FLUORINE CALORIMETRY

History, Applications, Results

Second Augmented and Revised Edition

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This book is dedicated by the authors to the memory of Gerald K. Johnson (1935–1997), a major contributor to the discipline of fluorine calorimetry, whose work is quoted extensively in these pages.

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FOREWORD

Ftornaya Kalorimetriya (Fluorine Calorimetry), originally published in Russian in 1978, was written by Vladimir Leonidov and Vadim Medvedev from the Data Center on the Thermodynamic Properties of Individual Substances (now known as the Glushko Thermocenter) of the Russian Academy of Sciences. They were founders of the Russian school of fluorine calorimetry who made a substantial contribution to thermochemistry, not only through their experimental investigations, but also as authors of the reference books *Thermodynamic Properties of Individual Substances* and *Thermal Constants of Substances* published in Russia and, later, in the United States (in English translation), principally thanks to Begell House, Inc.

The idea of updating *Ftornaya Kalorimetriya* and publishing it in English was conceived several years ago by Vladimir Leonidov (Vadim Medvedev had died in 1988) and Patrick O'Hare, a well-known specialist in fluorine calorimetry at the National Institute of Standards and Technology. They have added many new sections to the book, and have brought it completely up to date. O'Hare, in addition, has been responsible for editing the English text.

We have now an essentially new book that presents a comprehensive state-of-the-art disquisition on fluorine calorimetry and related topics.

This English edition of *Fluorine Calorimetry* appears a short time after the untimely death of Professor Leonidov. I believe that this book is a fitting tribute to his memory and an expression of the debt of respect we owe him.

Vladimir Yungman, Director
Glushko Thermocenter, Moscow, Russia

PREFACE

When, in 1891, Moissan and Berthelot* described the use of fluorine in a calorimetric experiment for the first time, they were pioneering a technique that survives today, more than a century later. So it is that fluorine calorimetry was continued by the schools of von Wartenberg, first in Danzig (Gdańsk) and later in Göttingen, by workers at the National Bureau of Standards in the United States, the Institute for High Temperatures and Moscow State University in the former Soviet Union, Fulmer Research Institute in the United Kingdom, and at Argonne National Laboratory in the United States. Several other, not so voluminous, contributions came from research groups in Switzerland, F.R.G., Japan, and the United States. One of the present authors has pursued the technique at the National Institute of Standards and Technology (formerly the National Bureau of Standards).

The book *Ftornaya Kalorimetriya* (Nauka: Moscow, 1978), published about twenty years ago with V. Ya. Leonidov and V. A. Medvedev as authors, is now updated and reissued as a second edition in English. The translation from Russian to English was made by N. S. Krivosheya (Russia). This book contains much new material, with surveys and analyses of the results obtained by fluorine combustion calorimetry over the past two decades. Sadly, one of the original authors, V. A. Medvedev, died in 1988, so all additions and changes are the responsibility of P. A. G. O'Hare and V. Ya. Leonidov. The entire text was edited by P. A. G. O'Hare.

This work addresses the present state and problems of fluorine calorimetry, a technique that occupies a special niche among modern thermochemical methods. This is so not only because it provides an independent way of determining enthalpies of formation of a wide range of (mostly inorganic) compounds; in addition, owing to the exceptional reactivity of fluorine, this method widens the scope of thermochemical research to include substances that could not previously be studied by conventional calorimetric methods. Thus, it is often possible to achieve complete reaction of a material with fluorine to form simple fluorides when, with another oxidant, the extent of reaction might be limited and lead, in all likelihood, to the formation of products in multiple oxidation states. Furthermore, combustion in fluorine often yields gases while, in other oxidizers, condensed products are formed that usually are more difficult to analyze.

Fluorine's high reactivity also presents difficulties and challenges to the experimentalist. Of those, the choice of suitable materials of construction, prevention of undesirable side reactions, and protection of samples from contact with fluorine during the fore-rating period of the calorimetric experiment are, perhaps, the most demanding. From the point of view of safe operations in the laboratory, the toxicity of fluorine, hydrogen fluoride, and many other fluorides presents unusual difficulties. All these problems are discussed in the book.

We have at our disposal extensive experimental information on calorimetric studies of fluorination reactions wherein, mainly, elemental fluorine was the oxidant. Much of this information has come, since 1978, from workers at Argonne National Laboratory and the

National Institute of Standards and Technology in the United States. At the same time, the search for new powerful fluorinating agents for calorimetry was an urgent task also (why use F_2 if a less hazardous, but effective, reagent is available?). Workers at the Institute for High Temperatures, Moscow, developed a technique by which fluorination is brought about through the use of crystalline xenon difluoride. This novel approach, and others, are also described here.

The present monograph consists of an introduction and two parts. The first is devoted to problems that dominated the development of fluorine bomb calorimetry: purification and analysis of fluorine; methods devised for the combustion of different substances and analysis of the reaction products; construction of calorimetric bombs; peripheral apparatus for the safe manipulation of F_2 and fluorides; and matters that address the treatment of experimental results.

In the second part, results of measurements of enthalpies of combustion of different substances in fluorine and other fluorine-containing oxidants are discussed individually. Separate categories deal with the fluorination of metals, nonmetals, oxides, chalcogenides, nitrides, phosphides, carbides, borides, silicides, lower fluorides, and other compounds. Particular attention was paid to the assessment of uncertainties, and their components, assigned to the thermodynamic quantities. All fluorine combustion calorimetric studies described in the literature to mid-1999 were considered for the purposes of this book.

It is only fitting that the present authors acknowledge the help and guidance of their mentors, among them Vadim Medvedev, an author of the first edition of this book, and Ward N. Hubbard, arguably the father of modern fluorine combustion calorimetry.

A significant part of the work on this book was completed by P. A. G. O'Hare, while he was a Visiting Scientist under the auspices of the Fundação para a Ciência e a Tecnologia (Portugal). He wishes to thank Professor M. A. V. Ribeiro da Silva and Dr. Maria D. M. C. Ribeiro da Silva (University of Porto), Dr. M. E. Minas da Piedade (Instituto Superior Técnico, Lisbon), and Professor J. A. Martinho Simões (University of Lisbon) for their hospitality and help during his stay in Portugal.

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[*] Berthelot, M.; Moissan, H. *Ann. Chim. Phys.* 1891, 23, 570–574.

INTRODUCTION

THERMOCHEMISTRY: ENTHALPIES OF CHEMICAL REACTIONS

Thermochemistry is a branch of physical chemistry that encompasses investigations of the thermal effects of chemical reactions and physico-chemical processes. Thermochemical values and their generalized relations are widely employed, for example, in engineering practice to analyze process heat balances and calculate equilibrium constants. This information is also used in pure chemistry, for example, to calculate enthalpies of dissociation of bonds in molecules.

Investigations of thermochemical processes are based on the first law of thermodynamics:

$$U_2 - U_1 = \Delta U = Q - W \tag{1}$$

where U_1 and U_2 are the internal energy values of a system in the initial and final states, respectively; Q is the quantity of heat absorbed between the initial and final states; and W is the work performed by the system. Frequently, the only work performed by a system is against the external pressure. In such cases:

$$U_2 - U_1 = Q - \int_{V_1}^{V_2} p \cdot dV, \tag{2}$$

where V_1 and V_2 are, respectively, the initial and final volumes of the system. For a process at constant volume (isochoric process), $W = 0$ and

$$Q_V = U_2 - U_1 = \Delta U. \tag{3}$$

Therefore, the quantity of heat absorbed by the system or released to the surroundings at constant volume is equal to the change of the internal energy of the system.

If a process occurs at constant pressure (isobaric process), Eq. (2) may be rewritten in the form:

$$U_2 - U_1 = Q_p - p \cdot (V_2 - V_1), \tag{4}$$

whence

$$Q_p = (U_2 + p \cdot V_2) - (U_1 + p \cdot V_1), \tag{5}$$

where p is the external pressure. After substitution of $H = U + p \cdot V$, one obtains:

$$Q_p = H_2 - H_1 = \Delta H. \tag{6}$$

Function H is called enthalpy. According to Eq. (6), an increase or decrease of the enthalpy equals the quantity of heat released or absorbed by the system in an isobaric process.

Thus, if a chemical reaction proceeds at constant volume or pressure, the energy or enthalpy of the reaction is equal to the change of state functions, as follows from Eqs. (3) and (6), and, consequently, is determined by the initial and final states of the system and is independent of the path of the process. This statement, which follows from the first law of thermodynamics, is of central importance in thermochemistry and is called Hess's law after G. I. Hess who first formulated it in 1836. By means of this law, one can calculate the overall enthalpy of a reaction as the sum of the enthalpies of the component intermediate reactions.

Change of molar enthalpy of a reaction $\Delta_r H^\circ_m$ (where r signifies that the change of H is associated with a chemical reaction, while m denotes a molar quantity) at constant pressure Q_p is, for brevity, called the "molar enthalpy of reaction", further abbreviated to the colloquial "enthalpy of reaction", a term that will recur frequently throughout this book. An enthalpy change is designated positive ($\Delta_r H^\circ_m > 0$) for endothermic reactions, and negative ($\Delta_r H^\circ_m < 0$) for exothermic reactions. The relation between Q_p and Q_V is the following:

$$Q_p = Q_V + p \cdot (V_2 - V_1) = Q_V + \Delta \nu^g \cdot R \cdot T, \tag{7}$$

where $\Delta \nu^g$ is the change in the amounts of gaseous substances involved in a reaction according to the stoichiometric equation; R is the universal gas constant; and T is thermodynamic temperature. Thus, for example, $\Delta \nu^g = -3.5$ for the reaction:

$$\mathrm{UP(cr)} + (11/2)\mathrm{F_2(g)} = \mathrm{UF_6(g)} + \mathrm{PF_5(g)}. \tag{8}$$

One of the most practical thermochemical quantities is the molar enthalpy of formation of a substance $\Delta_f H_m$, defined as the enthalpy of a reaction in which 1 mol of a given substance is formed from the elements in their most stable states at a given temperature. In many reference books on thermodynamics, values of standard molar enthalpies of formation are tabulated at $T = 298.15$ K and $p = 0.1$ MPa, which implies that all the substances participating in the process of formation are in their standard states. Standard molar enthalpy of formation is denoted by $\Delta_f H^\circ_m(T)$. When T is omitted, the function is usually taken to refer to $T = 298.15$ K. Values of $\Delta_f H^\circ_m(298.15\ \mathrm{K})$ are widely used in thermochemical evaluations, particularly in calculations where Hess's law is employed. One of the most valuable consequences of this law is that the enthalpy of a chemical process, the difference between the sums of enthalpies of formation of products and reactants, can often be predicted accurately and, therefore, need not be measured. For any chemical reaction, the enthalpy Q_p, or energy Q_V, is a function of temperature. This dependence is expressed by Kirchhoff's equation which, in the differential form, is:

$$\mathrm{d}Q/\mathrm{d}T = \Delta C_m, \tag{9}$$

where ΔC_m is the difference between the molar heat capacities $C^o_{p,m}$ (isobaric) or $C^o_{V,m}$ (isochoric) of reactants and products taken with regard to the stoichiometric coefficients. To obtain a formula for practical use, it is necessary to integrate Kirchhoff's equation. While doing this, it should be kept in mind that the C_ms of the substances participating in the reaction vary with temperature. After integrating Eq. (9) for constant pressure, one obtains:

$$\Delta_r H_m^\circ(T_2) - \Delta_r H_m^\circ(T_1) = \int (\Delta C_{p,m}^\circ \cdot dT). \tag{10}$$

The exact solution can be obtained from the temperature dependence of $\Delta C_{p,m}^\circ$, usually given by a power series in T:

$$\Delta C_{p,m}^\circ(T) = \Delta a + \Delta b \cdot T + \Delta c \cdot T^2 + ... \tag{11}$$

Thermodynamic values are very important for gaining insight into the spontaneity of any reaction under a given set of conditions, as well as for the determination of a numerical value of the equilibrium constant. The molar Gibbs free energy change (isobaric potential) of the reaction $\Delta_r G_m^\circ(T)$ is required for that purpose. When calculating $\Delta_r G_m^\circ(T)$ from the thermodynamic relation: $\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T) - T \cdot \Delta_r S_m^\circ(T)$, besides the value of $\Delta_r H_m^\circ(T)$, it is necessary to know also the value of $\Delta_r S_m^\circ(T)$, the change of molar entropy for the reaction at the temperature T of interest.

Throughout this book, the following notations are used (for a standard pressure of 0.1 MPa): $\Delta_f G_m^\circ$(298.15 K) is the standard molar Gibbs free energy (isobaric potential) of formation of 1 mol of a given substance from the elements in their standard states at T = 298.15 K; $\Delta_0^T S_m^\circ$(298.15 K) is the standard molar entropy of the substance relative to $T \rightarrow 0$ at T = 298.15 K; and $C_{p,m}^\circ$(298.15 K) is the standard molar heat capacity of the substance at T = 298.15 K and constant pressure.

In this book, the following symbols denote the states of substances: cr for crystal, am for amorphous, vit for glass, s for solid, l for liquid, g for gas, and sln for solution. The designation ($X \cdot nH_2O$, sln) is for 1 mol of the solution of solute X in n mol of H_2O. When the solution consists of more than two components, an analogous designation is used: for example, $KF \cdot 160KOH \cdot 1600H_2O$(sln).

In the International System of Units (SI), the recommended unit of energy for thermodynamic applications is the joule. The relation J = (1/4.1840) cal is used in this book to convert earlier thermochemical results to SI units.

SOME GENERAL INFORMATION ABOUT CALORIMETRY

Calorimetry (from the Latin *calor*, meaning heat; and Greek, *metron*, to measure) embraces those approaches and techniques used for measurements of thermal effects (quantities of heat) accompanying various chemical, physical, and other processes. Calorimetric methods are employed to measure *inter alia*: heat capacity, thermal effects of chemical reactions, and enthalpies of phase transitions, solution, wetting, adsorption, radioactive decay, and other phenomena. Such techniques are of paramount importance for the determination of thermodynamic quantities (such as entropies, enthalpies, and Gibbs free energies) of chemical reactions and thermodynamic properties of substances. Creation of new technologies and the rapid growth of science during recent decades stimulated the development of calorimetry, expanded the varieties of substances under investigation, and increased the demand for more accurate measurements.

Determinations of the quantity of heat absorbed or released during a process are usually carried out in a special apparatus called a calorimeter. Those parts of the calorimeter within which the total measured heat is disseminated are collectively called the calorimetric system. In the literature, the term “calorimetric system” is usually replaced by "calorimeter", which has, therefore, two meanings; usually, the abbreviated nomenclature is used in this book. Typically, but not invariably, calorimetric measurements consist of observations of the change in temperature of the calorimetric system during the experiment.

Designs of calorimeters are diverse and depend on the process to be studied and its duration, the temperature of the experiments, the quantity of heat to be measured, and the accuracy required. In modern calorimetry, the temperature interval can range from 0.1 K to greater than 10^3 K; the duration of the process may span $10^2 \cdot$ s to several days, and the quantity of measured heat may extend from $\approx 10^{-4}$ J to the kJ region. Accuracy of the measurements is dictated by the purpose of the investigation and in some cases is very high, from 0.01 to 0.1%.

In general, all calorimeters can be divided into two types: those of variable temperature in which the quantity of heat is determined by the temperature change of the calorimeter itself; and those of constant temperature (isothermal), in which the quantity of measured heat is related to the change of state of a substance (melting solid or vaporizing liquid). Most calorimeters belong to the first category. The quantity of heat Q released or absorbed in such a calorimeter during an experiment is calculated from the formula:

$$Q = \varepsilon \cdot \Delta T, \tag{12}$$

where ε is the energy equivalent of the calorimeter (the quantity of heat required to change the temperature of the calorimeter by 1 K), and ΔT is the (corrected) temperature change of the calorimeter during the experiment. As a rule, the value of ε is determined in calibration experiments. For that purpose, a known quantity of heat is released in the calorimeter by means of either a heater (electrical method) or chemical process, the heat effect of which is known exactly (comparison method). In both instances, a value of ΔT is determined. An example of the second method is the combustion of pure benzoic acid in pure oxygen. Special calorimetric mercury-in-glass thermometers with high sensitivity have been used in the past to determine ΔT, as have resistance thermometers, thermocouples, and optical pyrometers at high temperatures. More recently, thermistors and quartz-crystal thermometers, both of which provide highly accurate measurements, have been introduced.

A conventional calorimetric experiment usually consists of three observation periods. During the first (initial or fore) period, before the heat input, the temperature of the calorimeter changes uniformly because of heat exchange between it and its surroundings as well as secondary processes in the calorimeter (for example, stirrer friction and conduction along wires and thermometers). This change is shown by the temperature-against-time curve. The main period begins with the heat input into the calorimeter and is characterized by a rapid and relatively uneven change of temperature. The last (final or after) period begins when distribution of the heat input in the calorimeter is complete, and the temperature against time curve is again smooth.

It is essential that heat exchange between the calorimeter and its surroundings be taken into account as part of the experiment. To control this exchange meticulously, the system is usually enclosed within an outer jacket. In calorimeters with an isothermal jacket, temperature is maintained constant to within $\pm 10^{-3}$ K or less; even so, the heat exchange correction is not usually inconsiderable, as much as $(1 \text{ to } 5) \cdot 10^{-2} \cdot \Delta T$, but it can be calculated quite accurately.

Calorimeters with isothermal shields are used for investigations of comparatively fast processes (for example, combustion and many reactions in solution). For slow processes (duration > 1 h), it is preferable to employ calorimeters with an adiabatic shield, in which the jacket temperature is maintained as close as possible to that of the calorimeter. Here, the heat-exchange correction is substantially less, because it is due solely to the imperfection of the adiabatic conditions.

During the three rating periods for experiments with isothermally-shielded calorimeters, the temperature is usually measured at equal time intervals, and the measured temperature change ΔT is then adjusted for the heat exchange with the environment, δ. Corrected values are calculated from the formula:

$$\Delta T = T_n - T_0 + \delta, \tag{13}$$

where T_n and T_0 are the final readings of the temperature in the main and initial periods of the experiment, respectively. A number of methods have been proposed to calculate δ. The Regnault-Pfaundler formula, based on Newton's law of cooling, is most frequently used:

$$\delta = \left(v_n - v_0\right)/\left(\theta_n - \theta_0\right)\left\{\left(t_n + t_0\right)/2 + \sum_{1}^{n-1}\left(t_i - n \cdot \theta_0\right)\right\} + n \cdot v_0, \tag{14}$$

where v_0 and v_n are the mean rates of change of temperature of the calorimeter in the initial and final periods; θ_0 and θ_n are the mean temperatures of the calorimeter in the initial and final periods; and $\sum t_i$ is the sum of consecutive (1 through n) temperature readings in the main period. This formula takes into account not only the heat exchange of the calorimeter with the environment, but entirely excludes influences of the assumed constant heat input from, for example, stirrer friction or the current passing through a resistance thermometer.

In calorimeters with an adiabatic shield, differences between the temperature of the calorimeter and shield are measured during all three periods of an experiment, while the temperature of the calorimeter itself is measured only in the initial and final periods, when the drift is close to zero and the correction for heat exchange is comparatively small.

Most common calorimeters for room-temperature operations are immersed in a liquid, usually water. They have been successfully used for determinations of energies of combustion, enthalpies of reaction in solution, and other chemical processes. A weighed mass of water or other fluid is placed in the calorimeter vessel along with a special device in which the chemical reaction is to be conducted, for example, a sturdy bomb for determinations of energies of combustion at elevated pressures, a cell with a burner for combustion of gases in flowing oxygen or fluorine at pressures close to atmospheric, or a vessel of glass or metal for dissolution of solute in solvent. Combustion of substances in a bomb calorimeter, a technique introduced by Berthelot in 1881, has become widespread while being refined to a high degree of precision in modern research. This procedure has been of great importance in obtaining thermochemical values for various classes of substances, including investigations of thermal effects of reactions with fluorine, the subject of this book. The archetypal calorimetric bomb is an hermetically sealed thick-walled metal vessel capable of withstanding pressures as high as 15 MPa, and instantaneously greater, and equipped with a device to ignite a substance contained within the bomb.

Calorimeters in which the heat to be measured is transferred to a block of metal of high thermal conductivity (copper, aluminum, silver), are also widely used, especially in enthalpy increment studies. Typically, a substance heated to some accurately determined high temperature is dropped into the calorimeter maintained at $T = 298.15$ K. The enthalpy change is measured for a series of temperatures, and the relation between the enthalpy increment and temperature is deduced and usually represented as a polynomial in powers of T. Often, the first differential of this polynomial is taken to represent the heat capacity of the substance as a function of temperature.

Synthesis calorimeters are also quite common. These are thin-walled metal vessels in which reactants are placed and then heated electrically, or with a pyrochemical additive, to form the substance under investigation. Matched, so-called "twin calorimeters" (liquid or metal), are attractive because they make it possible to perform accurate measurements without having to make corrections for heat exchange.

Of "isothermal calorimeters", that with the most widespread application is the (Bunsen) ice calorimeter in which the quantity of heat released or absorbed is deduced from the observed change in volume of a mixture of ice and water at the melting temperature of ice. The Calvet calorimeter is also very popular; its operation is based on heat-flow measurement, and has a wide range of applicability.

For detailed descriptions of thermochemistry in general, and calorimetric measurement techniques in particular, the reader is referred to numerous authoritative books [1–10].

To solve varied and often complicated problems in calorimetry, thermochemists are constantly challenged to improve on familiar techniques and create novel methods and equipment, thus allowing up-to-date investigations of substances that are new or have new applications. In that respect, fluorine combustion calorimetry, the subject of this book, has proven to be a unique and powerful thermochemical probe.

ABOUT CALORIMETRIC INVESTIGATIONS WITH FLUORINE: AN HISTORICAL PERSPECTIVE

The idea of using elemental fluorine in calorimetry is not new. At the end of the 19th century, Berthelot and Moissan [11] carried out measurements of, in effect, the enthalpy of formation of HF(aq). Within a few decades, toward the end of the 1920s, von Wartenberg and coworkers published two articles in which they reported the results of determinations of the enthalpies of reaction of fluorine with hydrogen, [12] and silicon, carbon, and silicon carbide [13] in a flow calorimeter at constant pressure. Later, in 1939, von Wartenberg [14] used the same method to measure the energy of combustion of silver in a fluorine atmosphere. But, taking into account the extremely high reactivity of fluorine and the correlative side effects, as well as the lack of appropriate materials for work with elementary fluorine and, above all, the unavailability of the pure gas, the results obtained in Refs. 11 to 14 appear to be unreliable, and are now mostly of historic interest.

Systematic studies of the fluorination of substances began much later, in the middle of the 1950s. At about that time, techniques for obtaining and handling pure fluorine became much more sophisticated, and new materials and equipment with improved resistance to fluorine and fluorides appeared. This provided an optimistic outlook for the development of fluorine calorimetry and improvement of the accuracy of the results.

A number of measurements of the enthalpy of fluorination of substances in flow calorimeters at ambient pressure were performed by investigators that included Jessup and Armstrong at the U.S. National Bureau of Standards (NBS). In such apparatuses, gaseous fluorine was expanded into a special compartment where the reaction was initiated; the products that emerged were analyzed. Enthalpies of the reactions of fluorine with cobalt difluoride (1950) [15], methane (1955) [16], and ammonia (1960) [17] were determined. These investigations were pursued at the NBS for a number of years, and led to the introduction of novel techniques and equipment [18].

In 1959, the first results on the combustion of substances in fluorine in a sealed system emerged from the laboratory headed by Gross (Fulmer Research Institute, U.K.) [19]. Enthalpies of reaction of fluorine with titanium and sulfur were measured in a calorimeter that featured a glass combustion vessel with two chambers, one of which contained fluorine, and the other the substance under investigation. When ignition was desired, a frangible barb between the two compartments was broken, thus allowing fluorine to come into contact with the substance to be reacted. Over a period of several years, enthalpies of reaction of a number of materials with fluorine were measured in the Fulmer laboratories; they included boron, phosphorus, germanium, and some of their compounds.

In the late 1950s, Hubbard and coworkers (Argonne National Laboratory, U.S.A.) set out on the development of a new technique for measuring energies of combustion in fluorine in a calorimetric bomb. In retrospect, this approach has proven to be the most fruitful for a variety of reasons. Thus, Hubbard's group developed apparatus and methods and, beginning in 1961, determined the enthalpies of fluorination of approximately 100 substances (metals, nonmetals, refractory compounds, and gases).

Measurements of enthalpies of reaction in fluorine in a calorimetric bomb were subsequently undertaken by Armstrong and colleagues [20] in the Thermochemical Laboratory of the NBS. Arising from this work, enthalpies of fluorination of aluminium and Teflon, for example, were reported.

Margrave (Rice University, U.S.A.) and his group used the method to study a number of compounds. The first of their articles, published in 1967 [21], by coincidence also dealt with the fluorination of Teflon.

In 1970, Schröder and Sieben (F.R.G.) [22] described determinations of the energies of reaction in a bomb calorimeter of their own construction of fluorine with tungsten, sulfur, and WF_5. No further results on calorimetric combustions in fluorine were published by the German investigators.

Beginning in 1972, fluorine bomb calorimetric research was reported from the National Institute of Applied Sciences (Villeurbanne, France). Results given in the first publication [23], as well as those that followed [24–26], suffered from a lack of accuracy when compared with other modern fluorine calorimetry.

In the former Soviet Union, the practice of fluorine combustion calorimetry was begun in 1967 by Leonidov, Pervov, and coworkers at the Institute for High Temperatures and the Institute of General and Inorganic Chemistry of the Academy of Sciences, Moscow. The initial publication from these laboratories [27] reported the results of measurements on the fluorination of tungsten and appeared in the literature in 1971. Tungsten was recommended for the first time as a standard substance to be used in investigations with fluorine in calorimetric bombs. Later, the enthalpies of formation of SF_6 [28], CuF_2 [29], NiF_2 [30], tungsten borides [31–33], and other substances were determined by the same technique.

Although fluorine bomb calorimetry at the NBS was discontinued in the mid-1970s, this technique was revived in 1989 by O'Hare and colleagues at the same Institution, now known as the National Institute of Standards and Technology (NIST). Studies there encompassed the so-called "high-tech" materials [34].

Other, relatively short-lived, research efforts in fluorine calorimetry originated from laboratories at ETH (Zürich, Switzerland) [35], the University of Kyoto (Japan) [36], and Syracuse University (U.S.A.) [37].

Calorimetric techniques for the determination of accurate values of enthalpies of reaction with fluorine have evolved to a high degree of sophistication during the past 40 or so years. Because of considerable experimental difficulties and safety considerations, investigations have been carried out only in a few laboratories. However, even with those limitations, this technique has been instrumental in establishing enthalpy of formation values for a considerable number of substances of basic scientific and technological importance that would have been beyond the reach of the more conventional calorimetric techniques.

PART ONE

PROBLEMS ASSOCIATED WITH THE DEVELOPMENT OF FLUORINE CALORIMETRY

As mentioned in the Foreword, calorimetric investigations of the reactions of substances with fluorine offer novel possibilities for thermochemistry. Most advantages and features of the technique, as well as difficulties, stem from the extreme reactivity of fluorine. Almost everything reacts with fluorine, to a greater or lesser extent. Although the list of substances that can be studied is lengthened as a consequence, at the same time the likelihood of side reactions also increases, which introduces a number of experimental problems with which the thermochemist must cope. Of the numerous difficulties encountered to date, the following have been the most challenging:

1. Because of the possibility of side reactions with contaminants customarily found in fluorine, particular attention had to be paid to its purification and analysis.
2. A special apparatus constructed from one or more of the limited number of materials most resistant to fluorine was needed in order to perform precise evaluations of enthalpies of reaction. Construction of such an apparatus, and its preparation for the measurements, both time-consuming procedures, were essential for the successful implementation of this technique.
3. Of paramount importance, as in all variants of reaction calorimetry, was the development of successful procedures for the combustion of substances to be investigated and analysis of the products. Choice of optimum reaction conditions usually led, *ipso facto*, to a high combustion yield, and thereby minimized, or eliminated, troublesome side reactions.

The high toxicity of fluorine and fluorides, and the concomitant hazards of working with them, caused the evolution of fluorine calorimetry to be rather tortuous. Treatment and interpretation of the results of measurements of the heat effects of the reactions frequently were arduous tasks.

These problems are carefully considered in the first part of this book. Various techniques, along with the main features of fluorine calorimetry, will be discussed. Then, a brief description of the production of fluorine will be given, along with a list of its physical and chemical properties.

1

APPLICATION OF FLUORINE TO CALORIMETRY

1.1 MODIFICATIONS AND MAIN FEATURES OF FLUORINE CALORIMETRY

Fluorine calorimetry involves direct measurement of heat effects of chemical reactions with F_2. It affords an independent and powerful method for determining the enthalpies of formation of numerous inorganic compounds. There are two general variants of fluorine calorimetry: combustion of substances in F_2 in a calorimetric bomb, and fluorination in calorimeters of the constant-pressure flow type. It is possible, instead of elemental fluorine, to use other compounds of fluorine that have significant oxidizing power (chlorine fluoride, oxygen fluoride, fluorides of inert gases, nitrogen trifluoride). Such variations give the method additional flexibility, and will be the subject of a later chapter.

Enthalpies of fluorination of solid elements and compounds have been primarily measured by bomb calorimetry. Most of the experimental results given in the second part of this book were obtained in this way. In some cases, the technique has been used to determine the enthalpies of fluorination of gases, for example, the reaction of phosphorus trifluoride PF_3 with F_2 to yield phosphorus pentafluoride PF_5 [38].

Simply put, a substance is burned in F_2 at constant volume and elevated pressure in the calorimetric bomb, and the quantity of heat released is measured. Pressures of F_2 have varied from ≈ 0.3 MPa to ≈ 3 MPa. Bombs to be used with F_2 have certain unique features. They are fabricated from special materials that are resistant to corrosion by F_2 (Section 1.3). In the construction of bombs and their internal parts, the extremely high reactivity of F_2, especially during the calorimetric experiment (elevated pressure and temperature), is a primary consideration. Almost all substances react with F_2 spontaneously, so two-compartment bomb-and-tank vessels are used to separate the reactants before the main period of the experiment. To initiate the reaction, F_2 is expanded from the tank into the vessel containing the compound to be burned. In a single-compartment bomb, used with substances that do not react measurably with F_2 or do so at a slow and reproducible rate at ambient temperature, ignition is usually brought about by passing an electric current through a thin, combustible wire contiguous to the sample.

A two-chambered Pyrex vessel was used at the Fulmer Research Institute. Since the distinction between the bomb and glass vessel concerns mainly the operating pressures, the Fulmer technique cannot be considered a separate one in fluorine calorimetry. Experiments at pressures up to 1.2 MPa were successfully carried out in the Pyrex apparatus [39]. However, because of complications, and even hazards, associated with the use of glass equipment for work with F_2, such calorimetry should preferably be conducted in metal bombs or containers.

A second generic fluorine calorimetric method for measurements of the enthalpy of combustion at constant pressure is most useful for reactions between gases. A burner constructed of fluorine-resistant material is positioned in a special compartment inside the calorimeter, and both gaseous reactants are expanded into the compartment, where they combine. Products flow from the compartment into the heat exchanger, where they reach the temperature of the calorimetric fluid. This method is often called fluorine flame calorimetry, because the combustion takes place close to the burner nozzle. Techniques for adjusting the input of reactants and analyzing products are of vital importance in such calorimeters. When calculating the experimental results, corrections are made, for example, for the frictional heat generated in the calorimeter by the flowing gases, for corrosion, and ignition, when necessary. In some rare cases, this method was employed for measurements on solids [40,41].

Thus, each modification considered above has its own idiosyncrasies. Nevertheless, the principal problems listed in the Introduction to Part One remain the same, independent of the method.

Quantification of the extent of reaction of a substance and the composition of the products can prove to be a complicated task because the intrinsic aggressiveness of F_2 and some fluorides can lead to extraneous reactions. In most experiments, however, only the fluorides of highest oxidation state are formed. This is one of the advantages of the method; by comparison, multiple oxides may be produced in combustions of inorganics in oxygen. Furthermore, many higher fluorides, unlike oxides, are gases or substances with substantial vapor pressures under ambient conditions. Gaseous products, and those that sublime from the reaction zone and then condense on the cooler parts of the bomb, simplify identification and analyses, and also facilitate complete combustion.

Calorimeters and methods for measurements in F_2 do not differ in basic detail from those used for calorimetry with O_2 (see, for example, Ref. 3). The main distinction is in the construction of bombs and reaction vessels. In fluorine calorimetry, the most frequently used calorimetric vessels are immersed in liquids (usually water) and have isothermal environments.

Figure 1 shows a cutaway diagram of the calorimetric apparatus designed and formerly operated at Argonne National Laboratory [4] and currently installed at the National Institute of Standards and Technology for fluorine bomb calorimetric studies. This system is of the constant-temperature environment kind, and consists of three basic components: the constant-temperature bath, the calorimeter, and the thermometer.

On the outside, the constant-temperature bath is cylindrical in shape with an irregular opening in the center to accommodate the calorimeter. There is also a two-piece hollow lid hinged to the top of the bath and connected to it with internal tubing. The outer surface is shiny and made of nickel-plated brass. Inside, the surface is made of thin copper sheet, as is the calorimetric can, and both opposing surfaces, 1 cm apart to reduce convection, are chromium plated and polished to minimize heat transfer by radiation.

Two paddles connected to synchronous motors circulate the water in the bath, and a centrifugal pump at the base of one of the paddles forces water through the internal tubing into one section of the lid and, through the hinges, into the other, after which it is returned to the main body of the bath. A 100 W heater connected to a regulator maintains a constant temperature (± 0.001 K) that is monitored by a quartz crystal thermometer during the course of a measurement. Such stability is made possible by an airconditioned room maintained at a temperature close to 295 K, and a fan that improves air circulation in the part of the laboratory where the calorimeter is located.

Central to the calorimetric system is the calorimeter (sometimes called the bucket) which is suspended at three points from Lucite pieces attached to the inside surface of the bath, and is provided with a hermetically-sealed lid. Figure 1 shows the two-chambered reaction vessel (Figure 17) positioned within the calorimetric system. When in use, the

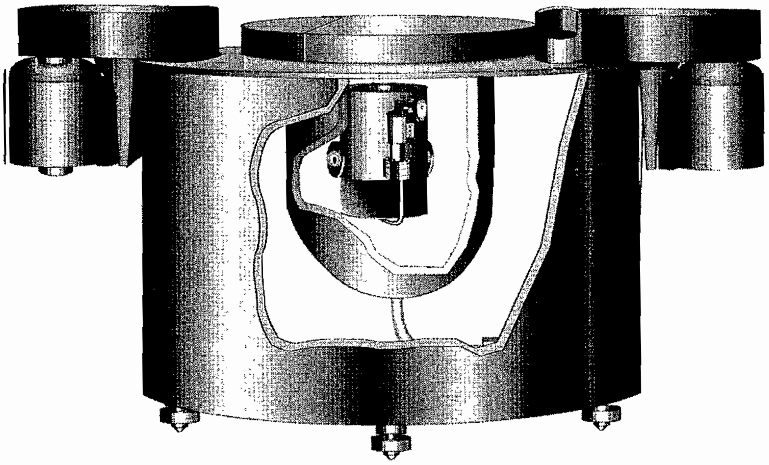

Fig. 1 Cutaway diagram of calorimeter for measurements of energy of combustion in fluorine.

sealed can contains an accurately weighed mass of stirred water whose temperature is measured as the experiment progresses.

There are five connections from the calorimeter to the outside: the quartz-crystal thermometer (and cable) to measure the calorimetric temperature passes through collinear openings in the jacket lid and the bucket; thin electrical leads to the ≈ 200 Ω heater that adjusts the starting temperature of an experiment; a Nylon collet that connects the calorimeter stirrer with an external synchronous motor; a second Nylon collet attached to the opening mechanism of the fluorine storage chamber of the reaction vessel; and two electrical connections to the ignition circuit of the calorimeter.

This calorimetric system was originally designed to accommodate rotating bomb experiments with organo-sulfur compounds, but the reaction vessel has not had to be rotated during any combustions performed to date in fluorine.

Much of the travail associated with temperature measurement in combustion calorimetry is now a thing of the past, thanks to the quartz crystal thermometer. At NIST, the Hewlett-Packard 2804A model is used. In principle, this instrument measures the response to changes in temperature of the resonant frequency of a precisely cut quartz disk mounted inside the probe of the thermometer. In practice, temperature resolution of approximately $1 \cdot 10^{-4}$ K is obtained. Calorimetric temperatures are displayed digitally at precise intervals of 10.7 s. At NIST, those data are simultaneously fed to a computer which records them and calculates the corrected temperature change of the experiment and other indices of performance of the calorimeter.

In fluorine calorimetry, the calorimetric system is generally calibrated by the combustion in oxygen of thermochemical standard benzoic acid (C_6H_5COOH). According to the generally accepted recommendations [42], the following conditions are specified for calibration measurements with benzoic acid: the temperature to which the results of the measurements refer is 298.15 K; the pressure of oxygen in the bomb is 3.0 MPa; the ratio of the mass of benzoic acid to the internal volume of the bomb is 3 g · dm^{-3}; and the ratio of the mass of water placed in the bomb to the internal volume of the bomb is also 3 g · dm^{-3}.

The massic (formerly called "specific") energy of combustion of benzoic acid under those conditions is known with high accuracy. On the basis of results obtained at different standardizing laboratories, the adopted value is – 26434 J · g^{-1}, with an estimated uncertainty of ± 3 J · g^{-1}, according to the recommendations of the U.S. National Institute of Standards and Technology [42]. When experimental conditions differ from those mentioned above, the certified massic energy of combustion of benzoic acid is adjusted according to a formula supplied with the calibration certificate.

Because the passivating layer of fluoride which forms when the bomb is exposed to F_2 [3,4] is hygroscopic, the energy equivalent of the calorimeter is usually determined before fluorine bomb experiments are performed, and it is assumed that the heat capacity of the subsequently added layer of fluoride is negligible [3]. Some authors have washed the bomb thoroughly after the experiments with fluorine, calibrated the system once again, and taken a mean of the two closely agreeing values of the energy equivalent.

Usually, the energy equivalent of a flow calorimeter used for measurements of the enthalpy of fluorination at constant pressure is determined electrically. Time and the electrical energy input to the calorimeter must be measured with an accuracy of 0.01% or better. In some cases [41], electrical calibration has been used in determinations of the energies of fluorination reactions at constant volume.

1.2 PROPERTIES OF FLUORINE. PURITY REQUIREMENTS FOR COMBUSTION CALORIMETRY

1.2.1 Characteristics of Elemental Fluorine

The English name "fluorine" comes from the occurrence of the element in the mineral fluorite, while the Russian word has its origin in the Greek *ftorios* which means "destroying". Fluorine is located in group 17 of the Periodic Table, and is the first element in the halogen group. Its electronic configuration in the ground state is $1s^22s^22p^5$. Because seven electrons are present in the outer electronic level, fluorine easily adds an electron to form a negative ion with closed-shell structure. With its tightly bound outer electrons and rare-gas (Ne) structure, $F^-(g)$ is very stable, and fluorine has the highest electronegativity of all elements. This is also demonstrated by the ionization energy of F, 1680 kJ · mol^{-1} (the greatest of any element). The normal electrode potential of fluorine is 2.85 V, whereas for chlorine and oxygen it is 1.36 V and 1.22 V, respectively. Among the halogens, F has the smallest atomic radius (0.064 nm), and F^- also has the smallest ionic radius (0.136 nm).

Those properties go hand-in-glove with fluorine's extremely high chemical reactivity and some characteristics of fluorine-containing substances. High reactivity is conditioned by the relatively weak bond in F_2; its enthalpy of dissociation, (154.4 ± 0.8) kJ · mol^{-1}, is small in comparison with the value for other diatomic halides. Since F_2 dissociates so readily, atomic fluorine participates in practically all fluorination reactions which, in turn, initiate a great variety of processes that proceed by chain mechanisms.

1.2.2 Physical and Chemical Properties of Fluorine

Fluorine is a gas; it is light-yellow in color with a strong irritating odor reminiscent of chlorine and ozone. On the basis of odor, one can detect the presence of volume fraction $\phi = 2 \cdot 10^{-8}$ of

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