THERMOCHEMICAL STUDIES OF PERFLUOROAROMATIC, HALOGEN SUBSTITUTED PERFLUOROAROMATIC, AND PERFLUOROCYCLIC COMPOUNDS.

HENRY JOSEPH. SAPIANO

University of Windsor

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THERMOCHEMICAL STUDIES OF
PERFLUOROAROMATIC, HALOGEN-SUBSTITUTED
PERFLUOROAROMATIC, AND PERFLUOROCYCLIC COMPOUNDS

by

Henry Joseph Sapiano

A Dissertation
submitted to the Faculty of Graduate Studies
through the Department of Chemistry
in partial fulfillment of the requirements for the
Degree of Doctor of Philosophy
at the
University of Windsor

Windsor, Ontario, Canada
1978
ABSTRACT

The method which was previously developed in this laboratory for the determination of the heats of combustion and subsequently the heats of formation of perfluoroaromatic and halogen substituted perfluoroaromatic compounds has been extended by this study to other perfluoroaromatic and halogen substituted perfluoroaromatic compounds, namely C\textsubscript{12}F\textsubscript{10} and C\textsubscript{6}F\textsubscript{5}Br, respectively, as well as the perfluorocyclic compounds, C\textsubscript{6}F\textsubscript{10} and C\textsubscript{6}F\textsubscript{12}. The basic difference from this method relative to previous methods is that no auxiliary substances are used and no water is present in the bomb. While a platinum lined bomb is normally used for these types of compounds, in the case of the combustion of bromopentafluorobenzene, a steel bomb had to be adopted and was used throughout the study of the rest of the compounds. The combustion of bromopentafluorobenzene in the steel bomb yields CO\textsubscript{2}, CF\textsubscript{4}, F\textsubscript{2}, Br\textsubscript{2} and BrF\textsubscript{3}. A material balance was obtained for carbon, fluorine and bromine. The combustion of decafluorocyclohexene and dodecafluorocyclohexane produced the products CO\textsubscript{2}, CF\textsubscript{4}, and F\textsubscript{2}. In both cases a portion of the compound remained unburned, so that it was necessary to collect the amount of unburned material after combustion. The combustion of decafluorobiphenyl yielded the same products as decafluorocyclohexene and dodecafluorocyclohexane. In this case a
material balance indicates that complete combustion is obtained. The value for \( \Delta H_f^{\circ} \)\textsuperscript{298} (C\textsubscript{6}F\textsubscript{5}Br, g) obtained by this method is \(-711.6 \pm 16.7\) kJ mol\(^{-1}\), for \( \Delta H_f^{\circ} \)\textsuperscript{298} (C\textsubscript{12}F\textsubscript{10}, g) \(-1906.6 \pm 7.2\) kJ mol\(^{-1}\), for \( \Delta H_f^{\circ} \)\textsuperscript{298} (C\textsubscript{6}F\textsubscript{12}, g) \(-2368.9 \pm 7.6\) kJ mol\(^{-1}\), and for \( \Delta H_f^{\circ} \)\textsuperscript{298} (C\textsubscript{12}F\textsubscript{10}, g) \(-1262.8 \pm 3.2\) kJ mol\(^{-1}\). The determination of enthalpies of formation for C\textsubscript{6}F\textsubscript{5}Br, C\textsubscript{6}F\textsubscript{10}, C\textsubscript{6}F\textsubscript{12}, and C\textsubscript{12}F\textsubscript{10} allow for the calculation of \( D(C_6F_5 - Br) \) (435.9 kJ mol\(^{-1}\)), the heats of reaction of C\textsubscript{6}F\textsubscript{10} + F\textsubscript{2} = C\textsubscript{6}F\textsubscript{12} (\(-462.3\) kJ mol\(^{-1}\)) and C\textsubscript{6}F\textsubscript{6} + 3F\textsubscript{2} = C\textsubscript{6}F\textsubscript{12} (\(-1424.3\) kJ mol\(^{-1}\)), and \( D(C_6F_5 - C_6F_5) \) (488.0 kJ mol\(^{-1}\)).
DEDICATION

To Linda

... my love and my life

To my family

... I love them dearly

To my friends

... I am happy we met

yi
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CHAPTER ONE

INTRODUCTION

1.1. Historical Introduction

Thermochemistry is concerned with the energy changes of chemical reactions. It is regarded as a branch of the thermodynamic science.

Thermochemistry developed in the period of 1780-1840, when the first measurements of heats of chemical reactions were made by Lavoisier, de Laplace, and Hess. In the last half of the nineteenth century, thermochemistry was further developed by the work of Thomsen and Berthelot (1). The heats of a very great number of reactions were measured by these two men. Near the turn of the twentieth century, a new concept was realized -- that is, that the entropy change of a reaction was an additional factor in determining the driving force of the reaction. The study of thermochemistry seemed to have lost its momentous surge. It was not until the late 1920's that it was realized any further developments of chemical technology were dependent on the existence of reliable thermochemical data, e.g., heats of reaction. At that point in time it was known that the accuracy of the existing thermochemical data would have to be increased greatly before the data could be coupled.
with entropy values in order to be of interest to technology.

The "classical" period of thermochemistry may be viewed to have ended with this previous knowledge and the "modern" period was conceived with the publication of a series of papers from the National Bureau of Standards in Washington, D.C. which set a whole new set of rules for accuracy of thermochemical research.

Mention should be given to a number of authors whose contributions led to the advancement of modern organic thermochemistry.

a. Rossini, in 1931, published measurements of the heat of formation of water, which when corrected to standard state is the value accepted today (2).

b. Washburn, in 1933, gave the first detailed thermodynamic analysis of the processes occurring in a bomb calorimeter combustion experiment (3).

c. Popoff and Schirokich, in 1933, pioneered the development of the moving bomb calorimeter (4).

d. Jossup and Green, in 1934, gave an accurate value for the energy of combustion of benzoic acid (5).

e. Dewey and Harper, in 1938; Jessup, 1938; and Prossen and Rossini, 1944, determined the heat of formation of carbon dioxide (6, 7, 8).
f. Cox et al., in 1963, began the investigation of a series of organic fluorine compounds and evaluated the accuracy of the previously published thermochemical data (9).

1.2. Nature of the Present Research

There has been a limited amount of thermochemical work done on perfluoroaromatic, and halogen-substituted perfluoroaromatic compounds and only one study on perfluorocyclic compounds (9, 10).

Price and Yared (11, 12, 13) developed a combustion method of determining the enthalpies of formation of C₆F₆, C₇F₈, and C₆F₅I. These compounds were combusted in oxygen using no auxiliary materials and under anhydrous conditions whereas Cox et al. used auxiliary materials and water in the combustion process to study C₆F₁₀, C₆F₆ (9), C₆F₅CH₃, C₆F₅OH, C₆F₅H, and C₆F₅Cl (10). No previous thermochemical work is reported for C₆F₅Br, C₆F₁₂, and C₁₂F₁₀. The present work is a continuation of the series of perfluoroaromatic, halogen-substituted perfluoroaromatic, and perfluorocyclic compounds using the direct combustion method.
1.3.1. The Chemical Bond

The strength of the chemical bond is of prime importance for the quantitative treatment of chemical reactions. There are various possible interpretations of bond strength. It can be viewed as the amount of energy required to break a bond or as a bond energy term, characteristic of each bond which, when summed over all the bonds in the molecule, will yield its heat of formation from atoms.

When the "bond dissociation energy" is used as a measure of bond strength, it becomes necessary for the determination of the bond strength to specify sufficiently the exact fragments into which the molecule is broken. The dissociation energy, \( D(R_1 - R_2) \), is the energy absorbed when the molecule \( R_1R_2 \) is decomposed into fragments \( R_1 \) and \( R_2 \) where \( R_1R_2 \), \( R_1 \), and \( R_2 \) are in their ground state (14). This change in energy is calculated for both reactants and products at absolute zero in the ideal gas state.

\[
R_1R_2(g) = R_1(g) + R_2(g)
\]  

[1.1]

Considering equation [1.1] the result is (assuming zero energy of activation for the recombination of \( R_1 \) and \( R_2 \))
\[ D(R_1 - R_2) = \Delta H_f^0(R_1, g) + \Delta H_f^0(R_2, g) - \Delta H_f^0(R_1R_2) \]  \[1.2\]

where \( \Delta H_f^0 \) is the heat of formation. It should properly be referred to \( 0^\circ K \). Using equation \[1.2\], \( D(R_1 - R_2) \) is determined, depending on whether the data for \( \Delta H_f^0(R_1, g) \) and \( \Delta H_f^0(R_2, g) \) are available. \( \Delta H_f^0(R_1R_2) \) is generally known from thermochemical results. Thus, the derivation of one bond dissociation energy can be used to deduce a series of dissociation energies involving a common radical by successive use of Hess's Law. Therefore, bond dissociation energies and enthalpies of formation are both inter-related and thus lead up to a body of knowledge and information.

1.3.2. Determination of Enthalpies of Formation

The most widely used experimental method of determining the heats of formation of organic compounds is to determine them calorimetrically. The type of calorimeter used depends upon the type of reaction involved, the amount of heat exchanged, and the duration of the reaction (15).

There are several different types of calorimeters used, which have different particular applications. The
flame calorimeter (15, 16) measures the heat generated by the combustion of various vapours or gases in oxygen at constant pressure. The apparatus is best suited to gases or substances with very high vapour pressure.

The reaction calorimeter is the term used for an apparatus which measures the heat liberated when a substance reacts with something other than oxygen. These reactions may employ hydrogenation, hydrohalogenation, halogenation and hydrolysis. The apparatus is of the constant pressure type and can operate under isothermal or adiabatic conditions. This type of calorimetry is often used where compounds are not suitable for reactions with oxygen but is often at a disadvantage due to a lack of necessary auxiliary data.

The bomb calorimeter is the oldest and best characterized of all the calorimeters known (15). It is used in the present work. It is a constant volume system in which a substance will combust under oxygen pressure to form products. The enthalpies of formation of the products formed are normally well established. The energy released is usually of the order of several thousand calories, thus making it possible to measure the energy released accurately.
CHAPTER TWO

THEORETICAL CONSIDERATIONS

2.1. General Principles.

A thermochemical investigation is one in which the thermochemist aims to determine the quantity of energy associated with a unit amount of a given chemical reaction or physical process (16). Important factors that must be taken into account include determination of the energy, determination of the amount of reaction, specification of the reaction, the nature of the thermodynamic properties involved, the characterization of the thermochemical method, assignment of the temperature of the reaction and a correction needed to refer the reaction to some standard or reference state.

The determination of the measured energy associated with a reaction will only be significant if attached to it is an adequate description of the given reaction with respect to all factors which may influence the value of the energy. Each factor should be specified with a precision appropriate to its measure of influence on the value of the energy. With the condition of each reactant and each product so defined, it becomes necessary to correct each
to the same specified standard state.

In addition to specifying adequately the given reaction or process and its components, it is important to define the thermodynamic property which is measured, either a change in internal energy $\Delta E$, or a change in the heat content or enthalpy, $\Delta H$. Depending upon whether the substances participating in the reaction are confined at a constant volume or a constant pressure will define the thermodynamic property of the heat of reaction measured $\Delta E$ or $\Delta H$.

According to the first law of thermodynamics, for any process,

$$\Delta E = q + w + u$$  \[2.1\]

where $q$ is the energy absorbed in the form of heat, $w$ is the PV work energy done on the system during the process, and $u$ is usually zero since it is involved with energy terms due to changes in motion of the entire system, or variations in electric or magnetic field strengths which are normally constant in a calorimetric experiment.

For a process in the case of a calorimetric system of constant volume $V$, $u$ is zero and $w$ is equal to $P\Delta V$ where $\Delta V$ is equal to zero then,

$$\Delta E = q$$  \[2.2\]
the heat absorbed associated with any chemical reaction taking place.

For a process, at constant pressure,
\[ w = -P \Delta V \]  \hspace{1cm} [2.3]

substituting in equation [2.1] gives,
\[ \Delta E = q - P \Delta V \]  \hspace{1cm} [2.4]

rearranging equation [2.4]
\[ \Delta E + P \Delta V = q \]  \hspace{1cm} [2.5]

and
\[ \Delta E + P \Delta V = \Delta (E + PV) = q \]  \hspace{1cm} [2.6]

Finally, since by definition
\[ E + PV = H \]  \hspace{1cm} [2.7]

then it can be written
\[ \Delta H = q \]  \hspace{1cm} [2.8]

Therefore, for a process in a calorimeter at constant pressure, the heat absorbed by the process is the change in heat content or enthalpy, \( \Delta H \).

For a specified reaction or process, the difference between the value \( \Delta H \) and \( \Delta E \) may be evaluated from the relation
\[ \Delta H = \Delta E + \Delta PV \]  \hspace{1cm} [2.9]

but
\[ \Delta (PV) = (\Delta n)RT \]  \hspace{1cm} [2.10]

therefore,
\[ \Delta H = \Delta E + \Delta nRT \]  \hspace{1cm} [2.11]
where \[ \Delta n = \sum_{\text{products}} n - \sum_{\text{reactants}} n \]  
\( n \) being the number of moles of gas.

Thus, \( \Delta H \) can be calculated from knowing the value \( \Delta E \) and the change in the number of moles of gases between the products and reactants.

A thermochemical investigation consists of two parts. One involves the calorimetric part where the determination of the quantity of energy evolved by the reaction or process is found. The other is the chemical part which is analytical in nature and involves the determination of the amount of reaction.

For a given calorimeter system, it is necessary to determine a quantity called the energy equivalent either by use of a known amount of electrical energy or a known amount of chemical reaction with a well-known reaction heat. The energy equivalent is defined as the known amount of energy divided by the temperature rise produced. Intuitively, for the same calorimeter an equal temperature rise produced by a reaction of unknown energy will have released the same energy.

In the chemical part of the thermochemical investigation, it is first necessary to establish the nature and completeness of the reaction and secondly, to measure the
quantities of the given reactions that occur for which the heat energies have been evaluated. It is preferable that the reaction produces a limited number of products in well defined thermodynamic states not only for simplicity of analysis but to enable the determination of the completeness of the reaction. This is done by either measuring the amount of one of the reactants consumed or more often, measuring the amount of products formed. In studying the chemical reaction, it should be demonstrated by physical or chemical means that the reaction, which actually occurs in the calorimeter vessel, is indeed not significantly different from the theoretical pure reaction and to evaluate the amount and effect of any side reaction(s).

As most calorimetric investigations are not carried out at the temperature commonly used in the definition of the standard state of a substance, namely 298 K, some method must be used for correcting the variation of the heat of reaction with temperature. For any process at constant pressure

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$  \[2.13\]

and differentiating with respect to temperature, T

$$\Delta H/\Delta T = \Delta H/\Delta T(\text{products}) - \Delta H/\Delta T(\text{reactants})$$  \[2.14\]

by definition, \(\Delta H/\Delta T\) the change in enthalpy with respect to temperature at constant pressure is the heat capacity
at constant pressure. Therefore,

\[ \frac{\Delta H}{\Delta T} = C_p^{\text{products}} - C_p^{\text{reactants}} = \Delta C_p \]  \[2.15\]

and similarly for a constant volume process,

\[ \frac{\Delta E}{\Delta T} = \Delta C_v \]  \[2.16\]

Thus, it is only necessary to know the difference in heat capacities of the products and reactants in order to determine the variation of the heat of reaction with temperature.

The thermochemist is concerned with matter in the gas, liquid, and solid states. For thermochemical reactions, the thermal corrections for the departure of actual states to standard states for a combustion reaction occurring in a bomb are calculated.

When a calorimetric investigation is not done at the defined pressure in the standard state, the combination of the first and second laws gives

\[ dE' = T \, dS - P \, dV \]  \[2.17\]

Expansion of perfect differentials of \( dF, ds \) and \( dV \) gives

\[ \frac{\partial E}{\partial T} \, dT + \frac{\partial E}{\partial P} \, dP = \\
- T \frac{\partial S}{\partial T} \, dT + T \frac{\partial S}{\partial P} \, dP - P \frac{\partial V}{\partial T} \, dT - P \frac{\partial V}{\partial P} \, dP \]  \[2.18\]

and rearranging

\[ (\frac{\partial E}{\partial P} - T \frac{\partial S}{\partial P} + P \frac{\partial V}{\partial P}) \, dP + \\
(\frac{\partial E}{\partial T} - T \frac{\partial S}{\partial T} + P \frac{\partial V}{\partial T}) \, dT = 0 \]  \[2.19\]
and for the relation to hold true
\[ \frac{\partial E}{\partial P} - T \frac{\partial S}{\partial P} + P \frac{\partial V}{\partial P} = 0 \]  \[2.20\]
and since,
\[ \frac{\partial S}{\partial P} = -\frac{\partial V}{\partial T} \]  \[2.21\]
therefore
\[ \frac{\partial E}{\partial P} = -T \frac{\partial V}{\partial T} - P \frac{\partial V}{\partial P} \]  \[2.22\]
hence it is necessary to find \( \frac{\partial V}{\partial T} \) and \( \frac{\partial V}{\partial P} \) data for the quantities concerned. Similarly for the enthalpy
\[ H = E + PV \]  \[2.7\]
and
\[ \frac{\partial H}{\partial P} = \frac{\partial E}{\partial P} + P \frac{\partial V}{\partial P} + V \]  \[2.23\]
with substitution and simplification,
\[ \frac{\partial H}{\partial P} = -T \frac{\partial V}{\partial T} + V \]  \[2.24\]

A thorough discussion of the corrections for the bomb combustion of C, H, and C, H, O, compounds were given by Washburn (17) and his approach has now been extended to other compounds. Details of the methods for correction (often called reduction) to standard state will be given in a separate chapter due to its significance in thermochemical evaluation.

In this work, it will be shown that the reduction to standard state is simplified due to lack of auxiliary materials used in the combustion process and the absence of water in the bomb.
2.2. Rotating Bomb Calorimetry

The rotating bomb calorimeter is equipped with a mechanism which causes the bomb to continuously rotate end-over-end and also about its cylindrical axis. The usual purpose of this is to cause the liquid in the bomb to wash all the internal surfaces and to dissolve all soluble products of combustion so that a homogeneous solution is produced in the bomb. In the present work the rotation was used solely to enhance the heat transfer by agitation of the water in the calorimetric bucket.

Often the limiting part of a thermochemical investigation is more the chemical part rather than the calorimetric part of the determination (18). It is necessary to have sufficient analytical and physicochemical data to precisely define the amount and states of reactants and products. This data includes: (i) the mass, purity, and state of the primary reactant and (ii) the masses, chemical nature and state of the products.

The reaction is usually carried out at constant volume under a pressure of approximately thirty atmospheres of oxygen in a reaction vessel termed a bomb.

The bomb containing the sample in a crucible suspended in a gimbal, is immersed in a can of water, the
temperature of which rises on ignition of the sample by electrical means. In an isoperibol calorimeter, the bomb and can of water are surrounded by a constant temperature bath. From the measured temperature rise of the water in the can, and a previous determination of the energy equivalent of the system, the amount of heat liberated by the combustion of the sample can be found.

2.3. Calibration of the Bomb

A reference substance for the determination of the energy equivalent of the calorimeter must satisfy certain minimum requirements: (i) it should be obtainable in a pure state; (ii) it should be stable; (iii) it should not be hygroscopic; (iv) it should not be too volatile; (v) it should ignite readily and burn completely in the bomb to give well defined products (18).

Benzoic acid has been used as the calorimetric standard substance. The certified value of benzoic acid can be used if it is combusted with the following conditions: (i) the combustion reaction is referred to 298 K; (ii) the sample is burned in a bomb of constant volume in pure oxygen at an initial pressure of 30 atmospheres at 298 K; (iii) the number of grams of sample burned is equal to three times the internal volume of the bomb in litres; (iv) the number of grams of water in the bomb prior
to combustion is equal to three times the internal volume of the bomb in litres.

The heat of combustion of the standard sample benzoic acid under conditions differing by small amounts from the standard conditions as outlined above can be obtained by multiplying the value of the certified heat of combustion of the benzoic acid as given by the National Bureau of Standards of 26.434 kilojoules per gram by the following factor (19),

\[ f = 1 + 10^{-6} \left[ 20(P - 30) + 42 \left( \frac{m_s}{V} - 3 \right) + 30 \left( \frac{m_w}{V} - 3 \right) - 45(\theta - 25) \right] \]  \[ 2.25 \]

where \( P \) is the initial pressure in atmospheres of oxygen at the temperature, \( \theta \), to which the reaction is referred, \( m_s \) is the mass in grams of sample burned, \( m_w \) is the mass in grams of water placed in the bomb, and \( V \) is the internal volume of the bomb in litres.

If a quantity of energy \( q \) is released in a fixed calorimetric system and produces a net temperature rise \( \Delta \theta \), then the energy equivalent of the calorimetric system, \( \epsilon \), is defined by

\[ \epsilon = \frac{q}{\Delta \theta} \]  \[ 2.26 \]

In the combustion of benzoic acid there are energy contributions to the actual bomb process: \( q_i \) is the energy used to ignite the charge and \( q_n \) is the energy
produced by the formation of nitric acid. Therefore the energy equivalent of the system after combustion is written as

\[ \varepsilon_f = \left( q + q_i + q_n \right) / \Delta \theta \]  

[2.27]

If \( \varepsilon_f \) represents the energy equivalent of the calorimetric system, then the standard final calorimetric system would be

\[ \varepsilon_{sf} = \varepsilon_f - \varepsilon_{cf} \]  

[2.28]

where \( \varepsilon_{cf} \) would be calculated from the heat capacities of the crucible, oxygen, carbon dioxide, and water in the bomb at the end of the combustion with benzoic acid and the specific heats and differences in mass of any other materials present in different amounts in the standard calorimetric system and the system as actually used.

2.4. Determination of the Corrected Temperature

Calorimeters used in combustion calorimetry undergo a change of temperature when a reaction takes place. If the calorimeter is surrounded by a jacket that is maintained at constant temperature this type of calorimeter is conventionally described as isoperibol and sometimes, incorrectly as isothermal. Some heat exchange (thermal leakage) occurs between the calorimeter and its surroundings, but may be accurately determined by analysis of the
temperature-time curve before and after reaction takes place, provided the reaction taking place is of a short duration. It is necessary that the calorimetric liquid be stirred adequately. The heat developed by the stirring must be corrected for in calculating the corrected temperature rise. The method generally used for making the correction is based on the assumption that the rate of heat of stirring is constant, thus it is an important necessity that the rate of stirring be kept constant.

In considering a combustion experiment, the temperature-time curve is ordinarily divided into three periods: the main period in which the principal part of the temperature rise takes place as a result of combustion taking place in the bomb; and the initial and final periods where the temperature rise is due to the stirring and exchange effects only.

In Figure 1, the relation between temperature, $\theta$, of the calorimeter and time, $t$, in an experiment in which combustion takes place in the bomb is illustrated. The sections of the curve ab, be, and eh are the initial, main, and final periods, respectively.

Assuming that the rate, $u$, of the temperature rise of the calorimeter due to the heat of stirring is constant and the rate of temperature rise due to thermal leakage, $k$,
Figure 1: A time-temperature curve for a bomb calorimeter experiment
is proportional to the difference between the temperatures of calorimeter and jacket. Then by Newton's law of cooling the total temperature rise due to the heat of stirring and thermal leakage is given by

\[
d\theta/dt = u + k(\theta_j - \theta) \tag{2.29}
\]

where \( \theta_j \) is defined as the temperature of the jacket.

Another expression for equation [2.29] is obtained when \( d\theta/dt = 0 \) when \( \theta = \theta_\infty \) then,

\[
\theta_\infty = \theta_j + u/k \tag{2.30}
\]

where \( \theta_\infty \) is defined as the convergence temperature of the calorimeter that is, the temperature which the calorimeter would attain in an infinite time if \( \theta_j \) and the rate of stirring remains constant. Substitution of equation [2.30] into equation [2.29] gives

\[
d\theta/dt = k(\theta_\infty - \theta) \tag{2.31}
\]

It is assumed that \( u, k, \) and \( \theta_j \) are constant and if \( g_i \) and \( g_f \) represent the values of \( d\theta/dt \) at the mean temperatures \( \theta_i \) and \( \theta_f \) of the initial and final periods respectively then from equations [2.29] and [2.31],

\[
k = (g_i - g_f)/(\theta_f - \theta_i) \tag{2.32}
\]

\[
\theta_\infty = (g_i \theta_f - g_f \theta_i)/(g_i - g_f) \tag{2.33}
\]

and

\[
u = g_f + k(\theta_f - \theta_j) \tag{2.34}
\]
by using equation [2.29] with
\[ g_f = u + k(\theta_j - \theta_f) \]  \[ 2.35 \]
or using equation [2.31] with
\[ g_f = k(\theta_\infty - \theta_f) \]  \[ 2.36 \]
then in either case we get
\[ \frac{d\theta}{dt} = g_f + k(\theta_f - \theta) \]  \[ 2.37 \]
The correction \( \Delta \theta \) is added to the observed temperature rise \( \theta_e - \theta_b \) to eliminate effect of heat of stirring and thermal leakage. Equation [2.38] is obtained by integration of equation [2.37]. That is,
\[ \Delta \theta = -g_f(t_e - t_b) - k \int_{t_b}^{t_e} (\theta_f - \theta_m) dt \]  \[ 2.38 \]
on solving
\[ \Delta \theta = -[(g_f + k(\theta_f - \theta_m))(t_e - t_b)] \]  \[ 2.39 \]
The value for \( \theta_m \) must now be found in order to solve equation [2.39]. The average temperature, \( \theta_m \) of the wall of the calorimeter in the main period must be found graphically or by numerical integration. No simple analytical expression of the relation between time and temperature in the main period can be expressed. Although, if \( n \) temperatures, \( \theta_x \) are measured or interpolated between observed values at equal time intervals, \( \Delta t \), during the main period, (16), then

\[ \text{...} \]
\[
\theta_m' = \sum_{r=2}^{n-1} \theta_r + (\theta_b + \theta_e)/2 \Delta t/(t_e - t_b)
\]  

[2.40]

Thus, from the preceding relations, the corrected temperature rise is given by

\[
\Delta \theta_{\text{corr}} = \theta_e - \theta_b + \Delta \theta
\]  

[2.41]

Dickinson's method (20) of obtaining the corrected temperature rise finds the time, \( t_x \) (figure 1) such that

\[
-g_b(t_x - t_b) - g_e(t_e - t_x) =
\]

\[
k \int_{t_b}^{t_e} (\theta - \theta_\infty) \, dt = \Delta \theta
\]  

[2.42]

Dickinson showed that this relationship holds if the two shaded areas in Figure 1 are equal. The time \( t_x \) is the time when the temperature rise has reached sixty percent of its total amount (21), and is the point where the calorimeter ceases to be heated at a rate equivalent to that in the initial period and begins to be heated at the rate as in the final period.

2.5. Calorimeter Design and Temperature Measurement

The constant-temperature-environment calorimeter is completely surrounded by a jacket of constant and uniform temperature. In a well-designed calorimeter and jacket system, the leakage modulus should be small as possible as
well as constant. The determination of the corrected temperature rise is based on the validity of equation [2.29]. It has been found that equation [2.29] is valid over the range of temperature differences usually encountered in bomb calorimetry (18). These requirements are met when the following points of design are satisfied: (i) no insulating material other than air can be used in the space between the calorimeter and the jacket; (ii) the jacket walls must be of constant temperature throughout the experiment; (iii) the thickness of the air space between the calorimeter and the jacket must not exceed 12 mm in order to minimize convection transfer; (iv) the stirring in the calorimeter must be adequate enough to ensure uniformity of the temperature in the calorimeter and the stirring rate must be kept constant to ensure constant heat of stirring throughout the experiment; (v) the evaporation of water from the calorimeter must be reduced to a minimum.

Calorimetric investigations require the measurement of the temperature of the calorimeter throughout the period of the experiment. The most commonly used temperature measuring instruments are mercury-in-glass thermometers, platinum or other metallic resistance thermometers, thermocouples, and thermistors.
The mercury thermometer has the advantage that it is direct reading and is relatively inexpensive. For highly accurate measurements, mercury thermometers are now inadequate since resistance thermometers, thermocouples, and thermistors are much more convenient and can produce results of higher accuracy. Short-interval mercury thermometers (e.g., Beckmann thermometers) are quite satisfactory for calorimetric measurements of moderate accuracy, since they can be read, with a lens to within 0.002 C. The mercury-in-glass thermometers are subject to several sources of error arising from secular changes in bulb volume, effects of pressure, exposure of the stem, and irregular movement of the meniscus.

The platinum resistance thermometers give results that are both accurate and very reproducible, and thus, these types of measuring device are able to be used for high accuracy work. A Wheatstone Bridge is used in conjunction with this type of thermometer. The main disadvantage of the platinum resistance thermometer is the expense of both the thermometer and resistance bridge.

For an acceptable degree of accuracy, thermocouples must be fabricated of wire of high quality that is homogeneous. The e.m.f. developed by the thermocouple is
generally quite small and thus the accuracy is dependent upon the type of potentiometer used.

Thermistors are semi-conductors of high resistance at room temperature, usually of the order of thousands of ohms. The most striking characteristic of the thermistor is the very high negative temperature coefficient of resistance. The greater response of the thermistor allows much more latitude in the choice of instruments for measuring the resistance changes. Thus an inexpensive Wheatstone Bridge and sensitive mirror galvanometer are quite adequate to detect a change of the order of 0.0001°C. While the thermistor is very sensitive, small in size, and rapid in response, it suffers from a minor degree of instability while aging and therefore must be recalibrated periodically.

For the relatively small temperature ranges used in calorimeter work, as is the case in the present work, the relationship given by Daniels et al. (22) between the natural logarithm of the thermistor resistance, \( R \), and the absolute temperature, \( T \), should be valid,

\[
\ln R = \frac{A}{T} + B \quad [2.43]
\]

The constants \( A \) and \( B \) may be determined by a plot of \( \ln R \) versus the inverse of the absolute temperature.
CHAPTER THREE
DETERMINATION OF ENTHALPIES OF FORMATION

3.1. Materials

3.1.1. Bromopentafluorobenzene

Bromopentafluorobenzene obtained from the Imperial Smelting Corporation was purified by fractional distillation. The final product had the following physical properties (the values in parentheses are those reported by the manufacturer): boiling point = 137°C (137°C); index of refraction, \( n_D^{25} = 1.4483 \) (1.4483) (23). Analysis by gas chromatography used a 6 ft. x 1/8 in. o.d. Durapak n-octane/Porasil C, 100-200 mesh column. The column temperature was 120°C and the flow rate of the nitrogen carrier gas was 60 cm³/min. Flame ionization detection was used. This showed the presence of a minor impurity which was found to represent a maximum of 0.05% of the sample.

3.1.2. Decafluorocyclohexene

Decafluorocyclohexene obtained from the Imperial Smelting Corporation was purified by preparative-scale
gas chromatography. The final product had the following physical properties (the values in parentheses are those reported by the manufacturer): b.p. = 53°C (53°C), n_D^{25} = 1.29 (1.29). Analysis by gas chromatography (6 ft. x 1/8 in. o.d. Durapak n-octane/Porasil C, 100-200 mesh, N_2, 60 cm³/min., column temperature 110°C, flame ionization detection) showed the presence of three impurities which represented a maximum of 0.02% of the sample. The impurities were collected and analyzed by mass spectrometry and N.M.R. They were identified to be C_6F_{11}H, C_6F_8 and C_6F_{10}H_2.

3.1.3. Dodecafluorocyclohexane

Dodecafluorocyclohexane obtained from the Imperial Smelting Corporation was used without further purification. Analysis by gas chromatography (same conditions as for C_6F_{10}) showed the presence of a minor impurity which represented a maximum of 0.01% of the sample.

3.1.4. Decafluorobiphenyl

Decafluorobiphenyl was supplied by the Imperial Smelting Corporation and used without further purification. The melting point was found to be 68°C in agreement with the reported value of 68°C (23). The mass spectrum of
decafluorobiphenyl was taken. No mass fragments heavier than those corresponding to the molecular ion was found in the mass spectrum of the sample and the spectrum obtained was in good agreement with that previously reported by Cotter (24a).

3.1.5. Carbon Dioxide, Tetrafluoromethane, and Fluorine

$\text{CO}_2$, $\text{CF}_4$ and $\text{F}_2$ were obtained from the Matheson Chemical Company and were used without further purification.

3.1.6. Bromine Pentafluoride and Bromine Trifluoride

$\text{BrF}_5$ and $\text{BrF}_3$ were obtained from the Air Products Chemical Company and Fluorochem Ltd., respectively. Both were stored as received in monel steel cylinders under their own vapour pressure. Before use the liquids were distilled into Pyrex traps and vacuum distilled. The vacuum distillation system used had taps equipped with Teflon barrels and Viton-o-rings and all joints and glass stopcocks were greased with halocarbon grease.

3.1.7. Bromine

Reagent A.C.S. bromine was dried over phosphorus pentoxide and vacuum distilled. A middle fraction was collected and stored under its own vapour pressure in a Pyrex tube.
3.1.8. Sodium Thiosulphate

Sodium thiosulphate pentahydrate (12.5 g) was dissolved in one litre of water that had been recently boiled and cooled. A few drops of chloroform were added as a preservative and the resulting solution was standardized with potassium iodate (24b).

3.1.9. Potassium Iodide

Reagent grade potassium iodide was used without further purification.

3.2. Apparatus

The calorimeter that was used in this work was made from plate brass (Figure 2). The design was similar to that of the U. S. Bureau of Mines (25) with some modifications.

The major modification was the rotating mechanism which involved the use of a low R.P.M. high torque motor attached to the rotating mechanism on the bomb by a series of gears and shafts. The shaft going through the lid of the calorimeter was capable of being raised or lowered which allowed linkage to the gear on the motor to engage when rotation of the bomb was necessary.

The high torque motor was a 115 V. Bodine motor, type
Figure 2: A photograph of the rotating bomb calorimeter
KYC-22RC, with a R.P.M. of 10, and a torque of 32 in. oz. The stirring and the circulation of the water in the jacket and lid of the calorimeter were done by blade stirrers and a circulating pump which were driven by two Electrohome 115 V., 1.25 amp. motors, with a R.P.M. of 1550. One of the motors that drives the circulating pump also supplied power to the stirrer for the water in the calorimeter bucket.

There are two circular heaters, one 500 watt and the other 125 watt heater along with a set of cooling coils contained inside the calorimeter jacket. Through the cooling coils, cool thermostated water was circulated from an external bath which was regulated to \(16 \pm 0.01^\circ C\). The temperature of this bath was controlled by a Haake unit temperature controller working against a cooling coil from a Portable Cooler Unit made by Precision Scientific Company. This system circulating through the coils inside the calorimeter jacket worked against the heaters, also inside the jacket to keep the calorimeter jacket constant at 25.000\(^\circ C\). Power to these circular heaters was supplied by a Thermodrol Proportional Temperature Controller, Model 1053 of the Shell Development Design, Hallikainen Instruments. This system would allow the temperature of the jacket to be controlled within \(\pm 0.001^\circ C\).
Figure 3: A photograph of the calorimeter bucket
Another added feature besides a 3-blade stirrer and the rotating mechanism was the calorimeter bucket (Figure 3) which housed a 15-watt rod heater and the mechanism for coupling the bomb with the ignition system. The rod heater was used to adjust the temperature to the desired starting point. The coupling mechanism between the bomb and ignition unit involved a spring clip which released when the rotating mechanism was initiated.

The ignition system consisted of two 250 mfd. capacitors, a 2000 ohm resistor, and a 250 V. diode. The diode rectified the current from a 115 V. A.C. Powerstat.

The bomb used in this work was a steel, high pressure Parr Bomb, Model 1004C (Figure 4). A sleeve and gear around the bomb produced a twisting end-over-end motion when the rotation mechanism was engaged through the exterior of the calorimeter. A special clamping handle was fitted into two holes near the bottom of the bomb to lower it in an inverted position into the calorimeter bucket. The inverted position was used so that the flame of the combustion would be directed towards the bottom of the bomb and therefore away from the interior fittings to avoid damage.

In order to work with the bomb in the inverted position, a brass ring was held around the bomb by three large
Figure 4: A photograph of the bomb
set screws that held the bomb inverted and steady while it was being prepared for a combustion experiment.

In sealing the bomb prior to combustion, the head was placed in the bomb and the cap screwed on. The sixteen screws in the head were tightened from side to side until all were secure in place. The bomb was allowed to sit for ten minutes in order for the teflon seal ring in the head to flow and then the screws were tightened once again.

The calorimeter bucket contained 3500 grams of water which was weighed to 0.1 g. accuracy. The bucket was placed in the calorimeter and the bomb set into place inside the calorimeter bucket and the ignition clip engaged for firing. A lid was placed on top of the bucket, the calorimeter was closed and the system was allowed to come to equilibrium for approximately twenty minutes.

3.3. Characterization of the Thermistor and Calorimeter

Calorimetric investigations in part require the measurement of the temperature increase with time and the subsequent calculation of the corrected temperature rise, $\Delta T$. For temperature measurements, a thermistor was used in this work which required calibration over the temperature range to be
used. This calibration is shown in Table 1.

For the thermistor used, the following formulae have been previously tested (26):

\[
\ln R = \frac{A}{T} + B \quad (22) \tag{3.1}
\]
\[
\ln R = \frac{C}{(T + \theta)} + D \quad (27) \tag{3.2}
\]
\[
T = A' \ln R \quad (28) \tag{3.3}
\]

where \( R \) is the resistance, \( T \) the absolute temperature and \( A, B, C, D, A' \), and \( \theta \) are constants. Of these relationships, equation [3.2] is reported to be the most accurate (29).

A plot of \( 1/\ln R \) versus \( T \), as shown in Figure 5, was necessary to determine \( \theta \) in equation [3.2] owing to the fact that thermistors undergo slight changes with age (30). Aging is now one of the standard processes in the manufacture of thermistors. A check on \( \theta \) is still warranted as a precaution to ensure reproducible behaviour.

Using equation [3.2] and the plot of \( 1/\ln R \) versus \( T \), a derivation of theta \( \theta \), is as follows:

\[
\ln R = \frac{C}{(T + \theta)} + D \quad (3.2) \tag{3.2}
\]

From the above relationship

\[
\ln R = \frac{D(T + \theta) + C}{(T + \theta)} \quad (3.4) \tag{3.4}
\]
Table 1: Thermistor Calibration

<table>
<thead>
<tr>
<th>Temperature $^\circ$K</th>
<th>Resistance ohm</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.351</td>
<td>2291.0</td>
</tr>
<tr>
<td>298.323</td>
<td>2293.9</td>
</tr>
<tr>
<td>298.136</td>
<td>2312.0</td>
</tr>
<tr>
<td>297.981</td>
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<td>296.951</td>
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<td>2481.3</td>
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<td>2532.4</td>
</tr>
<tr>
<td>295.890</td>
<td>2558.3</td>
</tr>
</tbody>
</table>
Figure 5: Thermistor calibration: A plot of $1/\ln R$ versus $T$
Therefore,

\[ 1/\ln R = (T + \theta)/(DT + D\theta + C) \]  \hspace{1cm} [3.5]

Now separating out terms, we get

\[ 1/\ln R = T/(DT + D\theta + C) + \theta/(DT + D\theta + C) \]  \hspace{1cm} [3.6]

Thus,

\[ 1/\ln R = T/(DT + K) + \theta/(DT + K) \]  \hspace{1cm} [3.7]

where \( K = D\theta + C \). In a plot of \( 1/\ln R \) vs. \( T \), the slope is equal to \( 1/(DT + K) \) and the \( y \)-intercept is equal to \( \theta/(DT + K) \). Therefore,

\[ \theta = \text{y-intercept/slope} \]  \hspace{1cm} [3.8]

The value obtained was confirmed to be 121.6 as was previously reported (26, 31).

In order to use the equations outlined in Chapter Two to determine the corrected temperature rise, the effects of stirring and heat exchange for the calorimeter had to be investigated. These studies, which were previously conducted by Clark (26), involved time-temperature readings for the calorimetric system with an empty bomb, over a range of temperatures with and without the bomb rotating. The slopes of the readings were plotted against the mid-temperature of each interval done and a representation of the data on the calorimeter used in the present work is shown in Figure 6. This shows a valid linear relation-
Figure 6: Characterization of the calorimeter: A plot of $dT/dt$ versus $T$ [ $\bullet$ = bomb rotating; $\circ$, $\cdot$ = bomb stationary]
ship for the calorimeter whether or not the bomb was rotating. Therefore, it was assumed that equation [2.29] -
that is,
\[
\frac{d\theta}{dt} = u + k(\theta_j + \theta)
\]  
[2.29]
holds true for the calorimeter for the temperature range used.

Clark (26) generated hyperbolae similar to the time-temperature curve produced in a combustion and developed a numerical method based on the following equation:
\[
\int_{x_o}^{x_m} y \, dx = \sum_{k=0}^{m} y_k / P_k(x_k) \int_{x_o}^{x_m} P_k(x) \, dx
\]  
[3.9]
by which it was shown to approximate the area under the curve the best. When time intervals of 0.07 minutes are taken, agreement is reached to five significant figures. The results of Clark's work are based on Lagrangian interpolation which is shown in program subroutine G05ARD (see appendix).

The critical factor in calculating the correct temperature rise \( \Delta T_{corr} \) is the decision of the time at the end of the main period. This problem was solved by Clark (26) by incorporating a feature into the calibration program of evaluating \( \Delta T \) over a time range judged to extend from the
main period into the final period of the time-temperature readings. At the point at which the end of the main period, tₑ (Figure 1) was reached, the Δ₀ corr values start to converge. This convergence is shown in Table 2. This also illustrates a refinement of Clark's original program in that the number of iterations was nearly doubled in an effort to follow the temperature rise through the main period and well into the final period.

3.4. Determination of the Energy Equivalent of the Calorimeter

The benzoic acid was standardized by and obtained from the Parr Instrument Company. It was used to determine the energy equivalent of the calorimeter. The benzoic acid was in the form of tablets weighing approximately 1 g. and was stored in a desiccator with calcium chloride. The results of the combustions of benzoic acid are shown in Table 3. Runs 1 to 4 represent determinations of the energy equivalent of the calorimeter where one cm³ of water was placed inside the bomb and thus nitrous and nitric acids were produced in the combustion and subsequently titrated with standardized sodium hydroxide solution. Runs 5 to 7 represent combustions where the bomb was flushed for fifteen minutes with analytical grade oxygen prior to sealing the
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bomb. This was done in an effort to remove all the nitrogen from the bomb and hence eliminate the need for corrections due to the enthalpies of formation of nitrous and nitric acids.

Table 3 also shows the percent recovery of carbon dioxide produced in the reaction of benzoic acid with oxygen. The carbon dioxide recovered was determined with Lithasorb, that was obtained from the Fisher Scientific Company.

Using the heat of combustion of benzoic acid as 26434 J/g., the average energy equivalent is calculated to be 17799.6 ± 9.4 J/°C.

3.5. Development of the Experimental Method

One of the purposes behind the present experimental work was to continue the application of the method devised by Price and Yared (31) to determine the enthalpies of formation of perfluoroaromatic and halogen-substituted perfluoroaromatic compounds and to extend this method to the determination of perfluorocyclic compounds without the use of any auxiliary materials. Previous experimental tests carried out in this laboratory (31) showed that for the combustion of C_6F_6, C_6F_5I, and C_7F_8, a platinum-lined bomb can be used and no auxiliary
Table 3. Determination of the Energy Equivalent of the Calorimeter

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<th>Mass of Benzoic Acid (g)</th>
<th>$\Delta T_{\text{cor}}$ (°C)</th>
<th>$q_1$ (J)</th>
<th>$C_{cf}$ (J)</th>
<th>$CO_2$ collected (g)</th>
<th>$CO_2$ theoretical (g)</th>
<th>Percent Carbon (%)</th>
<th>Energy Equivalent (J/°C)</th>
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materials other than the compound to be combusted are needed.

The first combustions of the compound under investigation were done in an open platinum crucible in a platinum lined bomb (32). The compound was weighed into a previously weighed platinum crucible and sealed immediately after removal from the balance into the platinum lined bomb which was in the upright position. This method was soon abandoned after several combustions because these combustions produced a red colouration on the inside of the bomb and a substantial weight loss of the platinum crucible gave indication that platinum fluorides were being formed. A test for platinum ions with KCNS proved to be positive (33). Hence a steel bomb and steel crucible were used in all combustions although it was stated (31) that a steel bomb and a steel crucible would form Fe\textsuperscript{+++} and Fe\textsuperscript{++} fluorides. A spectroscopic method was used to evaluate the amount of these fluorides formed.

Despite the fact that it had been previously reported (9) that it was not possible to obtain complete combustion of perfluoroaromatic compounds without containing them and
without the use of auxiliary materials, the method that was established which eventually with minor refinements, proved to be quite acceptable, involved no containment for the compound with the exception of the steel crucible and the use of no auxiliary materials whatsoever.

Before each combustion experiment the bomb was baked out in a drying oven at 110°C for thirty minutes to remove any traces of moisture. The bomb was then removed from the drying oven and was then allowed to come to room temperature before use. An empty steel crucible was weighed and approximately 1.5 grams of the liquid compound was pipetted into the crucible. The weight was recorded and a stopwatch was started. After several weight-time readings were taken, the crucible and compound were removed from the balance and fitted into the gimbal with a platinum fuse wire that was previously weighed and set. This illustration may be found in Figure 7. The lid assembly, including the crucible containing the compound, and the fuse wire was fitted as quickly as possible into the bomb which was securely clamped in an inverted position.

The bomb was then sealed by means of a screw cap which had sealing bolts. The length of time was recorded from taking the weight of the crucible and compound to the insertion of the lid into the bomb. This was measured with
1. Fuse wire
2. Crucible
3. Ceramic insulator
4. Inlet/outlet valve
5. Contact for ignition clip

Figure 7: A photograph of the bomb lid assembly.
a stopwatch to the nearest 0.1 seconds. The amount of compound lost by evaporation could then be calculated from the rate of evaporation of the compound which was determined from the weight-time readings taken prior to the removal of the crucible and compound from the balance.

Prior to and just up to the insertion of the lid containing the crucible, compound and fuse fire, analytical grade oxygen was flushed into the open bomb as was done for the benzoic acid combustions in an effort to eliminate the need for corrections due to the formation of nitric and nitrous oxides and any other products that may form in the combustion from the presence of nitrogen and combustion products in the bomb. After the bomb had been sealed, it was pressurized to 3273 kPa with analytical grade oxygen.

Since the sample undergoing combustion was not contained in any way, it was necessary (except in the decafluorobiphenyl study) in the computation of a valid $\Delta H^\circ_{f298}$(g), to determine the amount of compound which would exist in the vapour state at the conditions inside the bomb just before combustion. The use of Gibb's equation in the form of

$$\ln(P_1/P_2) = \frac{[\bar{V}_1(P_{e1} - P_{e2})]}{RT}$$  \[3.10\]

was used. In the above equation, $T$ represents the tempera-
ture in absolute degrees of the bomb at the beginning of a combustion experiment, $P_{el}$ is the pressure in kilopascals in the bomb when filled with the required amount of oxygen, $P_{e2}$ is 101.3 kilopascals, and $\bar{V}_1$ is the molar volume of the compound when the external pressure is $P_{e2}$. $R$ is the universal gas constant with the following value: 8.314 J mol$^{-1}$ deg$^{-1}$. It is a matter of solving for $P_1$ which is the vapour pressure of the compound under a pressure of $P_{el}$. The value obtained for $P_1$ in equation [3.10] is then substituted into

$$P_1V = nRT$$  \hspace{2cm} [3.11]

which can be rewritten as

$$P_1V = (w_g/M)RT$$  \hspace{2cm} [3.12]

were $w_g$ is the weight of the compound which will be in the vapour state, $M$ is the compound's molecular weight, $V$ is the internal volume of the bomb in m$^{-3}$ and $R$ is again expressed in J mol$^{-1}$ deg$^{-1}$.

Solving for $w_g$ will give a numerical value and hence allows for a determination of $\Delta H^0_{f298}$(liquid) for the compound which is to be combusted that represents only that portion of the compound in the liquid state when combustion occurs.
3.6. The Enthalpy of Formation of Bromopentafluorobenzene

The heat of combustion of bromopentafluorobenzene was determined by the method described in the preceding section and only the compound and oxygen were used in the bomb. Due to the compound being placed in an open crucible a weight loss from evaporation versus time curve for bromopentafluorobenzene was plotted as illustrated in Figure 8. The average rate of loss of bromopentafluorobenzene from the crucible in which it was weighed was 0.0207 mg s⁻¹. The time between weighing the crucible containing the liquid and closing the bomb was such that less than 0.04% of the total sample was lost by evaporation.

The correction for the evaporation is estimated to be accurate to better than ± 3%. The error generated by the correction procedure should therefore be less than ± 0.001%.

The bomb was placed in the calorimetric bucket containing water and prior to taking time and temperature readings which were taken every 10 to 15 seconds for approximately ten minutes, the bomb was allowed to sit in the calorimetric bucket for fifteen to twenty minutes in order for the bomb to reach thermal equilibrium with the water. Subsequent to the pre-combustion period, ignition
Figure 8: Weight loss from evaporation versus time plot for Bromopentafluorobenzene
was effected and time-temperature readings were taken as often as every 0.05 minutes for the remaining 25 minutes. Rotation of the bomb was started three minutes after ignition and was continued throughout the remainder of the calorimetric experiment. The time-temperature readings were then typed on I.B.M. cards and submitted with the program to calculate the corrected temperature rise.

Before the analysis of the combustion products, the exterior of the bomb's lid was thoroughly dried with acetone with special attention being given to the inlet and outlet valves to ensure no moisture was present. Vacuum was applied to both valves in order to remove all the acetone. The bomb was then connected by means of a steel tube to the analysis train which consisted of a glass or steel U-tube that had been previously dried, a Teflon bubbler, a drying tube containing magnesium perchlorate, a gas sample collection system, and a carbon dioxide collection vessel. The bomb's outlet valve now connected to the analysis train was opened and the gases were allowed to pass through. An acetone-dry ice bath was put into place around the glass or steel U-trap to collect any volatile liquids that may be present in the combustion products.

The gases were allowed to empty out of the bomb and
then analytical grade oxygen was passed through the inlet valve of the bomb and allowed to flush through the bomb, out through the outlet valve and on through the analysis train for about two to three hours. With an initial pressure of 3273 kPa of oxygen, the total bleeding and flushing of the bomb took approximately 24 hours.

The Teflon bubbler was a Teflon graduated cylinder that had a 2-hole rubber stopper which was fitted with two lengths of Teflon tubing. The one Teflon tube through which the effluent gases from the bomb enter the bubbler portion of the analysis train extends near the bottom of the Teflon graduated cylinder and there the Teflon tubing was drawn to a point. The second piece of Teflon tubing provided the exit of the gases after going through the solution contained in the bubbler. This tubing was extended just beneath the rubber stopper but not into the solution which was contained in the bubbler.

The bubbler contained 100 cm$^3$ of solution comprising of 5 cm$^3$ of concentrated hydrochloric acid and 95 cm$^3$ of distilled water. The hydrochloric acid was used as a precaution to prevent any of the carbon dioxide which was present in the effluent gases from dissolving in the bubbler solution.

A 10 cm$^3$ aliquot of this solution contained in the
Teflon bubbler was removed from the bubbler after the bomb had been emptied and flushed and added to 25 cm$^3$ of Total Ionic Strength Activity buffer solution (TISAB) from the Orion Company which causes the pH to be adjusted to 5.5. The mixture of the bubbler solution and the buffer solution was then analyzed for $F^-$ using a fluoride specific ion electrode in conjunction with an Orion, Model 701 digital pH meter, capable of reading to the nearest 0.1 millivolts. The meter was calibrated prior to each determination of $F^-$ using a series of standards ranging in concentration of $F^-$ from $1 \times 10^{-1}$ to $5 \times 10^{1}$ mol m$^{-3}$.

These were prepared by the addition of a 0.1 molar fluoride standard solution from the Orion Company to the appropriate amount of distilled water and TISAB solution.

The gas sample collection system consisted of a short length of Pyrex tubing with high vacuum stopcocks at each end. The stopcocks were obtained from the Ace Glass Company and had a Teflon barrel with Viton o-ring seals. The gas sample collection tube of 4 cm$^3$ volume was normally connected in the analysis train immediately after the drying tube but from time to time its position in the analysis train was altered to test the composition of the effluent gases at all stages of the analysis train. An alteration to this type of system was developed by using again a short piece of Pyrex tubing in the shape of
a "T" and a rubber septum was attached to it for a gas
tight syringe to be used to take the gas sample for gas
chromatographic analysis. This system was used for sim-
licity in handling the gas sample and to avoid any
leakage and loss of any effluent gases while changing the
gas collection tubes.

The analysis of the contents of the gas sample was
performed on a Perkin Elmer Model 154, gas chromatograph
equipped with a thermal conductivity detector. In this
study two types of columns were used. The first column
was a 6 ft. x ½ in. o.d. silica gel column, operated at
25°C and a helium carrier flow rate of 15 cc/min. The
chromatographic conditions employed gave separation of the
tetrafluoromethane peak from the massive oxygen peak and
thus permitted the determination of the ratio of carbon
dioxide to tetrafluoromethane. Uncorrected retention
times for O₂, CF₄, and CO₂ are 1 min., 30 s.; 3 min.,
12 s.; and 12 min., 36 s. respectively. In the first
five runs in Table 4, the CO₂/CF₄ ratio was found through
the use of this column.

The second column which was a 6 ft. x ½ in. o.d.
Porapak Q column operated at 25°C and a helium flow rate
of 48 cc/min. was used to determine the CO₂/CF₄ ratio
throughout the remaining work. Uncorrected retention times
for O₂, CF₄, and CO₂ are 1 min., 3 s.; 1 min., 54 s.; and 4 min., 57 s. respectively. An improved separation between oxygen and tetrafluoromethane occurred using this column. A sample chromatogram, obtained in the analysis of the contents of the gas sample for the combustion of bromopen-
tafluorobenzene is shown in Figure 9.

The vessel containing the magnesium perchlorate was used to remove any moisture from the effluent gases which might have been picked up from the Teflon bubbler. It was necessary for the effluent gases to be dry before entering the carbon dioxide collection tube; therefore, it was placed prior to the collection tube and after the Teflon bubbler in the analysis train.

A drawing of the U-shaped Pyrex carbon dioxide collection tube is shown in Figure 10. Lithasorb, an indicating high capacity carbon dioxide absorbant which was provided by the Fisher Scientific was used in the determination of carbon dioxide because of its ease of handling and its high capacity. When Lithasorb is used it must be followed in the carbon dioxide collection tube by a drying agent to retain the water that is liberated when Lithasorb reacts with carbon dioxide. Magnesium perchlorate was used for this purpose. The collection tube was evacuated to a constant weight prior to using it
Figure 9: A sample chromatogram for the analysis of the contents of the gas collection sample in a combustion of C₆F₅Br.
Figure 10: A diagram of the carbon dioxide collection tube
in the analysis train and was again evacuated to a constant weight subsequent to emptying and flushing procedure of the combustion gases. The carbon dioxide collection tube was evacuated through the magnesium perchlorate end to prevent any loss of liberated water.

Allowances were made for small amounts of carbon dioxide removed from the analysis train for determination of the \( \text{CO}_2/\text{CF}_4 \) ratio to the total yield of carbon dioxide.

While the calorimetric part of the investigation of bromopentafluorobenzene was similar to that previously reported (11, 12, 13), the nature of the reaction for this compound in the combustion products necessitated some alternation in the type of bomb used and in the chemical part of the investigation.

Preliminary combustions done in the platinum lined bomb resulted in the formation of a dark red to yellow-brown solid indicating possible formation of \( \text{PtF}_4 \). A noticeable loss in weight of the platinum crucible was observed after each combustion.

Combustions were then extended to test the suitability of a steel bomb. It has been observed that the combustion in this bomb with fluoroaromatic compounds produced the formation of a green coloration inside the
bomb (31). This was shown to be iron(II) and iron(III) fluorides (33). A determination of the amount of Fe(II) and Fe(III) fluorides after combustion of $C_6F_5Br$ was tested. A colorimetric determination (34) was used and the amount of iron fluorides were found after combustion. To ensure that iron fluorides were being formed, the bomb was rinsed with distilled water and a fluoride determination was done on the resulting solution and a calibration curve was used with standard fluoride solution. Agreement with the amount of iron found in the bomb as Fe(II) and Fe(III) fluorides corresponded with the amount of fluoride found by specific ion electrode method. The iron determination gave a ratio of 15 to 85% of Fe(III) to Fe(II) where the fluoride determination along with the total iron gave a ratio of approximately 20 to 80% of Fe(III) to Fe(II).

The amount of iron fluoride found after combustion of bromopentafluorobenzene was $(1.7 \pm 0.1)\text{mg}$. The correction to the heat of formation of $C_6F_5Br$ caused by the formation of FeF$_2$ and FeF$_3$ was less than $3.3 \pm 0.5 \text{kJ mol}^{-1}$ per experiment. All subsequent combustions were therefore carried out using the steel bomb and steel crucible.

The combustion of bromopentafluorobenzene led to the formation of products that were identified as CO$_2$, CF$_4$, F$_2$, Br$_2$, and BrF$_3$. 
The gaseous products (CO₂, CF₄, F₂) were identified in the same manner previously used for the combustion of C₆F₆. There was ample evidence that a liquid had formed in the combustion products. Condensible products were collected in either a glass or steel trap which was immersed in a dry-ice acetone bath set at -80°C within the analysis train. To ensure all the products volatile at 25°C were removed from the combustion bomb, the system was flushed with ultra high pure oxygen for two to three hours and the bomb was then evacuated through the trap. Two immiscible liquids were observed. The major portion (lower phase) had a characteristic colour of free bromine and the upper phase had a colorless to grey-yellow colour. Since a carbon balance had already been established, the possibility of any halo-carbon products were unlikely and the fact that all of the bromine oxides (35) are unstable at room temperature indicated that the remaining products would be halogen or interhalogen compounds such as Br₂, BrF, BrF₃, and BrF₅.

By vacuum distillation the liquids were easily separated. The more volatile substance was dark red in colour and appeared to be free bromine. This was confirmed by mass spectral analysis using a MAT CH5 mass spectrometer. Major peaks were obtained at m/e 162, 160, and 158 with a peak height ratio of close to 1:2:1. In addition, peaks
of approximately equal height (about 7% of the m/e = 160 peak height) were observed at m/e = 81 and 79.

The molecular constituents in order of increasing volatility at 25°C are BrF₃, Br₂, BrF₅, and BrF. Any BrF₅ and/or BrF would have been collected in the "bromine" fraction. In addition to the mass spectral analysis the fraction was tested by adding water to the distilled sample. If any halogen fluoride were present, they would have reacted with water to form a complex mixture of HF, HBr, HBrO₃, Br₂, and O₂ (36). Fluoride analysis of the solution with a specific fluoride ion electrode proved to be negative.

Based on colour and volatility, it appeared possible that the remaining liquid was BrF₃. The liquid was distilled under vacuum into a carefully dried quartz capillary tube while the tube was immersed in liquid nitrogen. The capillary was then sealed under vacuum and removed for subsequent NMR fluorine analysis. The fluorine NMR analysis indicated a single peak corresponding to liquid BrF₃ at -55.2 p.p.m. (literature value -54.3 p.p.m.) relative to trifluoroacetic acid (31).

The amount of Br₂ was analyzed by either weighing the sample collected in a small ampoule and/or by iodometric analysis (38). The BrF₃ was reacted with KI solution
and analyzed for fluoride using the corresponding specific ion electrode. In these runs the BrF₃ fraction was also determined directly by weighing the fraction. Good agreement was obtained between specific ion and gravimetric determination.

From Table 4 the average molar ratio of carbon dioxide to tetrafluoromethane is 7.29 ± 0.07. Since only the relative amounts of CO₂ and CF₄ are important, many of the possible errors normally associated with gas chromatographic calibrations are negligible. However, in establishing the relative response factor it is necessary to use a tetrafluoromethane-oxygen mixture whose composition is similar to that of the sample from the combustion experiment. With the silica gel column, use of pure CF₄ yields a response factor that is low by 4.6% with respect to that obtained with a CF₄-O₂ mixture. With the Porapak Q column, the response factor is low by 1%. The carbon dioxide was unaffected by the presence of oxygen for both columns.

The net result is that if the relative response factor determined with pure CF₄ and CO₂ is used, a maximum value for ΔH°₂₉₈(C₆F₅Br,g) is obtained that is about 17 kJ mol⁻¹ too high.

From the material balance shown in Table 5 along with the average CO₂/CF₄ molar ratio reaction [3.13] may be
Table 4: Combustion Data and Calculated Enthalpy of Formation for Bromopentafluorobenzene

<table>
<thead>
<tr>
<th>Run</th>
<th>Mass C₆F₅Br g</th>
<th>$\Delta T_{\text{cor}}^\circ C$</th>
<th>CO₂/CF₄ *</th>
<th>CO₂ collected g</th>
<th>BrF₃ collected g</th>
<th>Total F₂ collected g</th>
<th>$\Delta H^o_f$ (C₆F₅Br,g) kJ mol⁻¹</th>
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</thead>
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<td>7.35</td>
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<td></td>
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</tr>
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<td>0.7449</td>
<td>7.24</td>
<td>1.432</td>
<td>0.240</td>
<td>-717.1</td>
<td></td>
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<td>0.7582</td>
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<td>7.24</td>
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<td></td>
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<td>1.600</td>
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<td>-718.7</td>
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</tbody>
</table>

*Molar Ratio.

*From F₂ and BrF₃.*

**Runs 1 to 7 glass trap used to collect liquid products, runs 8 to 13 steel trap used to collect liquid products.
Table 5: Combustion Recovery Data for Bromopentafluorobenzene

<table>
<thead>
<tr>
<th>Run</th>
<th>Mass C₆F₅Br (g)</th>
<th>% theoretical yields</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C(%)</td>
<td>F(%)</td>
</tr>
<tr>
<td>1</td>
<td>1.504</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.527</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
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<td>102</td>
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<td>99</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.308</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>1.040</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.508</td>
<td>101</td>
<td>98</td>
</tr>
<tr>
<td>10</td>
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<tr>
<td>13</td>
<td>1.391</td>
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<td>87</td>
</tr>
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</table>

*Runs 1 to 7 glass trap used to collect liquid products, runs 8 to 13 steel trap used to collect liquid products.*
written to represent the combustion of bromopentafluorobenzene. However, as will be discussed later, it is unlikely that free bromine exists in the bomb.

\[ \text{C}_6\text{F}_5\text{Br} + 5.276 \text{ O}_2 \rightarrow 5.276 \text{ CO}_2 + 0.724 \text{ CF}_4 + 0.923 \text{ F}_2 + 0.086 \text{ BrF}_3 + 0.457 \text{ Br}_2 \quad [3.13] \]

In treating a complex mixture of products possible interactions between the compounds must be taken into account. No detectable heat of mixing was observed when \( \text{F}_2, \text{ O}_2, \text{ CF}_4, \) and \( \text{CO}_2 \) were mixed under anhydrous conditions (31).

However, it was found from studies of the mixing of bromine and fluorine in the bomb that a correction of \(-130 \pm 13 \text{ kJ mol}^{-1}\) is required for the interaction between \( \text{Br}_2 \) and \( \text{F}_2 \). Based on \( \Delta H_f^{\circ} \text{(BrF, g)} = -74.1 \text{ kJ mol}^{-1} \) (39), approximately \(-68.2 \text{ kJ mol}^{-1}\) of the correction is due to reaction (3.14).

\[ \frac{1}{2}\text{F}_2(g) + \frac{1}{2}\text{Br}_2(l) \rightleftharpoons \text{BrF}(g) \quad [3.14] \]

With the excess \( \text{F}_2 \) present the equilibrium should be far to the right (39). It should be noted that during the slow bleeding of the bomb over a period of approximately 20 hours to recover the combustion products for analysis, the BrF equilibrium shifts to the left in quantitative
conversion of BrF to Br$_2$ and F$_2$. In an all metal system (steel trap) the reaction may be somewhat inhibited as indicated by the apparent slight shortfall in bromine recovery (see Table 5). The shortfall was always accompanied by the appearance of a light yellow coloration in the F$_2$ absorbing solution in the bubbler.

In applying equation [3.13] to the experimental combustion process it must be remembered that the bromopentafluorobenzene sample is not contained in any way other than in the steel crucible. The combustion occurs in a 320 cm$^3$ bomb with an initial pressure of 3273 kPa. Application of the Gibb's equation in conjunction with the ideal gas law as outlined in equation [3.10], [3.11], and [3.12] and the necessary ancillary data produces a value of $w = .074$ g as the amount of bromopentafluorobenzene which is in the vapour state at the time of combustion. Thus, only $(W - .074)$ g of the liquid bromopentafluorobenzene are involved in a combustion where $W$ is the total liquid sample weight initially present in the bomb. This presence of slightly over 7.4% of the bromopentafluorobenzene in the vapour state undoubtedly aids combustion and may in fact be responsible for the complete combustion in the absence of any auxiliary materials.
In carrying out the thermochemical calculation for 
\( \Delta H_{f298}^\circ (C_{6}F_{5}Br, g) \) as shown in Table 4, the standard enthalpies of formation of the combustion products were taken as:

\[
\Delta H_{f298}^\circ (CO_2, g) = -393.512 \text{ kJ mol}^{-1} \quad (40)
\]

\[
\Delta H_{f298}^\circ (CF_4, g) = -933.0 \text{ kJ mol}^{-1} \quad (41)
\]

\[
\Delta H_{f298}^\circ (BrF_3, g) = -255.60 \text{ kJ mol}^{-1} \quad (36)
\]

and the required correction for bromopentafluorobenzene in the liquid state

\[
[(W - .074)/W] \Delta H_{298}^\circ (C_{6}F_{5}Br) \quad [3.15]
\]

was based on the heat of vaporization of 43.05 kJ mol\(^{-1}\).

Based on the preceding data and the average value of 
\( \Delta H_{f298}^\circ (C_{6}F_{5}Br, g) \) from runs 1 to 13 inclusive and an estimated correction to standard state of 5.5 kJ mol\(^{-1}\), the value of 
\( \Delta H_{f298}^\circ (C_{6}F_{5}Br, g) = -711.6 \pm 5.6 \text{ kJ mol}^{-1} \).

However, when the uncertainty in the auxiliary experiments are taken into account the overall limit must be set at about \( \pm 16 \text{ kJ mol}^{-1} \).

3.7. The Enthalpy of Formation of Decafluorocyclohexene and Dodecfluorocyclohexane

The heat of combustion of decafluorocyclohexene and
dodecfluorocyclohexane were determined by the direct combustion method previously developed and used for hexafluorobenzene and related compounds (11, 12, 13).

Figure 11 and Figure 12 illustrate a weight loss by evaporation versus time curve for decafluorocyclohexene and dodecafluorocyclohexane, respectively. The average rate of evaporation of $C_{6}F_{10}$ from the crucible in which the compound was weighed was 0.833 mg s$^{-1}$ and similarly for $C_{6}F_{12}$, an average of 0.667 mg s$^{-1}$. The time between weighing the crucible containing the sample and closing the bomb was such that less than 1.7% of the total sample for $C_{6}F_{10}$ and 1.3% for $C_{6}F_{12}$ was lost by evaporation. The correction for the evaporation is estimated to be better than ± 3%. The error generated by the correction procedure for $C_{6}F_{10}$ and $C_{6}F_{12}$ should therefore be less than ± 0.05% and ± 0.04%, respectively.

The same procedures were followed both in the calorimetric and analytical parts of the thermochemical investigation for $C_{6}F_{10}$ and $C_{6}F_{12}$ as for the compounds $C_{6}F_{6}$ (11) and $C_{7}F_{8}$ (12).

Gas chromatographic analysis of the products contained in the gas sample gave peaks for oxygen, tetrafluoromethane, and carbon dioxide.
Figure 11: Weight loss from evaporation versus time plot for Decafluorocyclohexene
Figure 12: Weight loss from evaporation versus time plot for Dodecafluorocyclohexane
Gas chromatographic and mass spectrometric analysis indicate that observed unburned material in the study of both C$_6$F$_{10}$ and C$_6$F$_{12}$ is a portion of the original material. The mass spectrum of unburned C$_6$F$_{12}$ was compared to that of an authentic sample and to API 0201 (42). No literature spectra could be found for C$_6$F$_{10}$. Table 6 represents the major peaks (R.A. > 4% base peak) for both an authentic sample and the recovered unburned material.

In the combustion of C$_6$F$_{10}$ and C$_6$F$_{12}$ in the steel bomb it was observed that the formation of a green coloration seemed to be less extensive in both cases as compared to the amount observed in the study of C$_6$F$_5$Br (32). The amount of iron fluorides were determined by the procedure described for the study of the combustion of bromopentafluorobenzene. In both cases the quantity found was 1.23 mg. The correction to the heat of formation of C$_6$F$_{10}$ and C$_6$F$_{12}$ caused by the formation of FeF$_2$ and FeF$_3$ was less than 1.5 kJ mol$^{-1}$ and 1.6 kJ mol$^{-1}$, respectively.

The total material balance based on CO$_2$, CF$_4$, F$_2$ and unburned material was in general low by about 0.25%. This was shown to be due to small losses from the trapping system used to recover the unburned material. Subsequent thermochemical calculations were therefore based on the CO$_2$-CF$_4$ recovery.
TABLE 6: Main peaks (R.A. > 4% base peak) for C$_6$F$_{10}$ and for unburned material from the combustion of C$_6$F$_{10}$ (isotope peaks omitted).

<table>
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<th>m/e</th>
<th>ion</th>
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<th>unburned material</th>
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<td>CF</td>
<td>6.5</td>
<td>6.2</td>
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<tr>
<td>69</td>
<td>CF$_3$</td>
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<td>21.6</td>
</tr>
<tr>
<td>74</td>
<td>C$_3$F$_2$</td>
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<td>93</td>
<td>C$_3$F$_3$</td>
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<td>4.9</td>
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<tr>
<td>243</td>
<td>C$_6$F$_9$</td>
<td>74.0</td>
<td>70.0</td>
</tr>
<tr>
<td>262</td>
<td>C$<em>6$F$</em>{10}$</td>
<td>26.0</td>
<td>30.9</td>
</tr>
</tbody>
</table>
From the average CO$_2$/CF$_4$ molar ratio (Table 7) along with the material balance shown in Table 8, reaction [3.16] may be written to represent the combustion of decafluorocyclohexene,

$$C_6F_{10} + 4.024 \text{ O}_2 \rightarrow 4.024 \text{ CO}_2 + 1.976 \text{ CF}_4 + 1.048 \text{ F}_2 \quad [3.16]$$

From the average CO$_2$/CF$_4$ molar ratio (Table 9) along with the material balance shown in Table 10, reaction [3.17] may be written to represent the combustion of dodecafluorocyclohexane,

$$C_6F_{12} + 3.452 \text{ O}_2 \rightarrow 3.452 \text{ CO}_2 + 2.548 \text{ CF}_4 + 0.904 \text{ F}_2 \quad [3.17]$$

In applying equation [3.16] and equation [3.17] to the combustion process to calculate $\Delta H_{f298}^\circ(C_6F_{10}, g)$ and $\Delta H_{f298}^\circ(C_6F_{12}, g)$, allowance must be made for that portion of the total liquid sample originally placed in the bomb which is in the vapour state when combustion occurs.

It must be remembered that C$_6$F$_{10}$ and C$_6$F$_{12}$ samples are not contained in any way and that the combustion occurs in a 320 cm$^3$ bomb with an initial temperature of 23.5°C and an initial pressure of 3273 kPa. The experimental procedure therefore involves combustion of 1.23 g C$_6$F$_{10}$ vapour and $(W - 1.23)$ g C$_6$F$_{10}$ liquid where $W$ is the weight of
Table 7: Combustion Data and Calculated Enthalpy of Formation for Decafluorocyclohexene

<table>
<thead>
<tr>
<th>Mass $C_6F_{10}$</th>
<th>$\Delta T_{corr}$</th>
<th>$CO_2/CF_4$</th>
<th>CO$_2$ collected</th>
<th>F$_2$ collected</th>
<th>$\Delta H^0_f$</th>
<th>$C_6F_{10}$ g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.364</td>
<td>0.3437</td>
<td>2.03</td>
<td>0.709</td>
<td>0.158</td>
<td>-1905.8</td>
<td>1.364</td>
</tr>
<tr>
<td>1.671</td>
<td>0.3928</td>
<td>2.05</td>
<td>0.821</td>
<td>0.187</td>
<td>-1913.8</td>
<td>1.671</td>
</tr>
<tr>
<td>1.468</td>
<td>0.3541</td>
<td>2.04</td>
<td>0.731</td>
<td>0.167</td>
<td>-1905.8</td>
<td>1.468</td>
</tr>
<tr>
<td>1.501</td>
<td>0.4178</td>
<td>2.03</td>
<td>0.860</td>
<td>0.194</td>
<td>-1901.6</td>
<td>1.501</td>
</tr>
<tr>
<td>1.443</td>
<td>0.3954</td>
<td>2.03</td>
<td>0.817</td>
<td>0.184</td>
<td>-1906.2</td>
<td>1.443</td>
</tr>
</tbody>
</table>

$^a$Mass of $C_6F_{10}$ placed in the bomb.

$^b$Molar Ratio.
Table 8: Combustion Recovery Data for Decafluorocyclohexene

<table>
<thead>
<tr>
<th>Mass $C_6F_{10}$</th>
<th>% theoretical yields</th>
<th>Mass $C_6F_{10}$</th>
<th>% theoretical yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td></td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>C(%)</td>
<td>F(%)</td>
<td>C(%)</td>
<td>F(%)</td>
</tr>
<tr>
<td>1.364</td>
<td>77.0</td>
<td>1.050</td>
<td>100.0</td>
</tr>
<tr>
<td>1.671</td>
<td>72.5</td>
<td>1.212</td>
<td>100.0</td>
</tr>
<tr>
<td>1.468</td>
<td>73.6</td>
<td>1.083</td>
<td>100.0</td>
</tr>
<tr>
<td>1.501</td>
<td>84.9</td>
<td>1.274</td>
<td>100.0, 100.2</td>
</tr>
<tr>
<td>1.443</td>
<td>83.9</td>
<td>1.211</td>
<td>100.0, 100.1</td>
</tr>
</tbody>
</table>

aMass of $C_6F_{10}$ placed in the bomb.

bPercent yield based on amount of $C_6F_{10}$ placed in bomb.

cBased on recovery of carbon (from CO$_2$ and CF$_4$).
Table 9: Combustion Data and Calculated Enthalpy of Formation for Dodecafluorocyclohexane

<table>
<thead>
<tr>
<th>Mass (C_{6}F_{12}) (^{a}) g</th>
<th>(T_{cor}) (^{b}) °C</th>
<th>(CO_{2}/CF_{4})</th>
<th>(CO_{2}) collected (g)</th>
<th>(F_{2}) collected (g)</th>
<th>(\Delta H_{f}^{o}(C_{6}F_{12},g)) (kJ\cdot mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.815</td>
<td>0.3485</td>
<td>1.37</td>
<td>0.696</td>
<td>0.160</td>
<td>-2365.2</td>
</tr>
<tr>
<td>1.696</td>
<td>0.3349</td>
<td>1.35</td>
<td>0.660</td>
<td>0.147</td>
<td>-2371.5</td>
</tr>
<tr>
<td>1.981</td>
<td>0.4082</td>
<td>1.36</td>
<td>0.806</td>
<td>0.183</td>
<td>-2361.4</td>
</tr>
<tr>
<td>1.741</td>
<td>0.3349</td>
<td>1.36</td>
<td>0.666</td>
<td>0.150</td>
<td>-2371.1</td>
</tr>
<tr>
<td>1.501</td>
<td>0.2653</td>
<td>1.35</td>
<td>0.521</td>
<td>0.113</td>
<td>-2362.3</td>
</tr>
<tr>
<td>1.945</td>
<td>0.3973</td>
<td>1.35</td>
<td>0.786</td>
<td>0.174</td>
<td>-2374.4</td>
</tr>
<tr>
<td>1.588</td>
<td>0.3065</td>
<td>1.35</td>
<td>0.607</td>
<td>0.133</td>
<td>-2376.5</td>
</tr>
<tr>
<td>1.790</td>
<td>0.3259</td>
<td>1.35</td>
<td>0.642</td>
<td>0.143</td>
<td>-2369.0</td>
</tr>
</tbody>
</table>

\(^{a}\)Mass of \(C_{6}F_{12}\) placed in bomb.

\(^{b}\)Molar ratio
Table 10: Combustion Recovery Data for Dodecafluorocyclohexane

<table>
<thead>
<tr>
<th>Mass ( C_6 F_{12} ) (^a) [g]</th>
<th>% theoretical yields (^c)</th>
<th>Mass ( C_6 F_{12} ) (^d) [g]</th>
<th>% theoretical yields (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.815</td>
<td>75.4 75.2</td>
<td>1.369</td>
<td>100.0 100.0</td>
</tr>
<tr>
<td>1.696</td>
<td>76.9 76.9</td>
<td>1.304</td>
<td>100.0 100.0</td>
</tr>
<tr>
<td>1.981</td>
<td>80.2 80.1</td>
<td>1.589</td>
<td>100.0 99.5</td>
</tr>
<tr>
<td>1.741</td>
<td>75.4 75.2</td>
<td>1.313</td>
<td>100.0 99.8</td>
</tr>
<tr>
<td>1.501</td>
<td>68.7 68.3</td>
<td>1.031</td>
<td>100.0 99.5</td>
</tr>
<tr>
<td>1.945</td>
<td>79.9 79.8</td>
<td>1.554</td>
<td>100.0 99.9</td>
</tr>
<tr>
<td>1.588</td>
<td>75.6 75.4</td>
<td>1.200</td>
<td>100.0 99.7</td>
</tr>
<tr>
<td>1.790</td>
<td>70.9 70.9</td>
<td>1.269</td>
<td>100.0 100.0</td>
</tr>
</tbody>
</table>

\(^a\) Mass of \( C_6 F_{12} \) placed in bomb.
\(^c\) Percent yield based on amount of \( C_6 F_{12} \) placed in bomb.
\(^d\) Based on recovery of carbon (from \( CO_2 \) and \( CF_4 \)).
C₆F₁₀ sample in grams and the combustion of 1.18 g C₆F₁₂ vapour and (W - 1.18) g C₆F₁₂ solid where W is the weight of C₆F₁₂ sample in grams. This means that on the average, approximately 74% of the C₆F₁₀ and 67% of the C₆F₁₂ are in the vapour state before combustion.

In carrying out the thermochemical calculations, the following heats of formation have been used:

\[ \Delta H_{f298}^o (\text{CO}_2, \text{g}) = -393.512 \text{ kJ mol}^{-1} \]  \hspace{1cm} (40)

and

\[ \Delta H_{f298}^o (\text{CF}_4, \text{g}) = -933.0 \text{ kJ mol}^{-1} \]  \hspace{1cm} (41)

The allowance for the amount of decafluorocyclohexene in the liquid state before combustion, that is

\[ [(W - 1.23)/W] \Delta H_{298}^o (\text{C}_6\text{F}_{10}) \]  \hspace{1cm} [3.18]

was based on the enthalpy of vaporization of 30.96 kJ mol⁻¹ which is in good agreement with the value of 30.75 kJ mol⁻¹ reported by Cox et al (9).

Again, allowance was made for the amount of dodecafluorocyclohexane in the solid state before combustion, that is,

\[ [(W - 1.18)/W] \Delta H_{298}^o (\text{C}_6\text{F}_{12}) \]  \hspace{1cm} [3.19]

was based on the enthalpy of sublimation of 35.98 kJ mol⁻¹.

Based on the preceding data and an estimated correction to standard state of 3.4 kJ mol⁻¹, \( \Delta H_{f298}^o (\text{C}_6\text{F}_{10}, \text{g}) = -1906.6 \pm 7.2 \text{ kJ mol}^{-1} \).
The value for $\Delta H^\circ_f$ (C$_6$F$_{12}$, g) based on the above data and an estimated correction to standard state of 2.9 kJ mol$^{-1}$ is $-2368.9 \pm 7.6$ kJ mol$^{-1}$.

3.8. The Enthalpy of Formation of Decafluorobiphenyl

The heat of combustion of decafluorobiphenyl was determined by the direct combustion method previously developed and used for hexafluorobenzene and related compounds (11, 12, 13).

The application of rate of loss of evaporation was not taken into account for no measurable loss of decafluorobiphenyl sample in the crucible in which it was weighed was observed.

The same procedure was followed in the calorimetric and chemical parts of the thermochemical investigation for C$_{12}$F$_{10}$ as was used for C$_6$F$_6$ (11) and C$_7$F$_8$ (12).

The only products of combustion were CO$_2$, CF$_4$, and F$_2$. Again, the gas chromatographic analysis of the products were done on a Porapak Q column.

In the combustion of C$_{12}$F$_{10}$ in a steel bomb the formation of a green coloration was again observed. The amount of iron fluorides was determined using the same procedure.
as described for the study of the combustion of bromopentafluorobenzene. In this case, approximately 1.30 mg of iron fluorides were formed. The correction to the heat of formation of C_{12}F_{10} caused by the formation of FeF_2 and FeF_3 was less than 2.5 kJ mol^{-1}.

From the material balance shown in Table 11, along with the average CO_2/CF_4 molar ratio, reaction [3.20] may be written to represent the combustion of decafluorobiphenyl,

\[ C_{12}F_{10} + 10.248 \ O_2 \rightarrow 10.248 \ CO_2 + 1.752 \ CF_4 + 1.496 \ F_2 \]  \[ [3.20] \]

With the exception of C_{12}F_{10} all reactants and products are in the gaseous state. The decafluorobiphenyl is present in the bomb solely as a solid at the time of combustion.

In treating a complex mixture of products possible interactions between the compounds must be taken into account. No detectable heat of mixing was observed when F_2, O_2, CF_4, and CO_2 were mixed under anhydrous conditions (12).

For the calculation of \( \Delta H^\circ_{f298} (C_{12}F_{10}, g) \), the standard heats of formation of the combustion products were again taken as
Table 11: Combustion Data and Calculated Enthalpy of Formation for Decafluorobiphenyl

<table>
<thead>
<tr>
<th>Mass C_{12}F_{10}</th>
<th>ΔT_{cor} (°C)</th>
<th>CO_2/CF_4* (by g.c.)</th>
<th>CO_2 (g)</th>
<th>F_2 (g)</th>
<th>% Theoretical Yields</th>
<th>ΔH^O_{f298} (C_{12}F_{10}, g) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.245</td>
<td>0.9073</td>
<td>5.82</td>
<td>1.677</td>
<td>0.222</td>
<td>99.9</td>
<td>101.6</td>
</tr>
<tr>
<td>1.054</td>
<td>0.7669</td>
<td>5.88</td>
<td>1.421</td>
<td>0.184</td>
<td>99.8</td>
<td>100.3</td>
</tr>
<tr>
<td>1.338</td>
<td>0.9777</td>
<td>5.78</td>
<td>1.830</td>
<td>0.226</td>
<td>101.5</td>
<td>101.5</td>
</tr>
<tr>
<td>1.176</td>
<td>0.8578</td>
<td>5.84</td>
<td>1.582</td>
<td>0.203</td>
<td>99.6</td>
<td>100.3</td>
</tr>
<tr>
<td>1.327</td>
<td>0.9664</td>
<td>5.88</td>
<td>1.803</td>
<td>0.225</td>
<td>100.6</td>
<td>98.7</td>
</tr>
<tr>
<td>1.410</td>
<td>1.0288</td>
<td>5.86</td>
<td>1.922</td>
<td>0.242</td>
<td>100.9</td>
<td>100.4</td>
</tr>
<tr>
<td>1.088</td>
<td>0.7940</td>
<td>5.84</td>
<td>1.504</td>
<td>0.189</td>
<td>102.4</td>
<td>102.4</td>
</tr>
<tr>
<td>1.212</td>
<td>0.8824</td>
<td>5.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Molar ratio
\[ \Delta H_{f298}^O (\text{CO}_2, g) = -393.512 \text{ kJ mol}^{-1} \quad (40) \]

and

\[ \Delta H_{f298}^O (\text{CF}_4, g) = -933.0 \text{ kJ mol}^{-1} \quad (41) \]

The required correction for decafluorobiphenyl in the solid state to the gaseous state was based on the heat of sublimation \( \Delta H_{298}^O = 85.27 \text{ kJ mol}^{-1} \) (43). This value was determined in the present work to be 85.60 kJ mol\(^{-1}\) which is in good agreement with that of the reported value.

Based on the preceding data and an estimated correction to standard state of 5.0 kJ mol\(^{-1}\), \( \Delta H_{f298}^O (\text{C}_{12}\text{F}_{10}, g) = -1262.8 \pm 3.2 \text{ kJ mol}^{-1} \).
CHAPTER FOUR

DISCUSSION OF THERMOCHEMICAL RESULTS

The method that has been devised by Price et al. (11, 12, 13) for the combustion of perfluoroaromatic and halogen substituted perfluoroaromatic compounds permits the determination of the enthalpies of formation of these compounds. The present work has enabled more thermochemical data to be found on these series of halocarbons and the method has been extended to perfluorocyclic compounds.

No published values for the enthalpies of formation of bromopentafluorobenzene, dodecafluorocyclohexane, and decafluorobiphenyl exist.

The present work calculates the enthalpies of formation of the compounds studied as follows:

\[ \Delta H_{f298}^o (C_6F_5Br, g) = -711.6 \pm 16.7 \text{ kJ mol}^{-1} \]
\[ \Delta H_{f298}^o (C_6F_10, g) = -1906.6 \pm 7.2 \text{ kJ mol}^{-1} \]
\[ \Delta H_{f298}^o (C_6F_{12}, g) = -2368.9 \pm 7.6 \text{ kJ mol}^{-1} \]
\[ \Delta H_{f298}^o (C_{12}F_{10}, g) = -1262.8 \pm 3.2 \text{ kJ mol}^{-1} \]
4.1. Destabilization Energies

The values given in Table 12 for $\Delta H_f^O(g)_{(\text{calc.})}$ have been calculated from the following relation (10),

$$
\Delta H_f^O(C_6F_5X, g) = 
\Delta H_f^O(C_6H_5X, g) + 5\Delta H_f^O(C_6H_5F, g) - 5\Delta H_f^O(C_6H_6, g) \quad [4.1]
$$

The above equation assumes that the difference between bond energy terms C-F and C-H are constant and are, therefore, transferable from one molecular structure to another. These values are shown in Table 12 and are compared to the experimentally derived values.

The large discrepancies between the experimental and calculated values of $\Delta H_f^O(g)$ indicates that the assumption made in deriving $\Delta H_f^O(g)$ calculated is not justified. The values of $\Delta H_f^O(g)_{(\text{experimental})} - \Delta H_f^O(g)_{(\text{calculated})}$ is referred to as $\Delta H$ destabilization (10). The values for $\Delta H$ destabilization for hexafluorobenzene, iodopentafluorobenzene, and octafluorotoluene are calculated. Also included is the $\Delta H$ destabilization of bromopentafluorobenzene based on the heat of formation determined in this work.
Table 12: Destabilization energies for $C_6F_5X^+$

<table>
<thead>
<tr>
<th>X in $C_6F_5X$</th>
<th>$\Delta H_f^0(g)$ kJ mol(^{-1}) (expt.)</th>
<th>$\Delta H_f^0(g)$ kJ mol(^{-1}) (calc.)*</th>
<th>$\Delta H$(destab.) kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>-843.3(10)</td>
<td>-945.6</td>
<td>102</td>
</tr>
<tr>
<td>H</td>
<td>-805.9(10)</td>
<td>-912.7</td>
<td>107</td>
</tr>
<tr>
<td>Cl</td>
<td>-810.0(10)</td>
<td>-944.8</td>
<td>134</td>
</tr>
<tr>
<td>OH</td>
<td>-957.1(10)</td>
<td>-1091.9</td>
<td>135</td>
</tr>
<tr>
<td>COOH</td>
<td>-1148.4(10)</td>
<td>-1288.2</td>
<td>140</td>
</tr>
<tr>
<td>F</td>
<td>-956.0(10)</td>
<td>-1111.8</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>-945.6(11)</td>
<td>-1111.8</td>
<td>166</td>
</tr>
<tr>
<td>Br</td>
<td>-711.6(32)</td>
<td>-891.4</td>
<td>180</td>
</tr>
<tr>
<td>I</td>
<td>-577.7(13)</td>
<td>-833.5</td>
<td>276</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>-1268.6(14)</td>
<td>-1594.8</td>
<td>326</td>
</tr>
</tbody>
</table>

† Reference numbers in parenthesis.

* From eq. [4.1]. Based on $\Delta H_f^0$($C_6H_5F$,g) = -116.15 kJ mol\(^{-1}\) (44) and $\Delta H_f^0$($C_6H_6$,g) = 82.98 kJ mol\(^{-1}\) (45)
4.2. Calculation of Bond Energies

The present work has produced the following data:

\[ \Delta H^O_{f298} (C_6F_5Br, g) \leq -711.6 \text{ kJ mol}^{-1} \]
\[ \Delta H^O_{f298} (C_{12}F_{10}, g) = -1262.8 \text{ kJ mol}^{-1} \]

With the preceding data and using the values for

\[ \Delta H^O_{f298} (C_6F_5, g) = -387.4 \text{ kJ mol}^{-1} \]  \hspace{1cm} (13)
\[ \Delta H^O_{f} (Br, g) = 111.7 \text{ kJ mol}^{-1} \]  \hspace{1cm} (46)

the relationship referred to 298°K and in the gaseous state can be used

\[ D(C_6F_5-X) = \Delta H^O_f(C_6F_5) + \Delta H^O_f(X) - \Delta H^O_f(C_6F_5X) \]  \hspace{1cm} [4.2]

where \( X = \text{Br} \), and \( C_6F_5 \).

The values of \( D(C_6F_5-\text{Br}) \) and \( D(C_6F_5-C_6F_5) \) are 435.9 kJ mol\(^{-1}\) and 488.0 mol\(^{-1}\), respectively.

In Table 13, a comparison is made between \( D(C_6F_5X) \) values based on thermochemical methods and appearance potential methods  \( (47) \). Agreement of the present value of \( D(C_6F_5-\text{Br}) \) with the value estimated from A.P. studies is well within the combined error limits.

In Table 14, calculations of \( D(C_6F_5-X) \) and \( D(C_6H_5-X) \)
Table 13: Comparison of $D(\text{C}_6\text{F}_5-X)$ values determined from thermochemistry with values derived from appearance potential studies

<table>
<thead>
<tr>
<th>X</th>
<th>From thermochemistry*</th>
<th>From appearance potentials†</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>608.8 ± 12.6</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>636.4 ± 12.6</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>642.7 ± 12.6</td>
<td>629.3 ± 8.4</td>
</tr>
<tr>
<td>Cl</td>
<td>543.9 ± 12.6</td>
<td>551.8 ± 8.4</td>
</tr>
<tr>
<td>Br</td>
<td>435.9 ± 12.6</td>
<td>443.1 ± 8.4</td>
</tr>
<tr>
<td>I</td>
<td>277.0 ± 4.2</td>
<td>277.0 ± 4.2§</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>595.0 ± 12.6</td>
<td></td>
</tr>
<tr>
<td>CF$_3$</td>
<td>404.2 ± 12.6</td>
<td></td>
</tr>
</tbody>
</table>

* All values in this column are based on $\Delta H^\circ_{f298}(\text{C}_6\text{F}_5, g) = -387.4$ kJ mol$^{-1}$ determined from the kinetic value of $D(\text{C}_6\text{F}_5-I)$ and $\Delta H^\circ_{f298}(\text{C}_6\text{F}_5, g) = -557.7$ ± 12.6 kJ mol$^{-1}$ (13)

† Based on the kinetic value of $D(\text{C}_6\text{F}_5-I)$ and differences in a.p. values.

§ Kinetic value. (48)
Table 14: Calculation of $D(C_6F_5-\text{X})$ and comparison with $D(C_6H_5-\text{X})\dagger$

<table>
<thead>
<tr>
<th>X</th>
<th>$\Delta H^O_{f298}(X,g)$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^O_{f298}(C_6F_5\text{X},g)$ (kJ mol$^{-1}$)</th>
<th>$D(C_6F_5-\text{X})$ (kJ mol$^{-1}$)</th>
<th>$D(C_6H_5-\text{X})$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>38.9(40)</td>
<td>-957.1(10)</td>
<td>608.8</td>
<td>460.2(50)</td>
</tr>
<tr>
<td>H</td>
<td>218.0(40)</td>
<td>-805.9(10)</td>
<td>636.4</td>
<td>460.2(50)</td>
</tr>
<tr>
<td>F</td>
<td>79.1(49)</td>
<td>-956.0(10)</td>
<td>647.7</td>
<td>514.6(50)</td>
</tr>
<tr>
<td>Cl</td>
<td>121.3(49)</td>
<td>-810.0(10)</td>
<td>543.9</td>
<td>393.3(50)</td>
</tr>
<tr>
<td>Br</td>
<td>111.7(46)</td>
<td>-711.6(32)§</td>
<td>435.9</td>
<td>313.0(51)</td>
</tr>
<tr>
<td>I</td>
<td>106.7(49)</td>
<td>-557.7(13)</td>
<td>277.0</td>
<td>263.6(50)</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>138.9(40)</td>
<td>-843.3(10)</td>
<td>595.0</td>
<td>418.4(50)</td>
</tr>
<tr>
<td>COOH</td>
<td>-223.0(46)</td>
<td>-1239.9(10)</td>
<td>538.0</td>
<td>394.6(50)</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>-477.0(10)</td>
<td>-1268.6(14)</td>
<td>404.2</td>
<td>435.1(52)</td>
</tr>
<tr>
<td>C$_6$F$_5$</td>
<td>-387.4(13)</td>
<td>-1262.8 §</td>
<td>488.0</td>
<td>*</td>
</tr>
</tbody>
</table>

† Reference numbers in parenthesis.
§ Value obtained in this work.
* Value cannot be determined.
are shown. These are compared in Figure 13 between the bond dissociation energies, D(C₆F₅-X) and D(C₆H₅-X).

In general, the enhanced electron density on the carbon attached to X in C₆F₅X leads to stronger C-X bonds.

The marked exception to the correlation shown in Figure 13 is where X = CF₃. In this and in similar groups where the carbon in X is bonded to highly electronegative atoms the sp³ hybrid orbitals on this carbon will be distorted to such an extent that the overlap with the ring carbon orbitals is drastically reduced. The low value for D(C₆F₅-CF₃) is therefore not unexpected (53).

4.3. Calculation of "Resonance Energy" of Hexafluorobenzene

It is possible from the data determined in this work and from the heat of formation of hexafluorobenzene (13) to calculate the enthalpies of reactions [4.3] and [4.4]

\[ C₆F₁₀(g) + F₂(g) = C₆F₁₂(g) \quad [4.3] \]
\[ C₆F₆(g) + 3F₂(g) = C₆F₁₂(g) \quad [4.4] \]

and subsequently to calculate a value for the "resonance energy" of hexafluorobenzene (defined as \( \Delta H^0_{298} \) (Rx[4.4]) - 3\( \Delta H^0_{298} \) (Rx[4.3])). Based on \( \Delta H^0_{298} \) (C₆F₆,g) = -945.6 kJ mol⁻¹ (13) this "resonance energy" is found to be -36.4 kJ
Figure 13: Comparison of $D(C_6F_5-X)$ and $D(C_6H_5-X)$ bond dissociation energies for $X = I(\bullet)$, $Br(\Theta)$, $Cl(\Theta)$, $COOH(\Theta)$, $CH_3(\Theta)$, $H(\Theta)$, $OH(\Theta)$, $F(\Theta)$, and $CF_3(\Theta)$.
mol\(^{-1}\), implying little difference in energy between hexa-
fluorobenzene and the hypothetical triene. This conclusion
seems to be in agreement with "destabilization" calculations
by Cox et al (10) which show that the destabilizing effects
of the C–F dipoles do not seem to be significantly moder-
ted by any "resonance" effect.

It is interesting to note that if the values of Cox
et al for \(\Delta H^\circ_{f298}(C_6F_{10},g)\) (1) and \(\Delta H^\circ_{f298}(C_6F_6,g)\) (10) are
used, the calculated "resonance energy" is \(-112.1\) kJ mol\(^{-1}\).
However, if the enthalpies of Cox are recalculated
using the older NBS selected value of \(\Delta H^\circ_{f298}(HF,20H_2O) =
-319.16\) kJ mol\(^{-1}\) (40) rather than the more recent result of
Hubbard, \(-322.1\) kJ mol\(^{-1}\) (54) then the resonance energy is
\(-44.7\) kJ mol\(^{-1}\) and \(\Delta H^\circ_{f298}(C_6F_{10},g) = -1908.1\) kJ mol\(^{-1}\),
both in good agreement with the present work.
APPENDIX A

REDUCTION TO STANDARD STATE

The energy evolved when combustion of a substance takes place in a bomb calorimeter may differ significantly from the decrease in internal energy for the combustion reaction under standard conditions. This fact was emphasized by Washburn (17) who treated in detail the corrections that must be applied to bomb calorimetric data. Extension of Washburn's corrections to apply to fluorine compounds are set out in this section. The form follows the pattern established in the first volume of Experimental Chemistry (16). The reduction to standard state for fluorine compounds have been laid out by Scott and Good (18). The approach taken here has a somewhat different form due to the nature of the compounds -- that is, the compounds contain only carbon and fluorine or carbon, fluorine and one other halogen. The other approach is due to the experimental method, namely, that no auxiliary materials are used and that the combustion is done under anhydrous conditions.

The computation is only for the correction to standard state and will use a general form for any of the perfluoroaromatic, halogen substituted perfluoroaromatic
and perfluorocyclic compounds. Starrèd item numbers denote input data and unstarred ones denote calculated quantities.

1. $C_{a}F_{b}X_{c}$, formula of the compound.

2. $m'$, mass of the compound.

3. $M'$, molecular weight of the compound.

4. $n' = m'/M'$, number of moles of the compound.

5. $\rho'$, density of the compound.

6. $V' = m'/1000\rho'$, volume of the compound in litres.

7. Data for any auxiliary materials used = none.

8. $a = n'a'$, total number of moles of carbon in the compound.

9. $b = n'b'$, total number of moles of fluorine in the compound.

10. $c = n'c'$, total number of moles of halogen in the compound.

In the equations to follow, subscripts i and f are used to designate the initial and final states, respectively.

**Initial State**

11. $V(bomb)$ is the internal volume of the bomb.
(12) \( V_i(H_2O) \) is the volume of water initially in the bomb which is zero since combustion was done under anhydrous conditions.

(13) \( P_i(gas) \), total pressure of the oxygen initially.

(14) \( V_i(gas) = V(bomb) - V_i(H_2O) - V' \)
\( V_i(H_2O) \) is zero and \( V' \) is considered negligible.
Thus,

(15) \( V_i(gas) = V(bomb) \).

(16) \( n_i(gas) = P_i(gas) V_i(gas)/24.465(1 - 0.00061 P_i(gas)) \).
This equation is used to calculate the number of moles of the gaseous mixture derived from the equation of state which fits the PVT data of \( O_2 \). The total number of moles of \( O_2 \) is calculated next.

(17) \( n_i[(O_2 + N_2)_{tot.}] = n_i(gas) - n_i(H_2O, \text{vap.}) \)

(17)' \( n_i[(O_2)_{tot.}] = n_i(gas) \).

**Final State**

The compound present in the bomb in the final state of the isothermal process and their distribution of the gases are represented as follows:
\[ C_{a'} F_{b'} X_{c'} + a' - a'/(Ratl + 1)O_2 = \]
\[ a' - a'/(Ratl + 1)CO_2 + a'/(Ratl + 1)CF_4 + \]
\[ [b' - 4a'/(Ratl + 1) - 3c]/2F_2 + cXF_{3/5} + \]
\[ (c' - c)/2X_2 \]

where Ratl and c are experimentally derived values and cXF_{3/5} is equal to cXF_3 or cXF_5, not both.

The volume of the gaseous mixture in the bomb is

\[ V_f(\text{gas}) = V(\text{bomb}) - V_f(\text{soln.}) \]

where \( V_f(\text{soln.}) \) is zero.

The number of moles of CO_2 and CF_4 produced in the combustion process is calculated from stoichiometry.

\[ n_f(CF_4) = a/(Ratl + 1) \]

\[ n_f(CO_2, \text{tot.}) = a - a/(Ratl + 1) \]

\[ n_f(CO_2, \text{gas}) = n_f(CO_2, \text{tot.}) \]

The number of moles of oxygen is calculated,

\[ n_f(O_2, \text{tot.}) = n_f(O_2, \text{tot.}) - n_f(CO_2, \text{tot.}) \]

The number of moles of gaseous mixture is

\[ n_f(\text{gas}) = n_f(O_2, \text{tot.}) + n_f(CO_2, \text{gas}) + n_f(CF_4, \text{gas}). \]

Items 24, 25, and 26 list the mole fraction of O_2, CO_2, and CF_4.

\[ X(O_2, \text{gas}) = n_f(O_2, \text{gas})/n_f(\text{gas}). \]
\[(25) \quad X(CO_2, \text{gas}) = \frac{n_f(CO_2, \text{gas})}{n_f(\text{gas})}.\]

\[(26) \quad X(CF_4, \text{gas}) = \frac{n_f(CF_4, \text{gas})}{n_f(\text{gas})}.\]

An equation for \(u\) in the equation of state \(PV = nRT(1 - \mu P)\), for \(O_2 - CO_2 - CF_4\) mixtures as a function of \(X(CO_2, \text{gas})\) and \(X(CF_4, \text{gas})\) is

\[(27) \quad \mu_f(\text{gas}) = 0.00061\left[1 + 3.21(CO_2, \text{gas})\right] \left[1 + 1.33(CO_2, \text{gas}) + 2.15(CF_4, \text{gas})\left[1 + 1.33(CF_4, \text{gas})\right]\right]\]

From this the pressure of the final gas mixture is found

\[(28) \quad P_f(\text{gas}) = \frac{1}{0.04875V_f(\text{gas})/n_f(\text{gas})} + \mu_f(\text{gas})\]

The change in internal energy when \(n_i(\text{gas})\) moles of mixture of oxygen gas and sample are compressed into the space of the bomb to the pressure \(P_i(\text{gas})\) can be represented by

\[(29) \quad \Delta E_i(\text{gas})\bigg|_{P_i(\text{gas})}^{P_f(\text{gas})} = \left(\frac{\partial E}{\partial P}\right)_T(O_2, \text{gas})P_i(\text{gas})n_i(\text{gas})\]

The gaseous phase containing \(O_2\), \(CO_2\), and \(CF_4\) is expanded to a negligible small pressure. The change in internal energy is

\[(30) \quad \Delta E_f(\text{gas})\bigg|_{P_f(\text{gas})}^{0} = 1.574(O_2, \text{gas}) + 2.691(CO_2, \text{gas}) + \]

\[ 1.69[(\text{CO}_2, \text{gas})^2] + 2.18(\text{CF}_4, \text{gas}), + \\
1.18[(\text{CF}_4, \text{gas})^2]] P_f(\text{gas}) n_f(\text{gas}). \]

The quantity \( \Delta E_z \) is the summation of \( \Delta E_i(\text{gas}) \) and \( \Delta E_f(\text{gas}) \), so by adding items 29 and 30 and adding this value to \( \Delta E_c \), the change in energy for the combustion as it occurs under actual bomb conditions is,

\[
(31) \quad \Delta E^0_c(C_a, F_b, X_c) = \Delta E_c(C_a, F_b, X_c) + \Delta E_z/n'.
\]
APPENDIX B

SUGGESTIONS FOR FURTHER WORK

The small differences found in the values of the heats of formation for $\text{C}_6\text{F}_6$ and $\text{C}_6\text{F}_{10}$ determined by Cox et al. (9, 10) and by the present work could be due to the value selected for the heat of formation $\Delta H^0_{\text{f}298}(\text{HF} \cdot 2\text{H}_2\text{O})$ used in Cox's work to determine the heat of formation for the forementioned compounds. Although the implication here is far from conclusive it may indicate that further study of the heat of formation of aqueous HF solutions is needed.

One of particular interest in this series of compounds that was determined by Cox is chloropentafluorobenzene. This would be an additional check on the procedure used. However, the possible formation of $\text{ClF}_3$, $\text{ClF}$, and $\text{Cl}_2$ may make in the study of this compound by combustion without any auxiliary materials rather complex.
APPENDIX C

COMPUTER PROGRAMS USED IN THE

ANALYSIS OF THERMOCHEMICAL DATA
$JOB WATVIV XXXXXXXXXXX, KP#29 LSQ. S.J. PRICE
C HENRY J. SAPIANO.
C PROGRAM FOR CALIBRATING THE CALORIMETER.
C NOTE MM, IC, ID MUST BE ODD NUMBERS.
C HENRY J. SAPIANO CHEMISTRY DEPARTMENT.
C MAIN PROGRAM FOR CALIBRATING THE CALORIMETER.
1 COMMON TEMP, TIME, QE, NO, MO
2 DIMENSION TEMP(500), TIME(500), QE(5, 5)
3 READ, INO
4 DO 66 NIJ=1, INO
5 A=4.023
6 B=-5.77328
7 NO=2
8 MO=3
9 VBOM=.32
10 EBENZ=6318.
11 EFUSE=2.3
12 READ, DH20, CH20, CO2, COO2, CPT, BASEN
13 PRINT, DH20, CH20, CO2, COO2, CPT, BASEN
14 READ, IRUN, MM, IC, ID, WBENZ, WFUSE, WCRCUC, WWIRE, VH20, V1,
15 PO2, VBASEx, T
16 PRINT462, (TIME(I), TEMP(I), I=2, MM)
17 READ, (TIME(I), TEMP(I), I=1, MM)
18 462FORMAT((1HO, F5.2, 1X, F6.1, 2X))
19 125CALL G05C P(TEMP, MM)
20 TEMP=TEMP(I)
21 DO 97 I=1, MM
22 97 TEMP(I)=TEMP(I)-TMP
23 JA=1
24 IA=IC
25 DO 120 I=1, 2
26 SLOPE=0.
27 YINT=0.
28 TAVE=0.
29 CALL G)5LSQ(TEMP, TIME, JA, IA, SLOPE, YINT, TAVE)
30 QE(I, 1)=1.
31 QE(I, 2)=TAVE
32 QE(I, 3)=SLOPE
33 JA=ID
34 IA=MN
35 120 CONTINUE
36 CALL G05SIM(QE, NO, MO):
37 DELT=QE(1, 1)*(TIME(ID)-TIME(IC))+QE(2, 2)*G05ARD(TEMP
1, TIME, IC, ID)
38 DELTC=TEMP(ID)-TEMP(ID)-DELT
39 PO2=(14.7+PO2)/14.7
40 WH20=DH20*VH20
41 F=1.+((20.*PO2-30.)*+42.*((WBENZ/VBOM)-3.)+30.*((WH2
10/VBOM)-3.))-45.*(TEMP(MM)-(8.0-TMP)))/(10.**6)
EBENZC=EBENZF
EIGN=(500.*V1*V1)/(4.18410.**6)
EACID=VBASE*BASEN*13.8
DQ=WBENZ*EBENZC+EIGN+EACID+WFUSE*EFUSE
13OCMEAS=DQ/DELT

BEN=WBENZ/122.12
O2Ni=(PO2*VBOM)/(0.082*(TMM(TC)+290.))
O2Nf=O2Ni-7.5*BEN
CO2N=7.0*BEN
H2ON=WH20/18.016.*BEN
PTN=(WCRUC+WIRE)/195.09
CSYS=CMEAS+CH20*H2ON-CO2*O2Nf-CCO2*CO2N-CPI*PIN
PRINT 250,IRUN,CSYS,UE(1,1),UE(2,2),DELT,DELT,CMEAS
ID=ID+2

IF(ID.EQ.MM) GO TO 3
230CONTINUE
66CONTINUE
250FORMAT (1X,I4,6E20.8)
3CALL EXIT

SUBROUTINE GO5LSQ(YYY,XXX,II,SLP,YNT,YAVE)
C SUBROUTINE TO DO LEAST SQUARES ANALYSIS ON LINEAR
C RELATIONSHIP
DIMENSION YYY(200),XXX(200)
SUMX=0.
SUMY=0.
DO 8 IG=1H,II
SUMY=SUMY+YYY(IG)
SUMX=SUMX+XXX(IG)
8CONTINUE
XII=II+1-IH
YAVE=SUMY/XII
SX=0.
SY=0.
SXY=0.
SXSQ=0.
DO 7 IE=IH,II
SX=SX+XXX(IE)
SY=SY+YYY(IE)
SXY=SXY+XXX(IE)*YYY(IE)
SXSQ=SXSQ+XXX(IE)*XXX(IE)
7CONTINUE
XII=II+1-IH
SLP=(SX*SY-XII*SXY)/(SX*SX-XII*SXSQ)
YNT=(SX*SXY-SXSQ*SY)/(SX*SX-XII*SXSQ)
RETURN
END
SUBROUTINE GO5SIM(Q,NP,MP)
C SUBROUTINE FOR SOLUTION OF SIMULTANEOUS LINEAR
C EQUATIONS
DIMENSION TX(200), TY(200), Q(5, 5)
Q(2, 2) = (Q(2, 3) * Q(1, 1) - Q(1, 3) * Q(2, 1)) / (Q(2, 2) * Q(1, 1) -
1 * Q(1, 2) * Q(2, 1))
Q(1, 1) = (Q(1, 3) - Q(1, 2) * Q(2, 2)) / Q(1, 1)
RETURN
END

FUNCTION GO5ARD(TE, TI, N, NM)
DIMENSION TE(200), TI(200)
C SUBPROGRAM FOR FINDING AREA UNDER CURVE USING
C LAGRANGIAN FORMULA
MM = NM - 2
GO5ARD = 0.0
DO 40 J = N, MM, 2
D = (TE(J) * (3.0 * TI(J+1) - 2.0 * TI(J) - TI(J+2))) / ((TI(J) - TI(J+1)) * (TI(J) - TI(J+2)))
E = (TE(J+1) * (TI(J) - TI(J+2))) / ((TI(J+1) - TI(J)) * (TI(J+1) - TI(J+2)))
F = (TE(J+2) - TI(J) * (TI(J+2) - TI(J+1)) / ((TI(J+2) - TI(J)) * (TI(J+2) - TI(J+1)))
TD = (TI(J+2) - TI(J) * (TI(J+2) - TI(J)) * (D + E + F) / 6.
GO5ARD = GO5ARD + TD
40 CONTINUE
RETURN
END

SUBROUTINE GO5COP(TEM, NN)
C SUBPROGRAM FOR CONVERSION OF RESISTANCE TO TEMPERATURE
DIMENSION TEM(200)
NN = NM
DO 22 I = 1, NN
XC = (A * LOG(TEM(I)) * 10.) - 77.8
TEM(I) = 1.6578123 + 2.5536824 * XC + 0.011885630 * XC * XC
22 CONTINUE
RETURN
END
ENTRY

$IBSYS
$JOB
WATFIV XXXXXXXXX,KP#29 LSQ. S.J. PRICE
C
PROGRAM FOR CALCULATING THE HEATS OF COMBUSTION AND
FORMATION OF BROMOPENTAFUOROBENZENE C6F5Br ALONG
WITH THE % YIELDS OF CARBON, FLUORINE, AND BROMINE
ALSO % RECOVERY OF CO2, F2 AND BR2.
C
PROGRAM FINDS THE CO2/CF4 MOLAR RATIO GIVEN THE
WEIGHT OF CO2 PRODUCED IN THE COMBUSTION.
C
PROGRAM FINDS THE CO2/CF4 MOLAR RATIO GIVEN THE
WEIGHT OF F2 FROM F2 AND BRF3 PRODUCED IN THE
COMBUSTION.
C
HENRY J. SAPIANO CHEMISTRY DEPARTMENT.
1
READ, INO
2
DO 10 I=1, INO
3
READ, IRUN, DELAT, WC6F5B, RAT1, WC02, WBRF3, WF2, WBR2
4
DATA EE, FC6F5B, FCW02, HCO2, HCF4, HBF3, FBF3, WF2, WBF
1R2/4254.13246.97, 44.01, -94.0517, -223.0, -61.09, 136.9,
237.996, 159.818/
5
  DW-=-(DELAT*EE*FC6F5B)/(WC6F5B*1000)
6
  RAT2=(RAT1+1.)/6.
7
  RAT3=RAT1+1/
8
  BRF3=WBRF3/FBF3
9
  AMCO2=WC02/FCW02
10
  AMF2=WF2/WF2
11
  AMCF4=AMCO2/RAT1
12
  AMBR2=WBR2/FBF3
13
  AMC6F5B=WC6F5B/FC6F5B
14
  FACT=1/AMC6F5B
15
  AMCARB=6*AMC6FB
16
  AMFLUO=5*AMC6FB
17
  AMBROM=1*AMC6FB
18
  THEOCO=(AMCARB-(AMCARB/RAT3))*FCW02
19
  THEOF2=(AMFLUO-(AMCARB/RAT3)*4)*WF2/2
20
  WTF2A=WF2+(BF3*1.5*WF2)
21
  CENT=((AMCO2+AMCF4)/AMCARB)*100
22
  CENTCO=(WC02/THEOCO)*100
23
  CENTF=((AMCF4*4)+(AMF2*2)+(BRF3*3))/AMFLUO)*100
24
  CENTF2=(WTF2A/THEOF2)*100
25
  CENTBR=((BF3+AMBROM)*100
26
  AMF23B=(WTF2A/WF2)*2
27
  F2LEFT=AMFLUO-AMF23B
28
  AMCF=F2LEFT/4
29
  COLEFT=AMCARB-AMCF
30
  RAT4=COLEFT/AMCF
31
  ACF4=AMC6FB*6-AMCO2
32
  RAT5=AMCO2/ACF4
33
  EQCO2=AMCO2*FACT
34
  EQO2+EQCO2
35
  EQCF4=AMCF4*FACT
36
  EQF2=AMF2*FACT
37
  EQBF3=BRF3*FACT.
EQBR2=AMBR2*FACT
HC6F5B=((RAT1*HCO2+HCF4+(BRF3*RAT2*HBRF3*FC6F5B/WC6
1EF5B))/RAT2) –DW
PRINTS,IRUN,DW,WC6F5B,DELAT,RAT1,WCO2,WBRF3,WF2,WBR2
5 FORMAT(///,10X,10HRUN NUMBER,I4,///,10X,21HHEAT OF C
1COMBUSTION IS,F31.2,///,10X,39HHEAT OF FORMATION OF
2C6F5BR(L) UNCOR IS,F13.2,///,10X,26HMASS OF C6F5BR I
3N GRAMS IS,F26.3,///,10X,42HDelta T CORRECTED IN DEG
4REES CENTIGRADE IS,F10.5,///,10X,32HCO2/CF4 MOLAR RA
5TIO CORRECTED IS,F20.2,///,10X,32HWEIGHT OF CARBON D
6IOXIDE(C)2 IS,F20.3,///,10X,38WEIGHT OF BROMINE TRI
7FLUORIDE(BRF3) IS,F14.3,///,10X,31HTOTAL FLUORINE GA
8S F2 COLLECTED,F21.4,///,10X,32HWEIGHT OF BROMINE (B
9R2) FOUND IS,F20.4,///)
PRINT5,THEOCO,WCO8,CENTC,CENT,THEOF2,WTF2A,CENTF2,CE
2NTF,WBR2,WBRF3,CENTB,EOQ2,EOQCO,EOQF4,EOQF2,EOQBF3,E
3QBR2
6 FORMAT(///,10X,27HTHEORETICAL CO2 IN GRAMS IS,F25.3,
1///,10X,22HACTUAL CO2 IN GRAMS IS,F30.3,///,10X,18HP
2ERCENT OF CO2 IS,F34.1,///,10X,30HPERCENT OF CARBON
3RECOVERED IS,F22.1,///,10X,45HTHEORETICAL F2 IN GRAM
4S (FROM F2 AND BRF3) IS,F7.3,///,10X,39HACTUAL F2 IN
5GRAMS (FROM F2 AND BRF3) IS,F13.3,10X,16HPERCENT OF
6F2 IS,F36.1,///,10X,32HPERCENT OF FLUORINE RECOVERED
7 IS,F20.1,///,10X,32HWEIGHT OF BROMINE (BR2) FOUND I
8S,F20.4,10X,39HWEIGHT OF BROMINE TRI FLUORIDE (BRF3)
9IS,F13.3,///,10X,21HPERCENT OF BROMINE IS,F31.1,///,
010X,6HC6F5BR,5X,F5.3,2HO2,10X,F5.3,3HCO2,5X,F5.3,3HC
1F4,5X,F5.3,2HF2,5X,F5.3,4HBRF3,5X,F5.03,2HF2,5X,F5.3
2,4HBRF3,5X,F5.3,3HBR2,///)
PRINT7,IRUN,WC6F5B,WTF2A,RAT4
7 FORMAT(1X,10HRUN NUMBER,I4,///,1X,22HWEIGHT OF C6F5BR
1IS,F10.6,///,1X,24HWEIGHT OF F2 PRODUCED IS,F10.6,///,1X
2,16HCO2/CF4 RATIO IS,F10.6,///)
PRINT8,IRUN,WC6F5B,WCO2,RAT5
8 FORMAT(1X,10HRUN NUMBER,I4,///,1X,22HWEIGHT OF C6F5BR
1IS,F10.6,///,1X,24HWEIGHT OF CO2 PRODUCED IS,F10.6,///,1
2X,16HCO2/CF4 RATIO IS,F10.6,///)
10CONTINUE
STOP
END
$ENTRY
$IBSYS
WATVIV XXXXXXXXXX, KP#29 LSQ. S.J. PRICE

PROGRAM FOR CALCULATING THE HEATS OF COMBUSTION AND
FORMATION OF DECAFLUOROCYCLOHEXENE C6F10

HENRY J. SAPIANO, CHEMISTRY DEPARTMENT

READ, INO

D) 10 I=1, INO

READ, IRUN, DELAT, WCF10, RAT1, WCO2, WF2

DATA EE, FWCF10, FWC02, HCO2, HCF4, FWF2/4254.13, 262.051,
*44.01, -94.0517, 223.0, 37.996/

DW=-(DELAT*EE*FWCF10)/(WCF10*1000)

RAT2=(RAT1+1.)/6

RAT3=RAT1+1.

AMCO2=WCO2/FWC02

AMF2=WF2/FWF2

AMCF4=AMCO2/RAT1

AMCF10=WCF10/FWCF10

FACT=1/AMCF10

AMCARB=6*AMCF10

AMFLUO=10*AMCF10

THEOCO=(AMCARB-(AMCARB/RAT3))*FWCO2

THEOF2=(AMFLUO-(AMCARB/RAT3)*4))*FWF2/2

CENTC=(AMCO2+AMCF4)/AMCARB*100

CENTCO=(WCO2/THEOCO)*100

CENTF=((AMCF4*4)+(AMF2*2))/AMFLUO)*100

CENTF2=(WF2/THEOF2)*100

F2LEFT=AMFLUO-(AMF2*2)

AMCF=F2LEFT/4

COLEFT=AMCARB-AMCF

RAT4=COLEFT?AMCF

ACF4=AMCARB-AMCO2

RAT5=AMCO2/ACF4

EQCO2=AMCO2*FACT

EQO2=AMCO2*FACT

EQCF4=AMCF4*FACT

EQF2=AMF2*FACT

HCF10=((RAT1*HCO2)+HCF4)/RAT2-DW

PRINT 1, IRUN, DW, HCF10, DELAT, RAT1, WCO2, WF2

FORMAT(///, 10X, 10HRUN NUMBER, I4.2, ///, 10X, 21HHEAT OF
1COMBUSTION IS, F31.2, ///, 10X, 39HHEAT OF FORMATION OF
2C6F10 (L) UNCOR IS, F13.2, ///, 10X, 28HM ASS OF C6F10 IN
3 GRAMS IS, F26.3, ///, 10X, 42HDELTA T CORRECTED IN DEGR
4EES CENTGRADE IS, F10.5, ///, 10X, 32H2CO2/CF4 MOLAR RAT
510 CORR IS, F20.2, ///, 10X, 32HWEIGHT OF CARBON DIOXIDE
6(CO2) IS, F20.3, ///, 10X, 31HTOTAL FLUORINE GAS F2 COLL
7ECTED, F21.4, ///)

PRINT2, WCO2, THEOCO, CENTCO, CENTC, WF2, THEOF2, CENTF2, CE
1NTF, EQO2, EQCO2, EQCF4, EQF2

FORMAT(10X, 22HACTUAL CO2 IN GRAMS IS, H30.3, ///, 10X, 2
17HTHEORETICAL CO2 IN GRAMS IS, F25.3, ///, 10X, 18HPERC E
2NT OF CO2 IS, F34.1, ///, 10X, 30HPERCENT OF CARBON RECO
3VERED IS, F22.1, ///, 10X, 33HACTUAL F2 IN GRAMS COLLECT
4ED IS, F19.3, ///, 10X, 26HTHEORETICAL F2 IN GRAMS IS, F2
56.3,///,10X,16HPERCENT OF F2 IS,F36.1,///,10X,32HPE
6RCENT OF FLUORINE RECOVERED IS,F20.1,///,10X,55HTHE
7 BALANCE EQUATION FOR DECAFLUOROCYCLOHEXENE C6F10 I
8S,///,10X,5HC6F10,2X,1H+,2X,F5.3,2HO2,3X,4H****,3X,
9F5.3,3HC)2,2X,1H+,2X,F5.3,3HCF4,2X,1H+,2X,F5.3,2HF2
0,///)

PRINT3,WCF10,WF2,RAT4

3FORMAT(10X,54HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN
1 THE WEIGHT OF F2,///,10X,18HWEIGHT OF C6F10 IS,F34.
.24,///,10X,24HWEIGHT OF F2 PRODUCED IS,F28.4,///,10X,3
30HTHE CO2/CF4 RATIO IS,F32.2,///).

PRINT4,WCF10,WCO2,RAT5

4FORMAT(10X,55HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN
1 THE WEIGHT OF CO2,///,10X,18HWEIGHT OF C6F10 IS,F34.
.24,///,10X,25HWEIGHT OF CO2 PRODUCED IS,F27.4,///,10X,
320HTHE CO2/CF4 RATIO IS,F32.2,///)

10CONTINUE
11STOP
12END
13$ENTRY

$IBSYS
$JOB  WATFIV  XXXXXXXXX,KP#29  LSQ. S.J. PRICE
C  PROGRAM FOR CALCULATING THE HEATS OF COMBUSTION AND
C  FORMATION OF DODECAFLUOROCYCLOHEXANE
C  HENRY J. SAPIANO  CHEMISTRY DEPARTMENT
1  READ,INO
2  DO 10*I=1,INO
3  READ,IRUN,DELAT,WCF12,RAT1,WCO2,WF2
4  DATA EE,WCF12,WCO2,HCO2,HCF4,FWF2/4254.13,300.040,
     144.001,-94.0517,-223.0,37.996/
5  DW=-(DELAT*EE*WCF12)/(WCF12*1000)
6  RAT2=(RAT1+1.)/6
7  RAT3=RAT1+1
8  AMCO2=WCO2/WCF12
9  AMF2=WF2/WCF12
10  AMCF4=AMCO2/RAT1
11  AMCF12=WCF12/WCF12
12  FACT=1/AMCF12
13  AMCARB=6*AMCF12
14  AMFUO=12*AMCF12
15  THEOCO=(AMCARB-(AMCARB/RAT3))*WCF12
16  THEOF2=(AMFUO-((AMCARB/RAT3)*4.))*WF2/2
17  CENTC=((AMCO2+AMCF4)/AMCARB)*100
18  CENTC0=(WCF2/THEOCO)*100
19  CENTF=((AMCF4*4)+(AMCF2*2))/AMFUO)*100
20  CENTF2=(WF2/THEOF2)*100
21  F2LEFT=AMFUO-(AMF2*2)
22  AMCF=F2LEFT/4
23  COLEFT=AMCARB-AMCF
24  RAT4=COLEFT/AMCF
25  ACF4=AMCARB-AMCO2
26  RAT5=AMCO2/ACF4
27  EQCO2=AMCO2*FACT
28  EQF2=AMCO2*FACT
29  EQCF4=AMCF4*FACT
30  EQF2=AMF2*FACT
31  HCF12=((RAT1*HCO2)+HCF4)/RAT2-DW
32  PRINT1,IRUN,DW,HCF12,WCF12,DELAT,RAT1,WCO2,WF2
33  1 FORMAT(///,10X,10HRUN NUMBER IS,I42,///,10X,21IHEAT O
34  1F COMBUSTION IS,F31.2,///,10X,39HHEAT OF FORMATION O
35  2F C6F12 (L) UNCOR IS,F13.2,///,10X,26HMASS OF C6F12
36  3IN GRAMS IS,F26.3,///,10X,42HDELTA T CORRECTED IN DE
37  4GREES CENTIGRADE IS,F10.5,///,10X,32HCO2/CF4 MOLAR R
38  5ATIO CORRECTED IS,F20.2,///,10X,32HWEIGHT OF CARBON
39  6DIOXIDE(CO2) IS,F20.3,///,10X,31HTOTAL FLUORINE GAS
40  7F2 COLLECTED,F21.4,///)
41  PRINT2,WCO2,THEOCO,CENTC0,CENTC,WF2,THEOF2,CENTF2,CO
42  print1,EQCO2,EQCF4,EQF2
43  2 FORMAT(10X,22FACTUAL CO2 IN GRAMS IS,F30.3,///,10X,2
44  17HTHEORETICAL CO2 IN GRAMS IS,F25.3,///,10X,18HPERCEN
45  2T OF CO2 IS,F34.1,///,10X,30HPERCENT OF CARBON RECOV
3ERED IS,F22.1,,/10X,33HACTUAL F2 IN GRAMS COLLECTED
4,IS,F19.3,,/10X,26HTHEORETICAL F2 IN GRAMS IS,F26.53,,/4,10X,17HPERCENT OF F2 IS,F36.1,,/10X,32HPERCENT OF FLUORINE RECOVERED IS,F20.1,AX,,10X,55HTHE BALANCE EQUATION OF DODECAFLUOROCYCLOHEXANE C6F12 IS,
8,,10X,5HC6F12,2X,1H+,2X,F5.3,2HO2,3X,2H***,3X,F5.3 9,3HCO2,2X,1H+,2X,F5.3,3HCF4,2X,1H+,2X,F5.3,2HF2,,/)
36 PRINT3,WCF12,WF2,RAT4
37 3 FORMAT(10X,54HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN THE WEIGHT OF F2,,/10X,18HWEIGHT OF C6F12 IS,F34.4, 2,,/10X,24HWEIGHT OF F2 PRODUCED IS,F28.4,,/10X,20HTHE CO2/CF4 RATIO IS,F32.2,,/)
38 PRINT4,WSP12,WCO2,RAT5
39 4 FORMAT(10X,55HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN THE WEIGHT OF CO2,,/10X,18HWEIGHT OF C6F12 IS,F34.4 2,,/10X,25HWEIGHT OF CO2 PRODUCED IS,F27.4,,/10X,20 3HTHE CO2/CF4 RATIO IS,F32.2,,/)
40 PRINT,AMCO2,AMF2,AMCF4,AMCF12,AMCARB,AMFLUO
41 10CONTINUE
42 STOP
43 END
$ENTRY
$IBSYS
$JOB WAIWIV XXXXXXXXXX,KP#29 LSQ. S.J. PRICE
C PROGRAM FOR CALCULATING THE HEATS OF COMBUSTION AND
C FORMATION OF DECAFLOUROBIPHENUL C12F10.
C HENRY J. SAPIANO CHEMISTRY DEPARTMENT
1 READ,INO
2 DO 10 I=1,INO
3 READ,IRUN,DELAT,WCF12,RAT1,WCO2,WF2
4 DATA EE,WFC12,WFCO2,HCO2,HCF4,WF2/4254.12,334.120,44
1.01,-94.0517,-223.0,37.996/.
5 DW=-(DELAT*EE*WFC12)/(WCF12*1000)
6 RAT2=(RAT1+1.)/12.
7 RAT3=RAT1+1.
8 AMCO2=WCO2/WFCO2
9 AMF2=WF2/FWF2
10 AMCF4=AMCO2/RAT1
11 AMCF12=WCF12/FWC12
12 FACT=1/AMCF12
13 AMCARB=12*AMCF12
14 AMFLUO=10*AMCF12
15 THEOCO=(AMCARB/RAT3)*WFCO2
16 THEOF2=(AMFLUO-((AMCARB/RAT3)*4.))*FWF2/2.
17 CENTC=((AMCO2+AMCF4)/AMCARB)*100
18 THEOCO=(((AMCF4*4)+AMF2*2)/AMFLUO)*100
19 CENTF2=(WF2/THEOF2)*100
20 F2LEFT=AMFLUO-(AMF2*2)
21 AMCF=F2LEFT/4
22 COLEFT=AMCARB-AMCF
23 RAT4=COLEFT/AMCF
24 ACF4=AMCARB-AMCO2
25 RAT5=AMCO2/ACF4
26 EQCO2=AMCO2*FACT
27 EQO2=AMCO2*FACT
28 EQCF4=AMCF4*FACT
29 EQF2=AMF2*FACT
30 HCF12=-(RAT1*HCO2+HCF4)/RAT2-DW.
31 PRINT1,IRUN,DW,HCF12,DELAT,RAT1,WCO2,WF2
32 1 FORMAT///,10X,10HRUN NUMBER,142,///,10X,21HHEAT OF C
33 LOBUSTION IS,F31.2,///,10X,39HHEAT OF FORMATION OF C
34 212F10(L) UNCOR IS,F13.2,///,10X,26HMMASS OF C12F10 IN
35 3 GRAMS IS,F26.3,///,10X,42DELTA T CORRECTED IN DEGRE
36 ESS CENTIGRADE IS,F10.5,///,10X,32HCO2/CF4 MOLAR RATI
37 SO CORRECTED IS,F20.2,///,10X,32HWEIGHT OF CARBON DIO
38 NXIDE(CO2) IS,F20.3,///,10X,31HTOTAL FLUORINE GAS F2
39 7COLLECTED,F21.4,///
40 PRINT2,WCO2,THEOCO,CENTCO,CENTC,WF2,THEOF2,CENTF2,CE
41 *NTF,EQQ2,EQQC2,EQQF4,EQQF2
42 2 FORMAT(10X,22HACTUAL CO2 IN GRAMS IS,F30.3,///,10X,2
43 17HTHEORETICAL CO2 IN GRAMS IS,F25.3,///,10X,18HPERCENT
44 2NT OF CO2 IS,F34.1,///,10X,30HPERCENT. OF CARBON RECO
3VERED IS, F22.1, ///, 10X, 33 HACTUAL F2 IN GRAMS COLLECT
4ED IS, F19.3, ///, 10X, 26 HTHEORETICAL F2 IN GRAMS IS, F2
56.3, ///, 10X, 16 HPERCENT OF F2 IS, F36.1, ///, 10X, 32 HPER
6CENT OF FLUORINE RECOVERED IS, F20.1, ///, 10X, 44 HTHE B
7ALANCE EQUATION DECAFLUOROBIPHENYL C12F10, 2X, 1H+, 2X,
8F6.3, 2HO2, 3X, 4H***, 3X, F6.3, 3HC2O2, 2X, 1H+, 2X, F5.3, 3HC
9F4, 2X, 1H+, 2X, F5.3, 2H2F2, ///)
36 PRINT3, WCF12, WF2, RAT4
37 3 FORMAT(10X, 54HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN
1THE WEIGHT OF F2, ///, 10X, 18 HWEIGHT OF C12F10 IS, F34.4
2, ///, 10X, 24 HWEIGHT OF F2 PRODUCED IS, F28.4, ///, 10X, 20H
3THE CO2/CF4 MOLAR RATIO IS, F32.2, ///)
38 PRINT 4, WCF12, WCO2, RAT5
39 4 FORMAT(10X, 55HTHIS IS THE CO2/CF4 MOLAR RATIO GIVEN
1THE WEIGHT OF CO2, ///, 10X, 18 HWEIGHT OF C12F10, F34.4, /
2, ///, 10X, 25 WEIGHT OF CO2 PRODUCED IS, F27.4, ///, 10X, 20HTH
3E CO2/CF4 RATIO IS, F32.2, ///)
40 PRINT, AMCO2, AMF2, AMF12
41 10 CONTINUE
42 STOP
43 END
$ENTRY
$IBSYS


35. N.V. Sidgwick. Chemical Elements and their Compounds. 


40. Selected Values of Chemical Thermodynamic Properties. 


42. E. Stenhagen, S. Abrahansson, and F.W. McLafferty, eds. 


45. Selected Values of Physical and Thermodynamic Properties 

46. R.C. Weast, ed. Handbook of Chemistry and Physics. 51st 


VITA AUCTORIS

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Son of John and Jane Sapiano

Primary Schools : Our Lady of Peace
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Determination of $\Delta H_{298}^0(\text{C}_6\text{F}_5\text{Br}, \text{g})$ from studies of the combustion of bromopentafluorobenzene in oxygen and calculation of $D[\text{C}_6\text{F}_5-\text{Br}]$

MICHAEL J. KRECH, STANLEY JAMES W. PRICE, AND HENRY J. SAPIANO

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Determination of $\Delta H_{298}^o(C_6F_5Br, g)$ from studies of the combustion of bromopentafluorobenzene in oxygen and calculation of $D(C_6F_5-Br)$

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Received July 4, 1977


The heat of formation of bromopentafluorobenzene has been determined through the use of the direct combustion method which has been applied to hexafluorobenzene, octafluorotoluene, and iodopentafluorobenzene. While a platinum lined bomb is normally used for these types of compounds a steel bomb had to be adopted in this work. The combustion of bromopentafluorobenzene in the steel bomb yields CO$_2$, CF$_3$, F$_2$, Br$_2$, and BrF$_3$. With a ten-fold excess of oxygen, the average CO$_2$ to CF$_3$ molar ratio is 7.29 ± 0.07. A material balance was obtained for carbon, fluorine, and bromine. The value of $\Delta H_{298}^o(C_6F_5Br, g) = -711.6 \pm 16.7$ kcal mol$^{-1}$ (−170.1 ± 4.0 kcal mol$^{-1}$) has been combined with $\Delta H_{298}^o(CF_3Br, g) = -387.4$ kcal mol$^{-1}$ (−92.6 kcal mol$^{-1}$) and $\Delta H_{298}^o(Br, g) = 111.7$ kcal mol$^{-1}$ (26.7 kcal mol$^{-1}$) to obtain a value for $D(C_6F_5-Br)$ of 435.9 kcal mol$^{-1}$ (104.2 kcal mol$^{-1}$).


On a déterminé l’enthalpie de formation du bromopentafluorobenzène par l’utilisation de la méthode de combustion directe qui a été appliquée à l’hexafluorobenzène, à l’octafluorotoluène et à l’iodopentafluorobenzène. Alors qu’une bombe couverte de platinne est généralement utilisée pour ce type de composé, on a adopté une bombe en acier dans le présent travail. La combustion du bromopentafluorobenzène dans la bombe d’acier conduit à la formation de CO$_2$, de CF$_3$, de F$_2$, de Br$_2$ et de BrF$_3$. Si on utilise 10 fois la quantité nécessaire d’oxygène, le rapport molaire moyen de CO$_2$ sur CF$_3$ est de 7.29 ± 0.07. On a obtenu une bonne balance de matériel pour le carbone, le fluor et le brome. On a combiné la valeur de $\Delta H_{298}^o(C_6F_5Br, g) = -711.6 \pm 16.7$ kcal mol$^{-1}$ (−170.1 ± 4.0 kcal mol$^{-1}$) à la valeur de $\Delta H_{298}^o(CF_3Br, g) = -387.4$ kcal mol$^{-1}$ (−92.6 kcal mol$^{-1}$) et $\Delta H_{298}^o(Br, g) = 111.7$ kcal mol$^{-1}$ (26.7 kcal mol$^{-1}$) pour obtenir une valeur de 435.9 kcal mol$^{-1}$ (104.2 kcal mol$^{-1}$) pour $D(C_6F_5-Br)$. [Traduit par le journal]

Introduction

To date no thermodynamic study for the heat of formation of C$_6$F$_5$Br has been reported. The combustion of C$_6$F$_5$X (X = F, H, CH$_3$, Cl, OH) has been determined by Cox and co-workers (1, 2). These studies involve the placement of fluoro compounds in polyester film bags. To ensure complete combustion hydrogen containing organic materials were added to the crucible. An alternate and successful approach involves open dish combustion under anhydrous conditions and without any auxiliary materials (3–5). This method has been adopted for the combustion of bromopentafluorobenzene through the use of a steel crucible in a steel bomb.

Materials

(i) Bromopentafluorobenzene C$_6$F$_5$Br obtained from the Imperial Smelting Corporation was purified by fractional distillation. The final product had the following physical properties (the values in parentheses are those reported by the manufacturer (6): bp = 173 C (137–139 C), n$_D$ = 1.4833 (1.483). Analysis by gas chromatography (6 ft × ¼ in. od Durapak n-octane/Porasil C, 100–200 mesh, N$_2$ carrier, 60 cm$^3$/min, column temperature 200 C, flame ionization detection) showed the presence of a minor impurity which was found to represent a maximum of 0.05% of the sample.

Vapour pressure measurements were taken over the range 10–75 C using the same modified Ramsay–Young system previously employed for C$_6$F$_5$ (3), C$_6$F$_5$CF$_3$ (4), and C$_6$F$_5$I (5). Over 50 vapour pressure measurements were made over three independent runs. The data may be represented by
The resulting heat of vaporization and average heat capacity differences (vapor - liquid) are \( \Delta H_{298}^\circ = 43.05 \pm 0.21 \text{ kJ mol}^{-1} \) and \( \Delta C^\circ_{p,298} \approx 0.954 \text{ J deg}^{-1} \text{ mol}^{-1} \).

(ii) CO\(_2\), CF\(_4\), F\(_2\), BrF\(_3\), and BrF\(_5\) were obtained from the Matheson Chemical Company and were used without further purification. BrF\(_3\) and BrF\(_5\) were obtained from the Air Products Chemical Company and Fluorchem Ltd., respectively. Both were stored as received in monel steel cylinders under their own vapour pressure. Before use the liquids were distilled into Pyrex traps and vacuum distilled. The vacuum distillation system used had taps equipped with Teflon barrels and Viton-O-rings and all joints and glass stopcocks were greased with halocarbon grease.

(iii) Bromine

Reagent A.C.S. bromine was dried over phosphorous pentoxide and vacuum distilled. A middle fraction was collected and stored under its own vapour pressure in a Pyrex tube.

(iv) Sodium Thiosulphate

Sodium thiosulphate pentahydrate (12.5 g) was dissolved in 1 L of water that had been recently boiled and cooled. A few drops of chloroform were added as a preservative and the resulting solution was standardized with potassium iodide (7).

(v) Potassium Iodide

Reagent grade potassium iodide was used without further purification.

Apparatus and Calorimetric Procedure

The apparatus and procedure used for the main combustion process were identical to those used for CsF\(_2\) (3), C\(_2\)F\(_6\) (4), and C\(_2\)F\(_6\)I (5). The sole exception was the use of a Parr model 1004 C steel bomb and steel crucible that contained the liquid C\(_2\)F\(_5\)Br. The rate of loss of C\(_2\)F\(_5\)Br from the steel crucible in which it was weighed was 0.0207 mg s\(^{-1}\). The time between weighing the crucible containing the liquid and closing the bomb was such that less than 0.04% of the total sample was lost by evaporation. The correction for the evaporation is estimated to be accurate to better than \( \pm 3\% \). The error generated by the correction procedure should therefore be less than \( \pm 0.001\% \).

Analysis of Reaction Products

The analytical procedures for CO\(_2\), CF\(_4\), and F\(_2\) have been described elsewhere (3-5). BrF\(_3\) was either weighed and/or reduced with KI and titrated with standardized 0.05 N sodium thiosulphate. Quantitative analysis of BrF\(_5\) was based on determination of F\(^-\) using a fluoride specific ion electrode in conjunction with an Orion 701 digital pH meter. Mass spectra were obtained using a Varian MAT-CHF-12F spectrometer controlled by an INCOS computer system. Fluorine nmr spectra were obtained on a nmr JELCO C60 HL spectrometer and are reported in ppm with trifluoroacetic acid used as an internal standard. A Bauch and Lomb Spectronic 20 colorimeter was used to determine iron with 1,10-phen.
The second column which was a 6 ft x 1 in. od Porapak Q column (25°C, He carrier, 48 cm$^3$/min) was used to determine the CO$_2$/CF$_4$ ratio for the remaining runs. Uncorrected retention times for O$_2$, CF$_3$, and CO$_2$ are 1 min 3 s, 1 min 54 s, and 4 min 57 s, respectively. An improved separation between oxygen and tetrafluoromethane occurred using this column. Use of pure CF$_4$ leads to a response factor that is low by only 1%.

Condensable products (at ~80°C) were collected in either a glass or stainless steel trap. To ensure all products volatile at 25°C were removed from the combustion bomb, the system was flushed with ultra high pure oxygen for 2 h and the bomb was then evacuated through the trap. The cold trap was allowed to come to room temperature. Two immiscible liquids were observed. The major portion (lower phase) had a characteristic colour of free bromine and the upper phase had a colorless to gray-yellow colour. Since a carbon balance had already been established the possibility of any halo-carbon products were unlikely and the fact that all the bromine oxides (11) are unstable at room temperature indicated that the remaining products would be halogen or interhalogen compounds such as Br$_2$, BrF$_3$, BrF$_4$, and BrF$_5$. BrF has not been isolated as of yet but there are indications that it does exist through spectroscopic studies.

By simple vacuum distillation the liquids were easily separated. The more volatile substance was dark red in colour and appeared to be free bromine. This was confirmed by mass spectral analysis using a MAT CHS mass spectrometer. Major peaks were obtained at m/e = 162, 160, and 158 with a peak height ratio of close to 1:2:1 in addition peaks of approximately equal height (about 7% of the m/e = 160 peak height) were observed at m/e = 160 and 79. Since the molecular constituents in order of increasing volatility at 25°C are BrF$_3$, Br$_2$, BrF$_4$, and BrF, any BrF$_5$ and/or BrF would have been collected in the 'bromine' fraction. In addition to the mass spectral analysis this fraction was tested by adding water to the distilled sample. If any halogen fluorides were present they would have reacted with water to form a complex mixture of HF, HBr, HBrO$_3$, Br$_2$, and O$_2$ (12). Fluoride analysis of this solution with a specific fluoride ion electrode proved to be negative.

Based on colour and volatility it appeared possible that the remaining liquid was BrF$_3$. The
TABLE 2. Comparison of \(D(C_8F_3-N)\) values determined from thermochemistry with values derived from appearance potential studies

<table>
<thead>
<tr>
<th>(X)</th>
<th>From thermochemistry*</th>
<th>From appearance potentials†</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>608.8 ± 12.6 (145.5 ± 3.0)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>636.4 ± 12.6 (152.1 ± 3.0)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>642.7 ± 12.6 (153.6 ± 3.0)</td>
<td>629.3 ± 8.4 (150.4 ± 2.0)</td>
</tr>
<tr>
<td>Cl</td>
<td>543.9 ± 12.6 (130.0 ± 3.0)</td>
<td>531.8 ± 8.4 (127.1 ± 2.0)</td>
</tr>
<tr>
<td>Br</td>
<td>435.9 ± 16.7 (104.2 ± 4.0)</td>
<td>445.1 ± 8.4 (105.9 ± 2.0)</td>
</tr>
<tr>
<td>I</td>
<td>277.0 ± 4.2 (66.2 ± 1.0)</td>
<td>277.0 ± 4.2 (66.2 ± 1.0)</td>
</tr>
<tr>
<td>CH₃</td>
<td>595.0 ± 12.6 (142 ± 3.0)</td>
<td></td>
</tr>
<tr>
<td>CF₃</td>
<td>404.2 ± 12.6 (96 ± 3.0)</td>
<td></td>
</tr>
</tbody>
</table>

*All values in this column are based on \(\Delta H_{f(0)}(C_8F_3,g) = -387.4 \text{ kJ mol}^{-1}\) and \(\Delta H_{f(0)}(C_8F_3,g) = -92.8 \text{ kJ mol}^{-1}\) determined from the kinetic value of \(D(C_8F_3-N)\).

†Based on the kinetic value of \(D(C_8F_3-N)\) and differences in AP values.

The liquid was distilled under vacuum into a carefully dried quartz capillary tube while the tube was immersed in liquid nitrogen. The capillary was then sealed under vacuum and removed for subsequent nmr fluorine analysis. The fluorine nmr analysis indicated a singlet peak corresponding to liquid BrF₃ at -55.2 ppm (literature value -54.3 ppm (13)) relative to trifluoroacetic acid.

The amount of Br₂ was analyzed by either weighing the sample collected in a small ampoule and/or by iodometric analysis (7). The BrF₃ was reacted with KI solution and analyzed for fluoride using the corresponding specific ion electrode. In three runs the BrF₃ fraction was also determined directly by weighing this fraction. Good agreement was obtained between specific ion and gravimetric determination.

From the material balance shown in Table 1, along with the average CO₂/CF₄ molar ratio, reaction 2 may be written to represent the combustion of bromopentafluorobenzene. However, as will be discussed later, it is unlikely that free bromine exists in the bomb.

\[ C_8F_3Br + 5.276O_2 \rightarrow 5.276CO_2 + 0.724CF_4 \\ + 0.923F_2 + 0.086BrF_3 + 0.457Br_2 \]

In treating a complex mixture of products possible interactions between the compounds must be taken into account. No detectable heat of mixing was observed when F₂, O₂, CF₄, and CO₂ were mixed under anhydrous conditions.

However, a correction of -130 ± 13 kJ mol⁻¹ is required for the interaction between Br₂, F₂, and BrF₃. Approximately -68.2 kJ mol⁻¹ of this correction is due to reaction 3.

\[ \frac{1}{2}F_2(g) + \frac{1}{2}Br_2(g) \rightarrow BrF(g) \]

With the excess F₂ present, the equilibrium should be far to the right (14). It should be noted that, during the slow bleeding of the bomb over a period of 20 h to recover the combustion products for analysis, the BrF equilibrium shifts to the left resulting in quantitative conversion of BrF to Br₂ and F₂. In an all-metal system (steel traps) the reaction may be somewhat inhibited as indicated by the apparent slight shortfall in bromine recovery (Table 1). The shortfall was always accompanied by the appearance of a light yellow coloration in the F₂ absorbing solution in the bubbler.

In carrying out the thermochemical calculations the following heats of formation have been used: CO₂(g), -393.512 kJ mol⁻¹ (15); CF₄(g), -933.0 kJ mol⁻¹ (16); and BrF₃(g), -255.60 kJ mol⁻¹ (12).

Based on the preceding data and an estimated correction to standard state of 5.5 kJ mol⁻¹, \(\Delta H_{f(0)}^{\circ}(C_8F_3Br,g) = -711.6 ± 5.6 \text{ kJ mol}^{-1}\) with a standard deviation of 5.6 kJ mol⁻¹. However, when the uncertainty in the auxiliary experiments are taken into account the overall limit must be set at about ±16 kJ mol⁻¹.

Defining \(D(C_8F_3-N)\) as \(\Delta H_{f(0)}^{\circ}\) for the reaction

\[ C_8F_3X_{g} \rightarrow C_8F_3g + X_{g} \]

and using the value for \(\Delta H_{f(0)}^{\circ}(C_8F_3,g)\) as -387.4 ± 12 kJ mol⁻¹ (5) and \(\Delta H_{f}(Br,g) = \)
111.7 kJ mol$^{-1}$ (17) and the present determined value of $\Delta H_{f,298}^{\circ}$(C$_8$F$_{3}$Br,g) = $-711.6 \pm 16.7$ kJ mol$^{-1}$ will yield a value of $D$(C$_8$F$_{3}$−Br) to be 435.9 kJ mol$^{-1}$.

In Table 2 a comparison is made between $D$(C$_8$F$_{3}$X) values based on thermochemical methods and appearance potential methods (18). Agreement of the present value of $D$(C$_8$F$_{3}$−Br) with the value estimated from the AP studies is well within the combined error limits.

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6. Highly fluorinated aromatic and alicyclic compounds.

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