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.

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