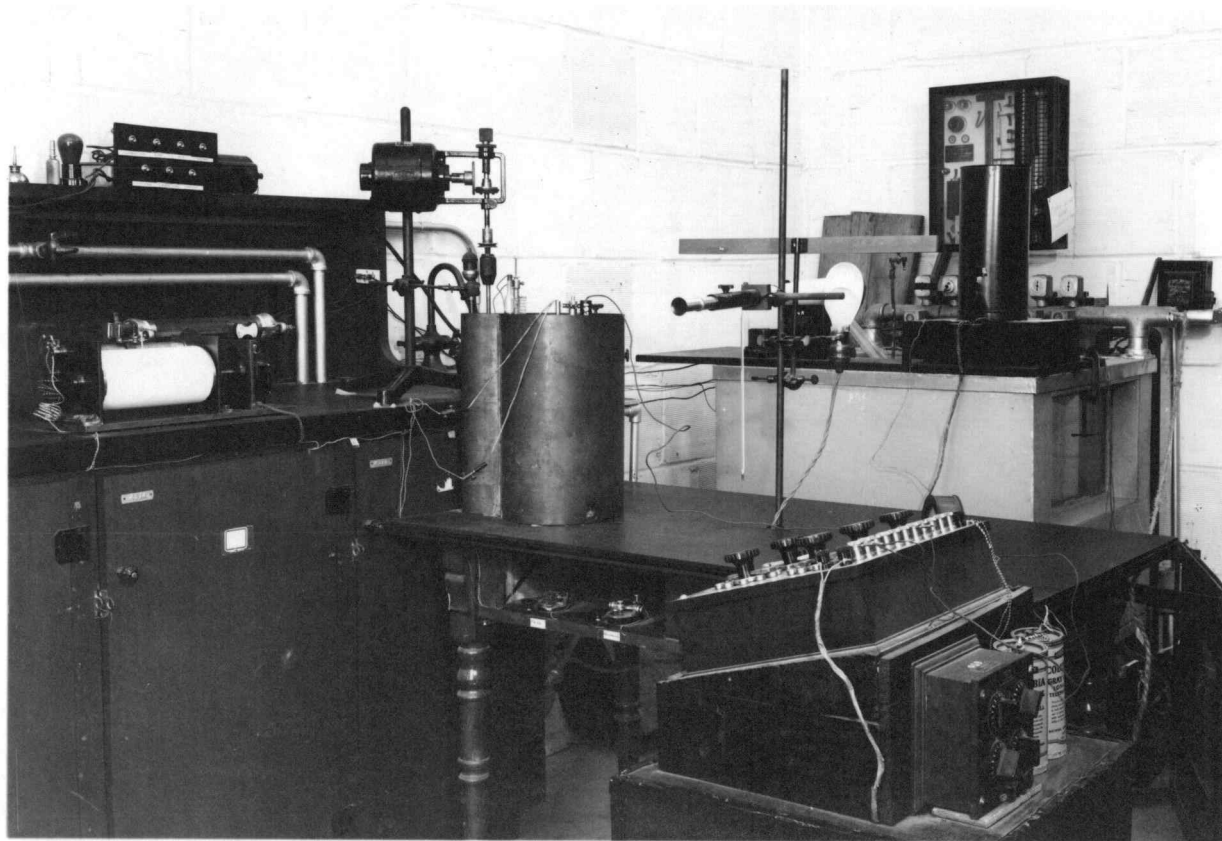
Figure 6: Photograph of the calorimeter assembled as for determinations of heats of combustion and showing relative positions of the auxiliary equipment.

Figure 1) and thus forms a seal around the stirrer shaft
to prevent evaporation of water from the calorimeter.
(This arrangement was later found to be unsatisfactory
due to rubbing of the stirrer in the oil pocket. It was
replaced by a cork gasket, G, placed on top of the
calorimeter around the stirrer hole and extending to the
jacket lid thereby forming a water tight seal. It is
believed that the oil seal is to be preferred providing
a stirrer shaft can be made to run straight enough to
eliminate rubbing.) The portion of the shaft which ex-
tends through the calorimeter top contains an inset of
lucite to cut down heat transfer to and from the calo-
rimeter. Immediately above the top of the calorimeter
a small disc is mounted on the stirrer shaft and contains
a small hole which may be made to engage a finger pro-
truding from the top of the jacket and thus serve as a
means of screwing the stirrer into the stirring tower of
the jacket cover after the cover is in place. A portion
of the calorimeter lid about the stirrer is a screw cover
(not shown in Figure 1) making it possible to remove the
stirrer and all its parts in one piece whenever desired.
The portion of the calorimeter top over the bomb compart-
ment contains a friction fitting lid through which the
bomb may be passed.

The bomb (360 mls capacity) is the illium double

valve type, obtained from the Parr Instrument Company,
Catalogue No. 1101, and modified by legs of bakelite
about one centimeter high to aid in circulation of water
under the bomb.

Near the stirring screw cap is a hole (T of Figure 2)
for insertion of the platinum resistance thermometer.
The thermometer is equipped with a rubber stopper about
its stem which closes the hole completely, and accord-
ingly the calorimeter, when the thermometer and the two
lids are in place.

Firing connections, F, are made near the top of the
calorimeter through the end nearest the bomb by means of
small indentures (one insulated) into which fit expansion
rivets soldered on the end of the firing leads. Connec-
tions inside the calorimeter from the opposite side of
the indentures are made by wires terminating in special
fittings for connecting to the bomb.

The bottom of the calorimeter contains three copper
discs which extend through the bottom and contain recess-
es on each side. The legs of the bomb fit into the
recesses on the inside and thus serve to obtain a repro-
ducible placing of the bomb. Lucite pegs from the bottom
of the jacket fit into the recesses on the opposite side.

The calorimeter jacket: The calorimeter jacket, W,
is also made of copper, nickel plated and highly polished

on the inside. The bottom contains the aforementioned
lucite pegs and the top, made from brass, is completely
removable, being held in place by means of six wing taps.
A rubber gasket made from a sample of Pure Gum Compound
#3825 obtained through the courtesy of the U. S. Rubber
Co., Passaic, N. J., is used to obtain a water tight
seal.

The top contains two openings built up in the form
of chimneys and coinciding with the stirrer and thermome-
ter holes in the calorimeter when it is in place. The
stirrer tower contains a coupling for connecting to the
stirrer shaft and then passes through a bearing and
terminates in a sprocket wheel for a chain drive.

A small nickel plated copper tube bent in a right
angle leads into the wall of the jacket below the top and
serves as a shield and guide for the firing leads. The
firing leads are very flexible being made from a number
of strands of No. 40 copper wire twisted together and
covered with glass spaghetti.

The outside of the calorimeter jacket is vaned
(Figure 5) to permit more rapid heat equalization between
it and the water bath. Four wooden positioners, (Figures
1 and 2, P) are cemented to the outside of the jacket to
assure reproducible and rigid positioning of it in the
water bath.

The water bath: The constant temperature water
bath, Figure 5, and B of Figures 1 and 2, consists of a
large copper can, oval in shape, and of about 22 liters
capacity. On one end is mounted a worm gear and cog
wheel arrangement for stirring the calorimeter by means
of a chain drive. The chain is driven by a synchronous
motor at a constant rate of 425 rpm. At the side of the
water bath is a well containing the stirrer M and heating
element H. The stirrer is a straight shaft on which are
mounted double bladed propellers that turn in such a
manner as to drive the water down through the stirrer
well, out under the calorimeter jacket, and return it
over the top. The heating element is a knife type, 225
watts, manufactured by CENCO. The auxiliary wiring is
such that the heater may be made to function at full
capacity, 225 W, until the bath is brought to temperature
and then approximately 180 ohms resistance may be placed
in series with it to reduce it to a 50 watt heater for
maintaining the temperature at a constant value,
$\pm 0.001°C$. The amount of heat furnished by the heater
is such as to balance that lost to the room through
leakage from the non-insulated walls of the bath and when
functioning properly with the bath set at approximately
1 - 1 1/2 degrees above room temperature, maintains a
constant temperature to approximately $\pm 0.001°C$., by

turning on and off practically continuously throughout its operation. A setting of 26°C. for the bath temperature proved satisfactory most of the time but had to be varied somewhat depending on the time of year.

The temperature of the bath is regulated by means of a mercury thermoregulator of the two finger type. See Figure 3 and R of Figure 2. The making and breaking of the mercury contact activates a very sensitive relay which in turn activates a larger relay which turns the heater on and off. A wiring diagram of the entire electrical circuit for the calorimeter system exclusive of the Mueller Bridge and galvanometer is shown in Figure 7.

Temperature measurements: Temperatures are measured by means of a Leeds and Northrup platinum resistance thermometer in conjunction with a Mueller Bridge and high sensitivity galvanometer placed at one meter from a scale. The sensitivity of the galvanometer is such that one mm. scale deflection corresponds to approximately 0.00005°C. The Mueller Bridge was calibrated in the manner described by The National Bureau of Standards (33) and the ice point resistance of the platinum resistance thermometer as given in the certificate by the National Bureau of Standards, November 27, 1939, duplicated.

The temperature of the bath was measured by means of
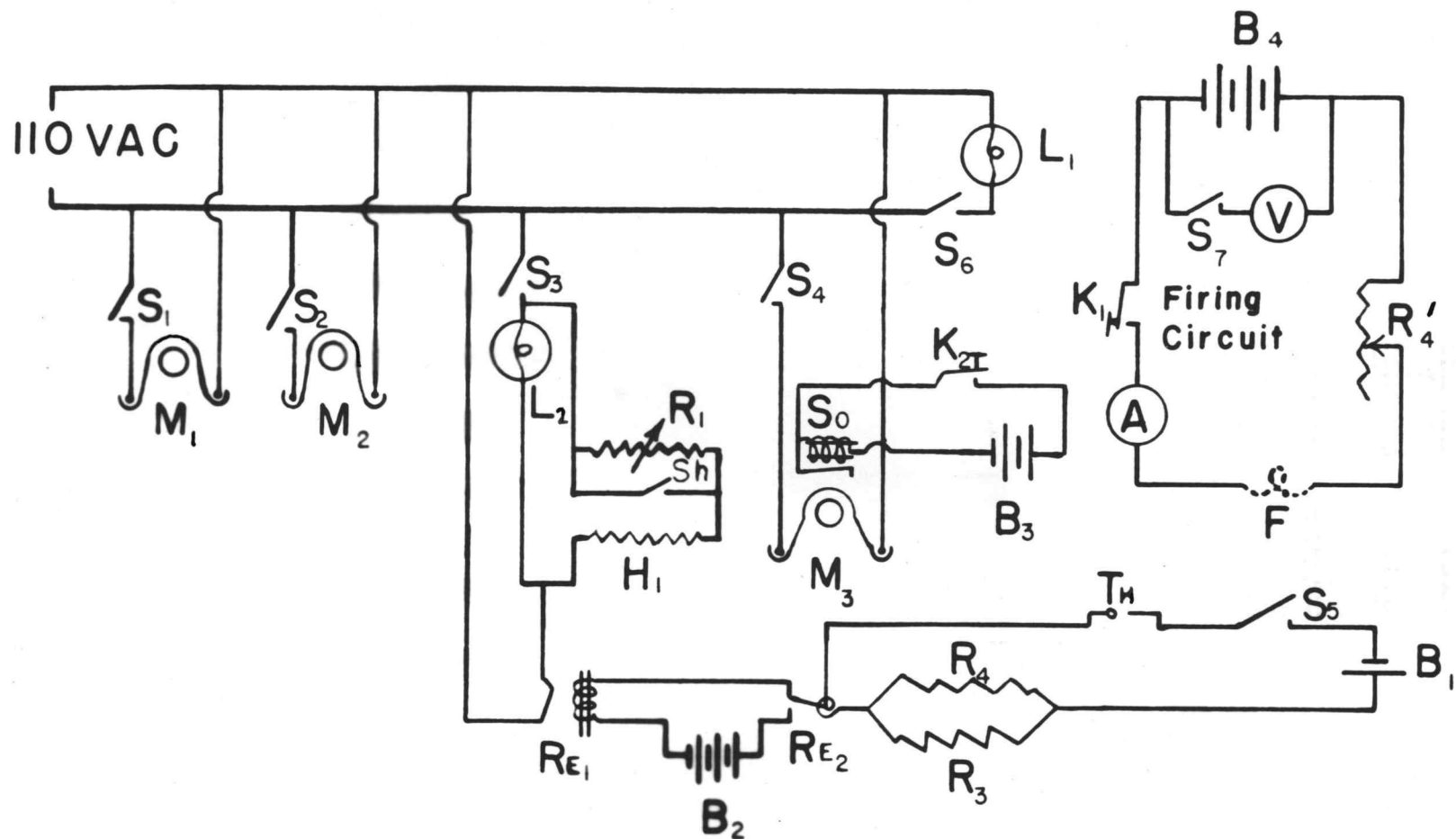
Figure 7: Schematic Wiring Diagram for Calorimeter
See next page for legend

LEGEND FOR FIGURE 7

S_1, S_2, S_3, S_4, S_5, S_6, S_7, Toggle switches for power
sources.
M_1, Motor for jacket stirrer; Cenco, 110VAC, Type SA-12,
60 cycle, 1725 rpm, 1.8 amp., 1/12 HP.
M_2, Motor for calorimeter stirrer; GE, 110VAC, Type SKS,
50/60 cycle, 1500/1800 rpm, 1.9 amp., 1/30 HP.
M_3, Chronograph Motor, Bodine, Type KYC-22, 115VAC, 60
cycles, 1 rpm, Torq. 120 in. oz.
L_1, Light for galvanometer, 60W bulb
L_2, Indicator light for heater, red bulb, 10W.
R_1, Variable resistor, 725 ohm set at approx. 180 ohm.
R_3, Resistor, 2.0 Meg.
R_4, Resistor, 0.25 Meg.
R_7, Variable resistor, 1 ohm set at approx. 0.5 ohm.
SH, Switch for shorting out resistance R_1, knife type,
single pole, single throw
H_1, Heater for water jacket, CENCO 225 W knife type
So, Solenoid, activating chronograph pen
K_1, Micro switch
K_2, Telegraph key
B_1, Battery, 2V
B_2, Battery, 6V
B_3, Battery, 8V
B_4, Battery, 6V
V, Voltmeter, 0----10VDC
A, Ammeter, 0-5 amps.
F, Firing leads and platinum wire
Re_1, Weston Magnetic Relay, Model 630
Re_2, Weston DC Relay, Model 534
Th, Thermoregulator

the platinum resistance thermometer at various points 1, 2, 3, 4, indicated in Figure 2 and found to be essentially constant. In an actual combustion experiment the temperature of the bath is observed at point 3 for a period of five to ten minutes both before and after the combustion in order to determine the constancy of the bath temperature. For determining the rate of heating or cooling and the temperature rise during the combustion, the thermometer is inserted into the calorimeter at point T of Figure 2.

The chronograph: It is necessary to have some automatic time recording device for observations made during the period just after ignition of the charge when the temperature is rapidly rising. A chronograph is a convenient instrument for such purposes. For these investigations a drum type chronograph pictured at the left in Figure 6, was used. The drum is turned at a rate of 1 rpm. by means of a synchronous motor. The circumference of the drum is thirty centimeters making it possible to read times to one-tenth second by placing the recorded tape over millimeter graph paper on a viewing box. A pen traces a steady line around the drum, and at times corresponding to certain predetermined resistances the pen can be made to deflect approximately one millimeter to the side of its regular path by tapping a telegraph key which

activates a small electromagnet to which the arm carrying the pen is attached. A spring is also attached to the pen arm so that a momentary depressing of the key causes the pen to move sideways and then return immediately to its normal position.

A worm screw on which the pen assembly is mounted causes the pen to move down the drum cylinder at approximately two millimeters per minute.

In order for a synchronous motor to be of value as a timing device it must be furnished with an electric current of constant frequency. Tests were made of the constancy of the frequency of the current furnished Oregon State College by attaching the electromagnet causing the pen to deflect to the master clock in the Physics Department. This clock was adjusted so as to send an impulse to the pen every second and cause a deflection from its normal straight course. Sixty such deflections should occur in one revolution of the drum, and providing the motor is functioning properly, the sixty deflections produced during the next minute should fall exactly beside those of the previous minute, and so on, for as long as measurements are being made. Thus a straight line of deflections should be plotted across the drum under ideal conditions.

It was found for observations of an hour's duration

made at various hours of the day from 8 AM to 8 PM and
on different days of the week that the frequency of the
current actually did fluctuate noticeably. The greatest
fluctuation which occurred at 8 PM on a Thursday was
0.6 second per hour, while the slightest fluctuation of
0.1 second per hour occurred at 5 PM on a Sunday. The
average fluctuation was 0.2 second per hour. No sen-
sible correlation was found between fluctuations and
hours of the day, or days of the week. As a rule no
general trend was observed in the fluctuations such as to
cause a continued loss or gain in time of the chrono-
graph during the hour. The fluctuations were always of a
gradual nature lasting for a period of perhaps twenty
minutes, after which the chronograph either regained its
normal speed, or fluctuated approximately the same amount
in the opposite direction. It was generally indicated
that the fluctuations were such as to average out to a
constant speed over a period of many hours. The observa-
tions during a combustion experiment last for approxi-
mately one hour and hence current fluctuation can cause
some error in the timing. It may be seen however from
the method of calculation (see section on Form of Records
and Calculations) that the error introduced in the value
for the heat of combustion is no more than 0.0001 percent
for the greatest fluctuation observed during the

chronograph calibration.

It was found during the calibration of the chronograph that a warm-up period of approximately twelve minutes for the motor was needed before any consistent results could be obtained. Hence it became normal procedure to start the chronograph motor, and also the stirring motors, well in advance of the time when data were being collected.

The firing circuit: The platinum wire-filter paper technique was used to fire the charge in the bomb (20). The ignition circuit is represented schematically in Figure 7. The dotted portion, F, represents a platinum wire between two electrodes in the bomb. Number 34, B. and S. gauge platinum wire, 0.006" diameter and 7.5 cm. in length, was first annealed by heating to redness in a flame and then wound twice around a 1/16" diameter rod to form a two coil spiral in which one end of the filter paper strip used to ignite the charge was placed. The electric current was furnished from a 6 volt storage battery and heated only the platinum spiral to incandescence. The current was kept low enough to avoid fusing the wire.

Since the resistance of cold platinum wire is less than that of the hot wire, a change in the current reading was observed during the time the circuit was

closed. After many observations it was concluded that this change took place in the first 0.1 sec. that the current was flowing. Hence current readings were made to determine an initial value and a steady state value, (after 0.1 sec.). The energy for the initial period was calculated by averaging the two readings of the current. A period of 0.6 sec. for closing the firing switch was found satisfactory for ignition and was timed by a 3-second-sweep stop watch. The electrical energy was calculated by using the formula, $EIt \div 4.183 = cal.$, and gave a correction of 1.28 cal.

CALIBRATION OF THE CALORIMETER

Fundamentally, a bomb calorimeter is a device for comparing the heat liberated in a combustion process with a known amount of electrical energy. In the electrical method of calibration a measured amount of electrical energy is supplied to the calorimeter and the corresponding rise in temperature determined. All conditions are maintained as nearly like those to be used in an actual combustion experiment as possible. In this way it is possible to determine the heat capacity of the calorimeter and its contents directly in joules per degree.

Very careful measurements (34) of the heat of combustion of benzoic acid have been made, and the bomb process clearly defined (35), so that it is possible without serious loss of accuracy to use the combustion calorimeter to compare the heat of combustion of some substance under investigation with that of benzoic acid and thus eliminate the equipment necessary for an electrical calibration. As in the case of the electrical calibration it is necessary to duplicate as nearly as possible in actual combustion determinations the conditions used in calibration. It is particularly important that the time-temperature curves for the two processes

be as nearly alike as possible. Inaccuracies in
.calorimetric observations, particularly those due to
heat leakage to the surroundings, are minimized in this
manner. This modern method of calibration, essentially
a substitution method, was first published by Rossini
(36) in 1931. By its use the advantages of the dif-
ferential twin calorimeter are introduced into the
simple calorimeter.

Combustion Procedure.

The following procedure was used in the calibration
with benzoic acid and subsequent determinations of heats
of combustion were made to adhere as closely as possible
to the calibration procedure.

The water bath was filled with water at approxi-
mately the correct temperature, and the stirring motors
and chronograph turned on. The full bath heater was
turned on by closing the shunt, Sh of Figure 7, and
allowed to function at full capacity until the bath was
at temperature as indicated by the red heater light,
which was turned off automatically when the bath was at
temperature. Then the shunt was opened and the heater
allowed to function as a 50 watt heater during the
remainder of the experiment.

While the bath was coming to temperature the

platinum crucible having been previously ignited and
plunged into distilled water twice while glowing, and
stored over phosphorous pentoxide in a dessicator, was
weighed on a micro-balance sensitive to a thousandth of
a milligram. The air of the balance was kept dry by
means of two containers of calcium chloride and the
temperature of the balance case was recorded before each
weighing. The weights used with this balance were
calibrated by the method of substitution and comparison
made with a set of weights calibrated by the National
Bureau of Standards. The small corrections found were
applied to the face value of the weights.

After weighing the crucible, the filter paper used
for ignition purposes was weighed, and finally the pellet
of benzoic acid.

The pellets of benzoic acid were made from powdered
benzoic acid dried over phosphorous pentoxide for at least
forty-eight hours and weighed approximately (before com-
pressing) on an analytical balance to achieve fair reproduc-
ibility in the size of the pellets. (Average 1.08 grams,
or a weight in grams equal to three times the volume of
the bomb in liters (37). The powdered acid was compressed
reproducibly into 3/8 inch pellets by means of a weight
falling four times from a given height on the plunger of
the press. Considerable difficulty was experienced in

the beginning in weighing and compressing pellets due to the electrostatic charge which accumulated on the benzoic acid in the process. It was discovered that a small amount of thorium placed in the dessicator with the benzoic acid when drying, eliminated the charge, so that no trouble was encountered thereafter in making pellets of benzoic acid.[*]

As soon as the weighings were complete, the crucible with its pellet were placed in the holder of the bomb head and the filter paper ignitor placed in position in the platinum wire loop above and to the side of the pellet. As much of the wire and loop as possible was placed around the outside and away from the lip of the crucible. Otherwise the wire is often melted by the combustion blast. The filter paper fuse was cut from Whatman Ashless Filter Paper No. 42 in the form of a strip approximately 2 mm. wide and 4.5 cm. long. One end was placed in the coil and the other end against the opposite side of the crucible, thereby obtaining a spring effect which tended to give the same type contact of paper to wire each time and in addition, to shove the platinum

wire and coil from the lip of the crucible (see Figure 1).

The water to saturate the bomb space was placed on the bottom of the bomb by means of a hypodermic syringe with an automatic adjustor set to deliver the same amount of water each time, namely 1.08 grams, or a value in grams equal to three times the volume of the bomb in liters (37). The reproducibility of the amount of water delivered by the syringe was checked several times by weighing on the micro-balance and found to vary not more than 0.2%. The syringe is to be recommended as an accurate and rapid method of placing a reproducible amount of water in the bomb.

After the bomb with its contents was closed it was flushed twice by filling to 10 atmospheres with tank oxygen and releasing to atmospheric pressure. The bomb was finally filled to a gage pressure of 30 atmospheres. An indication of the efficiency of the flushing process was given in some later experiments when the bomb was not flushed. The amount of sodium hydroxide required to titrate the nitric acid formed in the bomb process for an unflushed bomb was roughly twenty times that for a flushed bomb. During the flushing process, water at approximately 24.6°C. was weighed into the calorimeter. The balance used for weighing the water and calorimeter, is sensitive

to about 0.2 gram, and the total weight of the calorimeter
with water is 3335 grams. The accuracy of the weights
used in this weighing was not known and indeed, is not
important, since the weighing was made only to obtain the
same quantity of water in each experiment, and the same
weights were used each time.

The electrical connections were made to the calo-
rimeter and then it was placed in the jacket, whereupon
the bomb was placed in the calorimeter, the electrical
connections made to it, the ring seal around the stirrer
added, and the cover of the calorimeter put in place.

The calorimeter jacket cover containing the stirrer
was then lowered into position and screwed down against
a rubber gasket by means of six wing screws. A small
cork stopper with openings for the firing leads was
placed in the opening of the tube for the leads, and
another stopper was added to the thermometer chimney
until such time when the thermometer was inserted.

During these last operations it was convenient to
drain the water in the constant temperature bath to such
a height that the calorimeter jacket would be completely
immersed when placed in it and yet not overflow. When
this operation was complete the calorimeter and jacket
were put in place in the bath, the electrical connections
made, the chain drive connected, and the whole assembly

started. After such a disturbance the water bath requires about a minute to come to constant temperature as determined by the platinum resistance thermometer placed at position 3, Figure 2.

When the bath was again at constant temperature the thermometer was inserted in the calorimeter and after a few seconds had elapsed during which time the thermometer came to equilibrium and the chronograph pen was filled with ink, a series of readings were begun and recorded on the chronograph tape to determine the initial cooling rate (heating) of the calorimeter. See Figure 9.

After a sufficient number of readings had been taken to determine the initial cooling rate the charge was fired and the rise in temperature observed and recorded. When the temperature of the calorimeter had reached its peak and again leveled off, another series of readings were taken to determine the final cooling rate.

When these readings were complete the bath temperature was again read at position 3, after which time the apparatus was disassembled and the washings from the bomb titrated with standardized sodium hydroxide (approximately 0.1 N) using brom cresol green as indicator. The titration (about 0.6 ml. for a flushed bomb) was applied as a correction in calories for the formation of nitric acid from a small amount of nitrogen in the oxygen.

The platinum crucible was again ignited, quenched twice in water, and placed in the dessicator awaiting the next combustion.

Form of Records and Method of Computation.

The form of the records taken during a combustion experiment and the method of correcting for heat transfer are essentially those described by Dickinson (13).

Figure 8 shows a sample combustion record. The relation between resistance of the thermometer and time is represented by the curve in Figure 9. The correction for heat transfer consists in extrapolating the resistance-time curves of the initial and final periods to a time, t(m), so chosen that the areas BEF and FGC (Figure 9) are equal.

It may be remarked that the shape of the curve obtained in Figure 9 is a function largely of the design of the calorimeter vessel and the efficiency of stirring. It is necessary to fix the position of all parts of the calorimeter assembly so that flow conditions are reproduced. The circulation of water in the calorimeter must be complete and rapid enough to assure that the temperature observations reflect the average temperature of the calorimeter wall, otherwise an error is introduced into the correction for radiation.

COMBUSTION RECORD
OREGON STATE COLLEGE

Substance *NBS Benzoic acid*			Comb.No. 68	Obs. *GSH*	Date 6-13-49	
Wt. Xible +	6.916253	See	Wt. Fuse	0.008352	33.19	
Wt. Xible	5.819785	Reverse	Wt. Unburned Fuse	E/T	1.28	
Wt. Charge(a)	1.096468	Side	Wt. Carbon			
Wt. Charge(v)	1.097345		Wt. Oil			
Wt. System (air)	3335		Titration	0.678	0.82	
Temp. H_2O	24.8°		Total Excess		35.29	
H_2O in Bomb	1 cc		Calories			

Bomb flushed _2_ times at _10_ atm. & filled to _30_ atm.

Initial Jacket R.	8.2853	Final Jacket R.	8.2852
Initial Room Temp.	24.8	Final Room Temp.	25.9
Initial Bridge Temp.	23.4	Final Bridge Temp.	24.2

		Calculation					Time	Diff.	R	Time	Diff.	R
		Initial	Final		Initial	Final	0 - 14.6		8.0780	13-16.2	*fire*	0.0835
dR		0.0040	0.0009	t(run)	13-16.2	25-27.3			1			.10
dt		571.9	572.7	t(m)	14-31.5	14-31.5			2			2
r(obs)		0.6994	0.1572	Δt	75.3	655.8			3			4
R(mr)		8.0800	8.3328	rΔt	0.000520	0.001041			4			6
a		0.13389		R(obs)	8.083488	8.334241			5			8
a dr/2		0.6778	0.1526	R(cor)	8.084010	8.334241			6			etc
r(cor)		0.6926	0.1587	ΔR	0.250231				7			.3035
K		9.909605	C_v(cal)		10.51				8			4
ΔT		2.479690	Cal. Net		6932.61				9			3
C_p(cor)		2805.74	Mass(cor)		1.097345				90	25-27.3		2
C_pΔT		6957.39	Cal./gm.		6317.59				800			1
Cal. Excess		35.29	R̄		8.2105				10			etc.
Remarks:									1	34-60.0		.3323
									2			
									3			
									etc			
									8.0870			
									25			

Figure 8: Sample
Combustion Record

Figure 9: Typical Time-Temperature Curve from Combustion Observations

A particularly striking example of the efficiency of
stirring in the present work became evident upon analyzing
the curves from various combustions. It may be shown (13)
that if the heat generated in the bomb process were all
distributed to the walls of the bomb instantly, the rise
of temperature of the water would follow very nearly an
exponential law,

$$\theta = 1 - e^{-kt}$$

corresponding to the cooling constant of the bomb in
water. Actually the temperature does follow such a law
after the first few seconds immediately after firing.
Assuming the law to hold, t(m) may be calculated in terms
of θ, the temperature. In order for the condition of
equal areas to be satisfied:

$$\int_0^{t(m)} \left[1 - e^{-kt}\right] dt = \int_{t(m)}^{\infty} \left[1 - (1 - e^{-kt})\right] dt$$

whereupon t(m) = 1/k, and substituting to get the value
of θ_m corresponding to t(m),

$$\theta(m) = 1 - e^{-k/k} = 0.63.$$

Hence t(m) should coincide with the time for the observed

temperature rise to reach 0.63 of its final value.

Originally the calorimeter stirrer was designed with the lower propeller blade about one-half inch from the bottom of the calorimeter, and considerably below the bottom of the partition. The speed of stirring was 225 rpm.

Under these conditions the value of t(m) was determined to be 0.67. By raising the bottom propeller until it was just above the bottom of the partition and increasing the speed of stirring to 425 rpm a value of 0.63 was obtained.

The determinations of t(m) as 0.67 and finally as 0.63 were made by plotting curves of the data obtained from several combustions and constructing the areas BEF and FGC equal when measured by a planimeter.

The difference in temperatures (resistances) corresponding to the points E, and G gives the temperature rise of the calorimeter for the combustion process corrected for heat transfer between the calorimeter and its surroundings, and also for the heat of stirring.

This method of correcting for heat transfer is based on Newton's law of cooling, which may be written in the form:

$$\Delta R / \Delta t = -a \ (R - R')$$

where R is the resistance of the thermometer in the calo-
rimeter and R' its resistance at the constant bath tempera-
ture, the temperature toward which the calorimeter con-
verges if left alone.

In general it is found (38, 39) that for $\triangle R/\triangle t$
positive, i.e. for the temperature of the calorimeter
below that of the jacket, the agreement between observed
and calculated values is good. Probably increased evap-
oration of water from the calorimeter at temperatures
above that of the jacket causes discrepancies at positive
values of $\triangle R/\triangle t$. Accordingly, in calibration and com-
bustion experiments the initial temperature of the calo-
rimeter was adjusted so that after the rise due to the
combustion, the final temperature was only a few tenths
of a degree above that for the bath.

Probably the computation of the results of a com-
bustion can best be explained by a discussion of the en-
tries on the Sample Combustion record, Figure 8.

The items on the top half of the page are for the
most part self explanatory, with the possible exception
of "Wt Unburned Fuse". The form for the combustion
record was drawn up when it was thought that iron wire
would be used for ignition purposes and it was intended
to apply a correction for any wire remaining after a
combustion. The electrical energy, EIt, used to ignite

the filter paper was later recorded under the above
mentioned heading.

The times recorded under the "Time" column are those
read from the chronograph tape after the combustion is
completed. The "Diff" column was used only in case there
appeared to be irregularities in the recorded times from
their appearance on the chronograph tape. In such a case
the method given by Dickinson (Reference 13, Note 12) for
correcting the recorded times for slight variations in
observation and recording was used, and computed from the
variation of the quantities in the "Diff" column.

Under R is entered the resistance readings from the
Mueller Bridge corresponding to the times directly op-
posite. It is necessary during the main period when the
temperature is rising rapidly to have estimated and
recorded the resistances ahead of time. Then the times
are recorded when the galvanometer swings through zero
corresponding to the predetermined resistances. Other-
wise it is impossible to manipulate the bridge dials and
recording key and in addition, read and write down resist-
ances.

The items, dR, under the columns headed "Initial"
and "Final" are differences in resistances (corrected for
bridge corrections) as widely spaced as possible in the
fore and after periods, while the dt are the differences

in times (corrected if necessary for inconsistencies in recording) corresponding to the resistances dR. The next item, r(obs), is the apparent cooling rate during the interval above, and is equal to dR/dt.

The next three items are needed to compute a correction for the observed rate due to the fact that the resistance time curve in the initial and final periods is not quite linear. This correction, designated as $\underline{\frac{adR}{2}}$, is computed as follows:

R(mr) = average resistances in the initial and
final periods, corresponding to points
K and N, Figure 9.

$$a \approx \left[r(obs)_i - r(obs)_f \right] / \left[R(mr)_f - R(mr)_i \right]$$

$$= -\frac{d}{dR} \frac{dR}{dt} \approx -\frac{\left(\frac{dR}{dt}\right)_N - \left(\frac{dR}{dt}\right)_K}{R_N - R_K}$$

Note that $r(obs)_f$ is negative.

r(cor) = r(obs) ∓ adR/2, which is the cooling rate corresponding to the thermometer resistance represented by the point L, between B and E, Figure 9, or a corresponding point between G and C.

The item t(run) is the corrected time of firing

(Initial), or the time (Final) in the post period when a steady rate of cooling sets in, corresponding to point C, Figure 9, or the following point. $\triangle t$ is equal to $t(m) - t(run)$, where $t(m)$ has already been defined. The product of $r(cor)$ and $\triangle t$ is recorded as $r\triangle t$, the absolute value of which is to be added to $R(obs)$ to obtain $R(cor)$. The $R(obs)$ entries are the resistances at the time of firing and corresponding to $t(run)$, Final. $R(cor)$ is, then, the value of the resistance obtained by extrapolating the initial or final resistance-time curve to the time, $t(m)$.

$\triangle R$ is the corrected change in resistance of the thermometer corresponding to $R_G - R_E$ in Figure 9. The difference in the corrections to the bridge for the initial and final readings, $R(cor)$, must, of course, be applied in calculating $\triangle R$.

K is a factor to convert change in resistance to change in temperature and is obtained by differentiating the Callendar equation as described by Dickinson and Mueller (40). It is the value of $\triangle T/\triangle R$ corresponding to the mean value, $\bar{R}$, of $R(cor)$, initial and final, and consequently $\triangle T = \triangle R(K)$.

C_p (cor) is the water equivalent for the calorimeter and parts without the contents of the bomb as determined by the benzoic acid calibration. $C_p \triangle T$ is equal to the

product of C_p (cor) and ΔT. Calories excess is the sum of the heats liberated by the ignition energy, fuse, oil, nitric acid, etc. C_v (cal) is the Washburn correction for reduction of bomb calorimetric data to a common temperature (35) and is equal to

$$S_I (t_H - t_1) + S_F (t_2 - t_H) + \text{wt. pt.} (t_2 - t_1)$$

where the symbols are those defined by Washburn.

Calories net $= C_p \Delta T$ - cal. excess $+ C_v$ (cal)

Mass(cor) $=$ weight of charge in vacuo

Cal/gm $=$ calories net/mass(cor) $= -\Delta U_B /m$,

the actual heat evolved during the combustion per gram of substance burned, corrected to 25°.

The Energy Equivalent of the Calorimeter.

The energy equivalent of the calorimeter used in these investigations was determined by combustion of benzoic acid, National Bureau of Standards Standard Sample 39f. According to the National Bureau of Standards Certificate for Standard Sample 39f, December 17, 1948, the isothermal heat of combustion at 25°C., and under the standard specified conditions is 26428.4 ± 2.6 international joules per gram mass in vacuo. This value was converted to calories by the conversion factor, 1 calorie $=$ 4.1833 joule, yielding $6317.5_9 \pm 0.6_2$ calories per gram

mass. Since the conditions used in these experiments were so close to those defined for the standard bomb process, no correction was applied to the value given by the National Bureau of Standards.

When the calorimeter was first constructed it was planned to use iron wire for igniting the charge. Some twenty-four combustions were made using iron wire for ignition in an attempt to obtain a satisfactory value for the energy equivalent of the calorimeter. The average value so obtained was 2805.1 ± 2.8 calories/degree with a maximum deviation of 5.7 calories/degree. Since these results are obviously unsatisfactory for modern precision calorimetry some changes were necessary in the calorimeter system. The iron wire ignition technique and the stirring of the calorimeter were suggested as two possible sources of variation and both these were changed to the methods described earlier in this thesis (p. 31 and p. 44).

The results of six calibration experiments performed after the changes were made are presented in Table II, and show an average value of 2805.85 ± 0.28 calories/ degree for the energy equivalent. Only six calibration experiments were made; the last two listed were performed approximately three weeks after the first four during which time about forty combustions were made on other materials.

TABLE II

THE ENERGY EQUIVALENT OF THE CALORIMETER
at 25° Centigrade

NBS Benzoic Acid # 39 wt. in vacuo g.	Corr. temp. rise °C.	$C_p \Delta T$ Calc.	Heat from EIt+fuse Cal.	Heat from HNO_3 Cal.	Energy Equiv. Cal/degree	Deviation from mean
1.09601	2.47639	6948.72	34.30	0.76	2806.18	+0.33
1.09223	2.46873	6926.56	36.17	0.74	2805.71	−0.14
1.09168	2.46638	6918.93	32.09	0.76	2805.29	−0.56
1.09735	2.47969	6957.39	34.47	0.82	2805.74	−0.11
1.08836	2.45781	6897.30	31.21	0.81	2806.27	+0.42
1.08916	2.46129	6906.30	35.16	0.80	2805.96	+0.11

[a]Mean deviation

Mean = 2805.85 ± 0.28[a] cal/deg.

COMBUSTION DATA FOR SPIROPENTANE AND METHYLCYCLOBUTANE

Units of Measurement and Auxiliary Quantities.

The results of the combustion experiments are ex-
pressed in terms of the defined calorie, which equals
4.1833 N. B. S. international joules, and refer to the
isothermal process at 25°C. for true mass. The densities
used for obtaining buoyancy corrections to convert
weights in air to true mass were those reported for the
compounds. A table of 1948 atomic weights was used for
calculating molecular weights.

The correction for nitric acid formed in the combus-
tions was made using - 13,960 cal. per mole for the heat
of formation at constant volume from liquid water, gaseous
oxygen, and nitrogen. The heats of formation of water
and carbon dioxide at 25°C. were taken to be 68,317.4 ±
9.6 (41) and 94,051.8 ± 10.8 (42) cal/mole, respectively.

As in the case of the calibration experiments
Whatman Ashless Filter Paper No. 42 was used as fuse
material. The fuse strips were kept in a constant humid-
ity dessicator having a relative humidity of about 30%,
an average value (43) for Corvallis in the summer. The
heat of combustion was determined to be 3974 ± 3 calories
per gm. (Data from two combustions).

Standard White Oil No. 9, USP, obtained from the

Standard Oil Company of California, was used as kindler in some of the combustion experiments. Its heat of combustion was determined as $10,984.3 \pm 0.5$ cal/gm. (Data from two combustions.)

Materials.

The original sample of spiropentane was obtained from the National Advisory Committee for Aeronautics (NACA) and sent to the U. S. Bureau of Mines, Bartlesville, Oklahoma for further purification before the combustion measurements. Dr. Hugh M. Huffman of the Bartlesville Laboratory was kind enough to supply approximately 40 mls. of the purified material estimated from the index of refraction measurements (n_D^{20} 1.41201) to be pure except perhaps for some water. Upon freezing the sample in liquid air and thawing, one small "floater" was observed which was presumed to be ice. The spiropentane was then distilled through anhydrous magnesium perchlorate (Dehydrite) in a closed all glass distilling apparatus. The product so obtained showed no floaters upon freezing and was transferred in a dry box to a ground glass stoppered bottle and stored in a dessicator which was kept in a deep freeze unit. The physical constants given by Murray and Stevenson (44) are boiling point, $38.3 - 38.5°$ at 750 mm, n_D^{20} 1.4117, d_4^{20} 0.755.

The methylcyclobutane was a gift from the NACA Laboratories and labeled pure sample, freezing point -161.51°C, boiling point, 37.18°C at 760 mm pressure, n_D^{20} 1.3878, d_4^{20} 0.7014. Attempts to freeze solid the sample were unsuccessful even after an hour's cooling in liquid air. Upon warming, floaters were observed, and the mixture was then distilled through Dehydrite in a manner analagous to spiropentane. Collection of the product was made in liquid air and obtained in a solid state. Upon thawing no floaters were observed, and the liquid was then transferred in a dry box to its container and likewise stored in a dessicator in a deep freeze unit.

Technique for Burning Volatile Liquids.

The primary difficulty encountered in combustion work involving volatile liquids is determining accurately the amount of substance which enters into the reaction. Two methods have been used:

(1) direct determination by weighing the quantity of material used, and

(2) analysis of the combustion products.

The latter method is rather tedious and requires somewhat elaborate apparatus. Consequently the former method was chosen for the present work.

Considerable difficulty is encountered in construct-
ing, filling, and sealing ampoules for volatile liquids
which will withstand the pressure of the filled bomb and
yet break satisfactorily when ignited. Recently a method
(45) has been described for using unsealed ampoules for
heats of combustion of liquids, and good precision was
reported. The requirements for an acceptable glass
ampoule are not nearly so rigid in the case of unsealed
ampoules and practically any size or shape may be used
so long as the capillary is fine enough to produce negli-
gible evaporation.

A satisfactory design for an unsealed ampoule is
shown in Figure 4. The ampoules are blown from thin
walled glass tubing heated over a very small flame such
as that obtainable from the base of a Bunsen burner. The
tubing is first pulled to a capillary of the desired fine-
ness, the correct length of tubing left on the end of the
capillary to give an ampoule of the proper size,
(approximately 100 mg.) and the glass bulb fashioned by
heating the glass tubing and blowing through the
capillary. The approximate volume of the bulb may then
be determined by displacement of water in a graduated
cylinder.

It is desirable to curve the neck of the ampoule as
indicated in Figure 4 so that the opening is directed into

the crucible. As a consequence, when burning begins the liquid is sprayed into the crucible and not against the sides of the bomb.

A convenient method for filling such ampoules is to place them neck down in a container of frozen material, in a vacuum dessicator evacuate, and after the material has thawed, admit dry air. The ampoules should be dried, of course, in a similar fashion and weighed before filling.

After filling, the ampoule should be heated slightly to blow out a small amount of liquid from the neck. If a drop of combustion oil from a previously weighed container is then placed at the opening, capillary action draws the oil into the neck and the small region of oil helps to cut down diffusion of the volatile compound from the ampoule. The weight of the oil in the neck of the ampoule is determined by the difference in weights of the container. Providing the liquid is not too volatile and room temperature fluctuations not too great, the ampoule with its contents may now be weighed at leisure.

Combustion experiments on benzene using the unsealed ampoules yielded values for the heat of combustion in good agreement with those reported by Coops, et al. (46)

In order to gain experience in the unsealed ampoule technique for a compound with a boiling point closer to

that of spiropentane, ethyl ether was chosen. Again it was found possible to obtain combustions which appeared satisfactory (no data were taken). However an extremely small capillary was required for the ampoule neck and temperature fluctuations caused the loss of approximately 50% of the samples.

In applying the method to spiropentane, temperature fluctuations, and/or a great tendency for the material to syphon out of the ampoule until an air bubble appeared above the liquid surface, resulted in 100% loss of samples. No sample contained in an unsealed ampoule with an air bubble was found to burn without exploding. It was therefore deemed necessary to use sealed ampoules for spiropentane.

The construction of an ampoule for sealing differed from the unsealed ampoule only in that the neck was not curved as greatly and the sides were flattened slightly to give better breaking characteristic when ignited. Ampoules of approximately the correct size were dried by evacuating in a vacuum dessicator and admitting air through phosphorous pentoxide, (P_2O_5).

The introduction of dry and highly volatile liquid samples into dried and previously weighed ampoules deserves special mention. All the equipment necessary for filling ampoules was placed in a box made from lucite

sheet and containing two holes fitted with rubber gloves.
Several pieces of dry ice were placed in the box to reduce
the temperature and condense moisture. Air was admitted
to the box by passing first through calcium chloride and
then phosphorous pentoxide. The liquid samples were
allowed to remain in their closed containers from the
storage dessicators for about an hour during which time
all traces of moisture disappeared from the box. A
small quantity of liquid was then transferred to a glass
thimble and a small 10W electric light bulb located at one
side of the box turned on. The lighted bulb served as a
source of heat to drive air and vapor from the ampoules.
The ampoules were alternately heated and then cooled by
means of dry ice with their necks dipping in the liquid
sample until completely filled. They were then stored
away from the heater near a piece of dry ice until the de-
sired number of ampoules had been filled. After the fill-
ing operation was complete, the ampoules were removed
from the dry box and allowed to warm to room temperature
during which time a small quantity of liquid was forced
out. Sealing of the ampoules was accomplished by bring-
ing the ampoule in momentary contact with dry ice to
cause the liquid to recede about half way down the neck,
quickly placing it in a small cup lined with asbestos, and
passing the tip of the neck through a micro-flame made

from a glass tube drawn to a fine tip.

Sealed ampoules were then placed in numbered containers in the bomb and tested to 30 atmospheres pressure. Those withstanding the test were stored in a dessicator over P_2O_5 until the combustions could be made. The above procedure resulted in an average breakage of 20%.

The usual procedure of adding oil as kindler to initiate burning when employing sealed ampoules gave no satisfactory combustions in the case of spiropentane. Three attempts were made using oil and each resulted in more or less carbon deposited in the bomb. It was then suggested[*] that benzoic acid might have slower burning characteristics than oil, and a small pellet if included with the ampoule would cause it to break without exploding, and therefore spattering its contents over the interior of the bomb. Furthermore, longer burning would tend to "clean" the carbon from the bomb.

Three combustions in which there was no evidence of carbon were obtained using benzoic acid as kindler. However a larger number of combustions were found to contain carbon than not, even when benzoic acid was used to aid in combustion.

[*]
I am indebted to Professor E. C. Gilbert for suggesting benzoic acid as kindler.

Since the only combustions for spiropentane without evidence of carbon were made by means of benzoic acid, all combustions of methylcyclobutane were made in conjunction with benzoic acid. Fortunately, in view of the small quantity of material available (approximately 20 cc), six of the seven combustions appeared to be complete combustions.

Presentation of the Data.

Table III presents the results for the heat of combustion of spiropentane. The total heat evolved by the combustion, $C_p x \Delta t$, was calculated by multiplying the corrected temperature rise by the energy equivalent of the system. The observed temperature rise of the calorimeter was corrected for heat transfer and heat of stirring by the method of Dickinson as described earlier in this thesis. From the total heat evolved were substracted the energy of firing, the heat evolved by combustion of the filter paper fuse, and oil or benzoic acid, and the energy of formation of nitric acid. The quantity, $-\Delta U_B/m$, in this table (III), and Table V for methylcyclobutane, represents the heat evolved per gram in the isothermal bomb process at $25°C$. as calculated by the Washburn equations (35) for mixtures. The deviations listed are those from the average value of $-\Delta U_B / m$; the

TABLE III

Experimental Data for the Heat of Combustion of Spiropentane

Mass of Spiropentane g. (in vac.)	Mass of kindler g. (in air)	$C_p x \Delta t$ total heat evolved Cal.	Heat from EIt+fuse+ kindler Cal.	Heat from HNO_3 Cal.	$-\Delta U/m$ cal/g.	Dev. cal/g.
0.71779	0.33340[b]	10315.67	2135.43	1.22	11417.4	+1.9
0.67123	0.04005[a]	8122.52	474.82	0.97	11415.8[c]	+0.3
0.59767	0.19513[b]	8058.08	1260.76	0.92	(11395.5)	(−20.0)
0.58448	0.04096[a]	7130.85	484.26	0.93	(11397.5)	(−18.0)
0.52938	0.38939[b]	8525.19	2489.73	8.56[e]	11411.9	− 3.6
0.54575	0.28665[b]	8044.23	1841.31	0.94	(11390.6)	(−24.9)
0.52588	0.04685[a]	6516.97	542.94	0.87	(11388.8)	(−26.7)
0.46039	0.38417[b]	7702.80	2459.83	1.03	(11409.2)	(− 6.3)
0.44644	0.38542[b]	7540.33	2465.56	0.94	(11389.4)	(−26.1)
0.37826	0.39200[b]	6817.91	2519.56	0.65	11416.8	+1.3

Average 11415.5 ± 1.8[d] cal/g.

Those values enclosed in parentheses were obtained from incomplete combustions, as evidenced by carbon deposits, and are therefore not included in the average.
[a]Oil   [b]Benzoic Acid   [c]Faint trace of carbon   [d]mean deviation
[e]Bomb not flushed.

TABLE IV

Derived Data for Spiropentane in Kilocalories per Mole[a]

Formula	C_5H_8
Mol. wt.	68.114
$-\Delta U_B$	777.56 ± 0.31
$-\Delta U_R$	777.47 ± 0.31
$-\Delta H_R$ (liq)	778.65 ± 0.31
$-\Delta H_f^o$	-35.12 ± 0.57
$-\Delta H_{vap}$	6.6[b]
$-\Delta H_R$ (gas)	785.3

[a] Errors are uncertainty interval
[b] Unpublished data of Waddington and Williamson, Petroleum Experiment Station, U. S. Bureau of Mines, Bartlesville, Oklahoma, through private communication with Dr. J. P. McCullough of that station.

plus-minus value following the average $-\Delta U_B / m$ is the mean deviation from the average.

In Table IV are listed the calculated quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$, $-\Delta H_f^o$, for spiropentane and refer to one mole at 25^oC. $-\Delta U_B$ is the actual heat evolved under the conditions of the bomb, corrected to a constant temperature of 25^oC., $-\Delta U_R$, the decrease in energy for the combustion reaction when the reactants and products are in their standard states as defined by Washburn (35), $-\Delta H_R$ is the change in heat content at one atmosphere assuming the perfect gas laws to hold for oxygen and carbon dioxide, ΔH_{vap}, the heat of vaporization, and $-\Delta H_f^o$ represents the standard heat of formation from the elements at one atmosphere. The uncertainties given in Table IV correspond to the uncertainty interval of Rossini (47) and include the uncertainty in the value for the heat of combustion of benzoic acid (0.01%), and in the heats of formation of carbon dioxide (0.012%) and water (0.014%).

Table VI presents similar data for methylcyclobutane.

TABLE V

Experimental Data for the Heat of Combustion of Methylcyclobutane

Mass of Methyl-cyclobutane g. (in vac)	Mass of kindler g. (in air)	$C_p \times \Delta t$ total heat evolved cal.	Heat from EIt + fuse + kindler cal.	Heat from HNO_3, cal.	$-\Delta U_B/m$ cal/g	Dev. Cal/g
0.61455	0.38482	9463.36	2456.65	4.98[a]	11418.5[b]	-2.6
0.53486	0.15990	7146.91	1037.09	11.99	11422.0	+0.9
0.46279	0.38439	7742.64	2454.48	12.36	11421.5	+0.4
0.37669	0.39063	6781.35	2491.86	12.10	(11385.6)	(-35.5)
0.35448	0.39935	6590.36	2548.73	10.06	11420.9	-1.2
0.27440	0.37966	5558.37	2424.07	10.28	11422.7	+1.6

Average 11421.1 ± 1.3[c] cal/g.

The value enclosed in parenthesis was obtained from an apparently complete combustion, but since its deviation from the average is more than four times the average deviation, it is omitted from the average

[a]Bomb flushed once, remainder not flushed
[b]Faint trace of carbon
[c]Mean deviation

TABLE VI

Derived Data for Methylcyclobutane in Kilocalories per Mole[a]

Formula	C_5H_{10}
Mol. wt.	70.130
$-\Delta U_B$	799.96 ± 0.25
$-\Delta U_R$	799.66 ± 0.25
$-\Delta H_R$ (liq)	801.14 ± 0.25
$-\Delta H_f^o$	10.71 ± 0.32
$-\Delta H_{vap}$	7.0[b]
$-\Delta H_R$ (gas)	808.1

[a]Errors are uncertainty interval
[b]Estimated by Trouton's Rule

CORRELATIONS WITH THEORY AND DISCUSSION OF RESULTS

Let us now calculate by the use of bond energies according to the method suggested by Kilpatrick and Spitzer the values of $-\Delta H_R$ (gas) for spiropentane and methylcyclobutane in order to compare with the experimentally derived quantities listed in Tables IV and VI. The sum obtained directly by adding together the energies of all the bonds in a molecule is the value for the heat change $(-\Delta H)$ accompanying the formation of the gaseous molecule from gaseous atoms. The value so obtained for hydrocarbons must of necessity include any uncertainty in the heat of sublimation of carbon. A value of 125.7 kcal/mole has been chosen for the present calculations to be consistent with the normal C-C and C-H bond energies of Pauling (4) which give close agreement with the observed heats of formation of saturated hydrocarbons.

A consideration of the structure of spiropentane (30) shows that there are two C-C bonds of one type and four of another, as illustrated by the following diagram, and labeled a and b. All eight of the C-H bonds are of the same type, however.
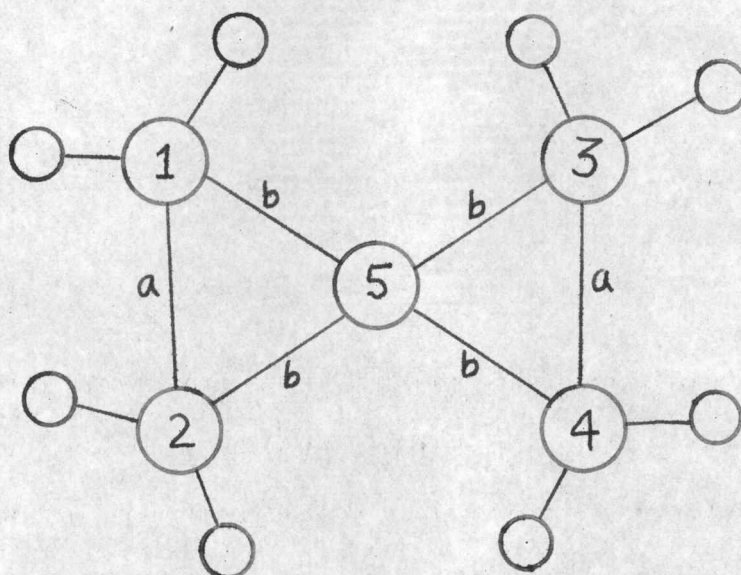
The total energy for the heat of formation of spiropentane may be represented by the equation,

$$-\triangle H = \sum_{1}^{2} D_i(a)_{C-C} + \sum_{1}^{4} D_i(b)_{C-C} + \sum_{1}^{8} D_i{}_{C-H} \qquad (1)$$

where D_i represents the bond energy for an individual bond. The quantities, D_i, required in the above equation may be calculated with the aid of data given in Table I, and the fundamental assumption of the bond orbital method that the angular part of an orbital along the bond axis is a measure of its relative bond forming power; i.e., bond strength. In addition, it is necessary to assume that the bond energy, D_{AB}, between two atoms, A and B, is

proportional to the product of the bond strengths, ψ_A with ψ_B.

Taking 59 and 87 kilocalories for the normal C-C and C-H bond energies, the values for $D(a)_{C-C}$ and D_{C-H} are,

$$D(a)_{C-C} = (1.887)(1.887)(59)/(2.000)(2.000) = 52.5 \text{ kcal.}$$

$$D_{C-H} = (1.000)(1.989)(87)/(2.000)(2.000) = 86.5 \text{ kcal.}$$

Carbon atom 5 (refer to the diagram) is in a unique position compared to carbon atoms 1, 2, 3, and 4. Since it is symmetrically located, it is logical to assume that its orbitals are symmetric and that the bond strengths in the direction of the other four carbon atoms are equal. Accordingly, the orbitals were assumed to have tetrahedral symmetry, and the bond strengths in the directions of the other carbon atoms (C-C-C $\measuredangle = 60^{\circ}$) calculated by means of the equation,

$$\psi_5 = 1/2 + 3/2 \cos \vartheta,$$

which has a maximum value 2.000 (the tetrahedral value) when $\vartheta = 0$. The value at $24^{\circ}58'$, the deviation from tetrahedral symmetry for a C-C-C angle of 60°, is 1.860.

Hence,

$$D(b)_{C-C} = (1.887)(1.860)(59)/(2.000)(2.000) = 51.8 \text{ kcal.},$$

and by equation (1),

$$-\Delta H = 2D(a)_{C-C} + 4D(b)_{C-C} + 8D_{C-H} = 1004.2 \text{ kcal.}$$

for the reaction,

$$5C(g) + 8H(g) = C_5H_8 (g).$$

Using the aforementioned value for the heat of sublimation of carbon, the accepted values for the heats of formation of $CO_2(g)$ and $H_2O(l)$, and 51.7 kcal/mole (4) for the heat of formation of hydrogen in the standard state from the monatomic gas, one obtains a value of 781.6 kcal/mole for $-\Delta H_R$ (gas). Adding to $-\Delta H_R$ (gas), 2 kcal. per opposed CH_2-group (29) brings the value to 785.6 kcal/mole to be compared with the value 785.3 kcal/mole listed in Table IV and derived from the combustion data.

Referring to the following diagram for methylcyclo-butane it is to be noted that there are four C-C bonds (a) of one type and one of another (b), while there are seven similar C-H bonds (c) in the ring and three probably normal C-H bonds (d) in the methyl group.
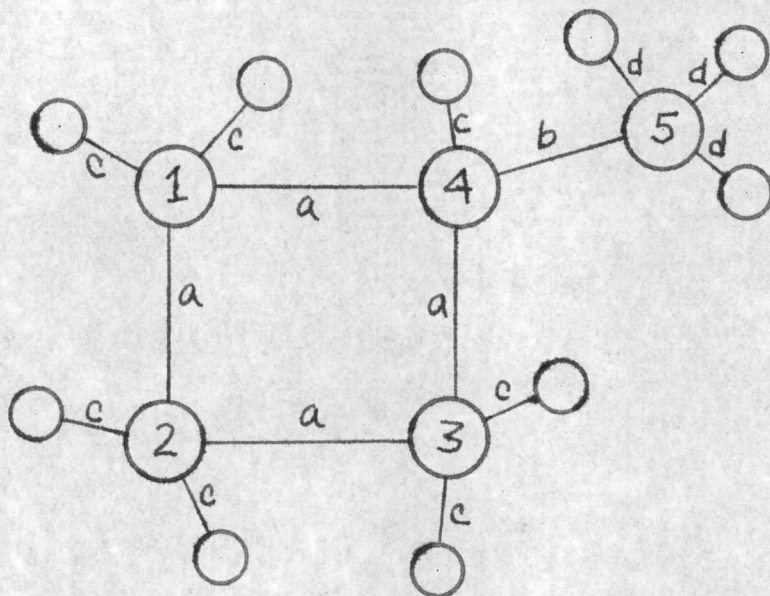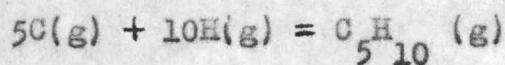
The corresponding values for equation (1) are then,

$$D(a)_{C-C} = (1.984)(1.984)(59)/(2.000)(2.000) = 58.1 \text{ kcal}$$

$$D(b)_{C-C} = (1.984)(2.000)(59)/(2.000)(2.000) = 58.5 \text{ kcal}$$

$$D(c)_{C-H} = (1.995)(1.000)(87)/(2.000)(1.000) = 86.8 \text{ kcal}$$

$$D(d)_{C-H} = (2.000)(1.000)(87)/(2.000)(1.000) = 87.0 \text{ kcal}$$

which lead to

$$-\Delta H = 4D(a)_{C-C} + D(b)_{C-C} + 7D(c)_{C-H} + 3D(d)_{C-H}$$

$$= 1159.2 \text{ kcal/mole}$$

for the reaction,

$$5C(g) + 10H(g) = C_5H_{10} (g)$$

Manipulation of the necessary equations gives a value of 798.3 for $-\Delta H_R$ (gas).

The corrections for torsional strain in methylcyclo-butane are not so straighforward as in the case of cyclo-propane, cyclobutane, spiropentane, etc., which have a definite number of opposed CH_2-groups. In methylcyclo-butane there are two pairs of opposed CH_2-groups between carbon atoms 1 and 2, and 2 and 3, which should contribute about 4 kilocalories to torsional strain. Between carbon atoms 3 and 4, and 1 and 4, are two "half-pairs" of opposed CH_2-groups which we shall assume contribute 2 kilocalories to the strain energy, and in conjunction with the above-mentioned 4 kilocalories, makes a total of 6 kilocalories to be added to the calculated value of $-\Delta H_R$(gas). The final value obtained for $-\Delta H_R$ (gas) by these methods is 804.3 kcal. per mole, or a difference of about 4 kilocalories between the calculated value and the experimentally determined value listed in Table VI.

Even if the CH_3-group were considered the same as a H-atom, and therefore expected to contribute about 2 kilocalories more to the strain energy, the methyl-cyclobutane molecule probably should not be considered rigid and may tend to be non-planar, thereby decreasing the strain energy, as in the case of cyclopentane (48).

Table VII lists further comparisons between $-\Delta H_R$(gas)

as derived experimentally and calculated from the theory.

It is evident that in the case of ethylene the theory does not give good results, but the decrease in interatomic distance due to the double bond between the carbon atoms has not been taken into account in the calculated value. Whereas the variation in the carbon-carbon bond length between 1.52A and 1.55A which is observed for aliphatic and alicyclic compounds is negligible for the assumption of constant interatomic distance, the decrease to 1.34A for ethylene is by no means negligible. This great shortening of bond distance is indicative of greater overlap of atomic orbitals which is not taken into account in the calculation.

Furthermore, it is well known that application of the bond energy method to benzene gives a value about 39 kcal/mole different from the heat of combustion data, and the difference has been termed the resonance energy of the molecule. Similarly rather large resonance energies are found for carbon dioxide and carbon monoxide. It is not unlikely that account of some resonance effects should be taken for ethylene. Such account would be in the proper direction to obtain agreement between the calculated and experimental values in Table VII.

The results for the other compounds listed are, indeed, excellent, except perhaps for methylcyclobutane.

TABLE VII

Comparison of Experimental and Calculated Values for
$-\Delta H_R$ (gas) at 25°C. for Various Strained Cyclic
Hydrocarbons.

Compound	Structure Representation	$-\Delta H_R$ (gas) experimental kcal/mole	$-\Delta H_R$ (gas) calculated kcal/mole[a]
ethylene	C=C	337.3	367.7
cyclopropane	C-C	504	503.9
cyclobutane	C-C	648[b]	647.6
cyclopentane	C-C	793.6	793.6[c]
spiropentane	C-C	785.3	785.6
menthylcyclobutane	C-C	808.1	804.3

[a] A torsional strain energy of 2 kilocalories per opposed CH_2-group has been included.

[b] Estimated from cyclobutane derivatives.

[c] Only 1 kilocalorie for torsional strain has been added to the calculated value for cyclopentane in view of the rotation of puckering about the ring (48)

Here again no correction has been made for the methyl group
attached to the ring. In all probability some torsional
strain effects are present because of it. However, un-
til further data are available on related compounds it
seems impractical to make any further corrections of the
calculated value for methylcyclobutane.

SUMMARY

An isothermal calorimeter for determination of heats
of combustion has been constructed and found by calibra-
tion with National Bureau of Standards benzoic acid to
have an energy equivalent of 2805.85 ± 0.28 cal/degree.
A detailed description of the construction, and operation
of the calorimeter together with the method of handling
data from a particular run is presented.

A discussion of the theory of non-tetrahedral carbon
atoms with applications to cyclic hydrocarbons is in-
cluded.

Combustion experiments on spiropentane and methyl-
cyclobutane yielded values for $-\Delta U_B/m$ of 11415.5 ± 1.8
cal/gm and 11421.1 ± 1.3 cal/gm, respectively. Comparison
of these values, converted to $-\Delta H_R$ (gas), with those
calculated from the theory of non-tetrahedral carbon
atoms gave 785.3 kcal/mole (expt'l) compared to 785.6
kcal/mole (calc'd.) for spiropentane, and 808.1 kcal/
mole (expt'l.) compared to 804.3 kcal/mole (calc'd.)
for methylcyclobutane. The calculated values contain
some corrections for torsional strain energies.

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