

## 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.