PART TWO

DETERMINATION OF ENTHALPIES OF FORMATION OF SUBSTANCES BY FLUORINE CALORIMETRY

This part of the book was written after all the literature on enthalpies of formation of binary fluorides and of many other substances obtained by the technique of fluorine calorimetry was systematized and carefully analyzed. Energies of combustion in fluorine were measured in most of the studies considered; results obtained by the application of other fluorine-containing oxidizers will be discussed separately.

When the stoichiometric reaction is given, the corresponding value of the enthalpy change refers to it in all cases. All numerical results included in the tables and text are, in essence, taken from the primary work. When original values were recalculated, that is so specified in the text. For example, many of the investigations cited were carried out over the past 35 to 40 years, so results were adjusted to correspond to the standard atomic weights of 1995 as promulgated by IUPAC [1]. The absence of such a recalculation implies that there was no intervening change in molar mass or that it had a negligible effect on the value of the thermochemical quantity. Many earlier thermochemical values were expressed in units of kcal $\cdot$ mol^{-1}; for conversion to SI units, the relation cal = 4.184 J was invoked.

Selected values of the auxiliary enthalpies of formation of binary fluorides required to recalculate the enthalpies of formation of compounds on the basis of their enthalpies of fluorination (chapters 2 and 3), were usually obtained by the same technique and investigators. This strategy is believed to lead to minimal systematic errors.

Special attention has been paid to the assessment of uncertainties of measurements. This is very important when the results obtained by different authors are compared and the most reliable value of a thermochemical quantity is to be selected. It is essential to use a uniform approach in such evaluations. In most cases, the uncertainties of measured values Δ_{tot} are expressed as twice the standard deviation of the mean and are calculated from the expression which includes errors Δ_i of all components: $\Delta_{tot} = \{(\Delta_1)^2 + (\Delta_2)^2 + ...\}^{1/2}$ [2]. Exceptions to this rule are indicated in the text. Uncertainties recalculated on the basis of the Student criteria [2] yield similar results. It is specifically mentioned when an uncertainty is expressed at the 95% confidence level. In analyses of individual studies, particular attention was paid to the contributions of different sources of error to the final uncertainties. If there was insufficient information concerning these matters in some articles, it was necessary to calculate or estimate the influence of different experimental and analytical factors on the final uncertainty.

When calculating the value of the enthalpy of formation of a substance by means of Hess's law, the final uncertainty was taken as the square root of the sum of the squares of the errors of all component enthalpies of formation and reaction. For substances of variable composition $AB_{x \pm \delta}$, the contribution of δ was considered as well.

In modern calorimetric investigations, the principal influence on the precision of the results often emanates not from the scatter of the experimental measurements but from the chemical analyses of starting substances and final products of reaction. Furthermore, in the

case of fluorine bomb calorimetry (as in some other kinds of calorimetry), one has to be cognizant of possible side reactions and how they are likely to contribute to the uncertainty. For that reason, it was helpful when complete details were given in the literature of the initial materials and final products, with special attention paid to those features of the technique employed to spur the desired reaction to completion.

To avoid repetition, requirements that are standard for all, or most, reliable fluorine calorimetric determinations, will not be mentioned *ad nauseam* during our consideration of individual publications. Thus, it is to be assumed that:

1. in all cases, the apparatus was carefully passivated before the measurements;
2. almost always, calorimeters for fluorine bomb studies were calibrated by the combustion in oxygen of pure benzoic acid;
3. in experiments with two-compartment reaction vessels, a "blank" correction was applied (Appendix) that took into account the net energy of expansion of fluorine into the empty combustion chamber (only the contribution to the overall uncertainty will be mentioned).

In addition, little mention will be made of certain other corrections, such as those that allow for: incomplete reaction; the energy of combustion of an auxiliary substance; and corrosion of the apparatus, if such occurred. Nor, as a rule, have corrections for trace impurities, for adjusting the results to the standard state (Washburn corrections), and for conversion of the experimental $\Delta_c U_m^\circ$ to $\Delta_c H_m^\circ$, been singled out. Usually, only the states of combination of impurities postulated in the original paper were considered, along with the parallel contribution to the total uncertainty of the final result.

In two special cases, $\Delta_c U_m^\circ = \Delta_c H_m^\circ$: when the measurements were carried out at constant pressure (usually in a flow calorimeter), and when the amounts of substance of gaseous reactants and products were, coincidentally, equal (for example, for combustions of polytetrafluoro-ethene, PTFE, in F_2).