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 $\Delta_r H_m^\circ$ (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 ($\Delta_r H_m^\circ > 0$) for endothermic reactions, and negative ($\Delta_r H_m^\circ < 0$) for exothermic reactions. The relation between Q_p and Q_V is the following:

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

where Δv^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, $\Delta v^g = -3.5$ for the reaction:

$$UP(cr) + (11/2)F_2(g) = UF_6(g) + PF_5(g). \tag{8}$$
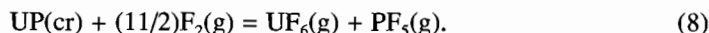
One of the most practical thermochemical quantities is the molar enthalpy of formation of a substance $\Delta_f H_m$, defined as the enthalpy of a reaction in which 1 mol of a given substance is formed from the elements in their most stable states at a given temperature. In many reference books on thermodynamics, 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 $\Delta_f H_m^\circ(T)$. When T is omitted, the function is usually taken to refer to $T = 298.15$ K. Values of $\Delta_f H_m^\circ(298.15$ 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:

$$dQ/dT = \Delta C_m, \tag{9}$$

where ΔC_m is the difference between the molar heat capacities $C_{p,m}^\circ$ (isobaric) or $C_{V,m}^\circ$ (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:

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

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 $T \to 0$ 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 $(X \cdot nH_2O, \text{sln})$ 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, $KF \cdot 160KOH \cdot 1600H_2O(\text{sln})$.

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 Σt_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.