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# Advances in Fluorine Calorimetry

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The development of a new area of thermochemistry (the calorimetry of fluorination reactions) is reviewed. The high reactivity of fluorine offers some important advantages over alternative reagents, but at the same time it introduces some experimental difficulties. We have attempted to generalise the practical problems of fluorine calorimetry by systematically examining a number of specific thermochemical investigations by the most widely adopted modification of the method: fluorine bomb calorimetry. Current developments and possible new applications are reviewed, and the basic experimental procedures and apparatus are described. 86 references.

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## I. INTRODUCTION

The method known as "fluorine calorimetry" includes two main modifications, differing in the details of the calorimetric measurement. The first modification relies on combustion of the sample in fluorine within a calorimetric bomb ("fluorine bomb calorimetry"). This is the latest and most important development in the fundamental thermochemical procedure of bomb calorimetry. The second modification relies on combustion in fluorine with formation of a flame in a special flow-through calorimeter ("fluorine flame calorimetry"). Its applications are more limited, since it is assumed that only gaseous products are formed.

The term "fluorine calorimetry" includes all thermochemical studies of fluorination reactions, whether or not the fluorine is in the elemental state. The replacement of fluorine by a fluorine compound of comparable oxidising power (inert gas fluorides, oxygen fluorides, halogen fluorides) is a mere extension of the method without any fundamental difference.

Thermochemical studies of fluorination reactions were first reported[1] in the 1930's, but precise measurements of the heats of reactions were not attempted until approximately 1960. In 1959 Gross[2], of the Fulmer Research Institute in Great Britain, published the results of his calorimetric measurements of the heats of formation of $SF_6(g)$ and $TiF_4(c)$, obtained by burning sulphur or titanium in fluorine in a special glass bomb. Important contributions to the development of the fluorine bomb came from Hubbard and coworkers[3] of the Argonne National Laboratory, USA, and from Armstrong and coworkers[4] of the National Bureau of Standards, USA. These workers demonstrated the precision attainable by this method, they developed new apparatus for general application, and they proposed new combustion procedures. At the same time Armstrong developed and successfully applied the method of "fluorine flame calorimetry".

Work on reaction calorimetry by using fluorine in a bomb began in the Soviet Union in 1967 at the Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences and also at the High Temperatures Institute of the USSR Academy of Sciences.

Whereas the combustion method using fluorine in a bomb has been used successfully in several laboratories in the USA, Great Britain, West Germany, France, and the Soviet Union, the work using fluorine flames remains the prerogative of a single laboratory (the National Bureau of Standards in the USA). Partly because of its limited applications, and partly because of the lack of direct experience in our own laboratory, we have thought it preferable not to include a discussion of fluorine reaction calorimetry in flames in the present review.

There can no longer be any doubt that fluorine calorimetry offers entirely new possibilities in experimental thermochemistry, since it allows the study of reactions involving substances too unreactive to be investigated by other methods. From the thermochemical point of view reactions with fluorine are more attractive than reactions with oxygen because of the higher oxidising power of elemental fluorine. They are more exothermic and more readily initiated under the conditions of a calorimetric experiment. Fluorides tend to have more definite compositions than oxides. In the great majority of cases combustion in a bomb under a high pressure of fluorine gives the higher fluoride, whereas calorimetric combustion in oxygen can yield crystalline or glassy protective oxide films which make the reaction diffusion-limited and can lead to products of indefinite composition such as mixtures of oxides or phases of variable composition. Effects of this type are responsible for the low precision of oxygen bomb measurements on compounds containing silicon, boron, germanium, and some multivalent transition elements.

Fluorides are "low-temperature" compounds compared with oxides. Most of the higher fluorides have a significant vapour pressure at normal temperature. The presence of gaseous or distillable products in the calorimetric bomb makes their identification and analysis much simpler.

For these reasons reliable values of the standard heat of formation of many compounds were not available before the advent of fluorine calorimetry. Precise measurements of the heats of formation of fluorides by the direct thermochemical method (reaction between the element and fluorine) are important in their own right because of the major role played by these compounds in chemistry, chemical technology, and industry.

The compounds which have been studied by fluorine calorimetry up to the time of writing are listed in the Table. It can be seen that combustion in a fluorine bomb is the main form of the fluorine calorimetry method, having been used successfully to measure the heats of formation of higher and lower fluorides, oxides, refractories, and some other compounds. After the fluorides, the most important group of compounds in the list includes those of silicon ($SiO_2$, SiC), germanium ($GeO_2$, GeS), and boron (Zr, Hf, Nb, and Ta borides, and $B_2O_3$), i.e. the compounds which cannot be studied accurately by oxygen combustion for the reasons stated above. The bomb combustion methods in which fluorine is replaced by other fluorinating agents are likely to be developed further.

Compounds whose heats of formation have been studied by fluorine calorimetry*.

| No | Compound | Reference | Notes |
|---|---|---|---|
| | Reactions with fluorine in a bomb calorimeter | | |
| 1 | $SF_6$(g) | 2, 5, 6, 7 | synthesis from the elements |
| 2 | $TiF_4$(c) | 2, 8 | |
| 3 | $ZrF_4$(c) | 9 | |
| 4 | $MoF_6$(g) | 10 | |
| 5 | $BF_3$(g) | 11, 12, 13, 14, 15 | |
| 6 | $HfF_4$(c) | 8 | |
| 7 | $UF_6$(g); $UF_6$(c) | 16, 17 | |
| 8 | $SiF_4$(g) | 18 | |
| 9 | $CdF_2$(c) | 19 | |
| 10 | HF(l) | 20 | |
| 11 | $ZnF_2$(c) | 21 | |
| 12 | $MgF_2$(c) | 22 | |
| 13 | $AlF_3$(c) | 23, 24 | |
| 14 | $NbF_5$(c); $TaF_5$(c) | 25 | |
| 15 | $YF_3$(c) | 26 | |
| 16 | $BeF_2$(c) | 27, 28 | |
| 17 | $RuF_5$(c) | 29 | |
| 18 | $AsF_5$(g) | 30 | |
| 19 | $SeF_6$(g); $TeF_6$(g) | 5 | |
| 20 | $WF_6$(g) | 31, 6, 32, 33 | |
| 21 | $PF_5$(g) | 34, 35, 36 | |
| 22 | $NiF_2$(c) | 37 | |
| 23 | $CF_4$(g) | 38, 39, 40 | combustion of lower fluorides to higher fluorides |
| 24 | $GeF_4$(g) | 41, 42, 43 | |
| 25 | $VF_5$(c) | 44 | |
| 26 | $CuF_2$(c) | 33 | |
| 27 | $1/n(C_2F_4)_n$(c) | 23, 38, 40 | |
| 28 | $UF_3$(c); $UF_4$(c) | 17 | |
| 29 | $GeF_2$(c) | 45 | |
| 30 | $WF_5$(c) | 6 | |
| 31 | $PF_3$(g) | 46 | |
| 32 | $SiO_2$(c) | 18 | reaction of oxide with fluorine |
| 33 | $GeO_2$(c) | 41 | |
| 34 | $B_2O_3$(c) | 47 | |
| 35 | $AlB_2$; $AlB_{12}$ | 48 | reaction with refractory compounds |
| 36 | BN | 15, 49 | |
| 37 | $ZrB_2$; $HfB_2$ | 50 | |
| 38 | $NbB_2$; $TaB_2$ | 51 | |
| 39 | $B_4C$ | 52 | |
| 40 | $UB_2$ | 53 | |
| 41 | BP | 36 | |
| 42 | SiC | 54 | |
| 43 | GeS | 55 | |
| 44 | $MoS_2$ | 56 | |
| 45 | $Si_3N_4$; GaN | 57 | |
| 46 | $W_2B$ | 58 | |
| 47 | $NSF_3$(g) ) | 59 | other compounds |
| | Reactions with other fluorinated oxidising agents in a bomb calorimeter | | |
| 48 | $OF_2$(g) | 60, 61 | reaction with $H_2$ |
| 49 | $NF_3$(g) | 62 | reaction with elemental sulphur |
| 50 | ClF(g) | 63 | reaction with $H_2$ |
| | $ClF_3$(g) | » | |
| | $ClF_5$(g) | 63,64 | |
| 51 | $ClF_5$(l) | 64 | ditto |
| 52 | $XeF_2$(c) | 65 | reaction with $PF_3$ |
| | $XeF_4$(c) | » | |
| | $XeF_6$(c) | » | |
| | Reactions in flames in a flow calorimeter | | |
| 53 | HF(g) | 4 | reaction of fluorine with $H_2$ and $NH_3$ |
| 54 | $OF_2$(g); HF (soln.) | 66 | reaction with $H_2$ followed by dissolution in water |
| 55 | $ClF_3$(g) | 67 | |
| 56 | ClF(g); $ClF_5$(g) | 67, 68 | ditto |

* Compounds within each group are listed in order of appearance of the first publication. The basis of the classification is stated in the Notes.

The use of fluorine compounds such as the inert gas fluorides often brings a number of advantages. However their exploitation requires some preliminary work: in particular, accurate measurements of the heats of formation of these fluorides, and the development of methods for causing combustion and for analysing the combustion products. Fluorine flame calorimetry is useful for determining the heats of formation of some reactive gaseous fluorides.

## II. SPECIAL FEATURES OF COMBUSTION IN FLUORINE IN A CALORIMETRIC BOMB

The high reactivity of fluorine and fluorides can induce various side reactions, leading to systematic errors in the measurement of the heat of the main reaction. One of the main features of fluorine calorimetry is the need to develop procedures for avoiding these side reactions or accurately correcting for them. We shall discuss this aspect in detail for the special case of combustion in fluorine within a calorimetric bomb.

Obviously, one of the main problems is to avoid side reactions involving fluorine. The fluorine is present in the bomb at a relatively high pressure, and it can interact with the container material. Corrosion of the apparatus during the measurement can be a serious problem†, but it can be minimised to a level which produces a negligible error (thermal effect of the corrosion reaction less than 0.01% of the thermal effect of the main reaction)[10,11] by suitable choice of materials and methods of passivation, and also by careful design and operation of the calorimetric bomb. Heavy corrosion of the other parts of the apparatus (connecting tubes, taps, storage vessels) is also unacceptable because the fluorine can be contaminated with oxygen and other impurities if it is allowed to come into contact with an oxidised metal surface. On the other hand, metal surfaces covered by a passivating film of fluoride can show increased adsorption and a tendency to hydrolysis. A passivating fluoride film on the inner wall of the calorimetric bomb may interact with the products of the main reaction.

The experimental substance can begin to react with the fluorine in the bomb even before the start of the main period of the calorimetric experiment. Hence the thermochemical experiment must be supplemented by tests for this interaction, and if necessary the bomb must be provided with two compartments or other means of isolating the reactants. All these precautions relate, to a greater or lesser extent, to apparatus design. Accurate measurements of the heat of fluorination reactions cannot be attempted without special fluorine-handling equipment, made of the smallest number of fluorine-resistant materials, and operated with careful attention to the special requirements of this procedure.

Let us now consider the possibility of side reactions with impurities in the fluorine used for the calorimetric experiment. A survey of all the papers published on fluorine bomb calorimetry shows that the purity of the fluorine used by different authors varies in the range 99.0–99.99 vol.%. The earlier workers[9,10,35] tended, as a rule, to purify their fluorine by low-temperature distillation[69]. By using laborious procedures with distillation apparatus operated under laboratory conditions they were able to prepare very pure fluorine containing only a few hundredths of one per cent of oxygen and nitrogen as the main impurities[9].

†Some measurements[66,68] by fluorine flame calorimetry have had to be corrected for the corrosion of the apparatus in $OF_2$ and $ClF_3$. In the $ClF_3$ experiment[68] the correction amounted to 0.33% of the measured thermal effect of the $ClF_3 + H_2$ reaction.

At the same time, Domalski and Armstrong[23] measured the heat of formation of $AlF_3$ with fluorine containing 1 vol.% of impurities (0.9% $O_2$, 0.08% $N_2$, 0.01% $CO_2$, traces of $SiF_4$, HF, and fluorocarbons). Later the same workers[70] gave detailed information on the impurity content of two samples of commercial fluorine (99.40 vol.% $F_2$ and 99.79 vol.% $F_2$) which they used for calorimetric combustions of aluminium borides and graphite. Thus, both specially purified fluorine and fluorine of commercial purity have been used in fluorine calorimetry. The tendency to use the latter is explained by recent improvements in industrial processes, which now enable a level of purity in excess of 99.5% to be reliably obtained in commercial fluorine. However, the spectrum of impurities in the material is not constant, and depends on many factors including the grade of the starting material and unavoidable process variations. We must therefore consider the extent to which various possible impurities could take part in side reactions during the calorimetric experiment.

There is general agreement[69-72] that the commonest impurities in fluorine are $O_2$, $N_2$, HF, oxygen fluorides, fluorocarbons, $CO_2$, $SiF_4$, $NF_3$, $SF_6$, $SO_2F_2$, and Ar. An analysis[68,69] of many samples of commercial fluorine suggests that the predominant impurities are $O_2$, $N_2$, $SiF_4$, and $CO_2$. For example, the combined amount of these impurities in two fluorine samples containing 0.60 and 0.21 vol.% of total impurity was found to be[70] >98% of the total. Although the most reactive impurities (oxygen fluorides and hydrogen fluoride) are not usually detected, it cannot be assumed that their concentration is so low as to guarantee freedom from side reactions, since the occurrence (or otherwise) of these reactions depends also on the chemical properties of the substance under study. For example, according to Leonidov and coworkers[32] tungsten reacts spontaneously in the bomb if the fluorine contains ~1 vol.% of oxygen impurity. Spontaneous reaction was not observed when the oxygen content was decreased to 0.1 vol.%. Similar effects may occur with other impurities in the fluorine, which may therefore affect the result to different extents depending on the use to which the fluorine is put.

Thus the required level of purity of the fluorine may vary according to the nature of the impurities and that of the experimental substance. It is not enough to have access to high-purity fluorine: a qualitative and quantitative analysis of the impurities is essential, both before and after the calorimetric experiment‡. This presupposes that a high-precision method of analysis of fluorine and of the impurities in the gas is available. The need exists even if fluorine of the highest purity is used (such as fluorine purified by low-temperature distillation). Thus, Gillardean and coworkers[73] have shown that even very low (>0.1 vol.%) concentrations of oxygen in the fluorine can affect the mechanism of fluorination of metallic copper.

‡As well as measuring the concentration of impurities in the fluorine before and after the calorimetric experiment, special experiments are necessary to prove that there has been no reaction of the main sample with the various impurity components. Thus Domalski and Armstrong[23], having used fluorine containing 0.9 vol.% of oxygen for the calorimetric combustion of aluminium, also burned a sample of aluminium in an equimolar mixture of fluorine and oxygen to show that aluminium oxide is not formed even at that concentration of oxygen.

It follows that an accurate method of fluorine analysis must be available, in addition to suitable calorimetric apparatus, in any laboratory attempting to use fluorine calorimetry.

The third essential precaution to avoid systematic errors through possible side reactions in the calorimetric bomb is a proper choice of the conditions under which the sample is burned in fluorine (combustion procedure).

The best combustion conditions in "oxygen" bomb calorimetry are those for which the oxidation reaction proceeds with a full yield of products of well-defined composition. When the sample is burned in a fluorine bomb calorimeter there is an additional requirement: freedom from side reactions by the fluorine or by the resulting fluorides. This requirement can introduce serious difficulties into the choice of the optimum method of combustion in fluorine. The combustion conditions cannot be really satisfactory unless the initial pressure of fluorine is as low as possible, since the probability of side reactions increases rapidly with pressure. The choice of optimum conditions for combustion in fluorine is further complicated by the likelihood of spontaneous reaction. Because of all these difficulties, we shall attempt a general discussion of the special features of calorimetric combustion in fluorine in relation to the type of sample used, and we shall make some general recommendations on the best experimental conditions in each case.

Thus, the following sections will deal in detail with the analytical determination of fluorine and its impurities, with non-standard apparatus for calorimetric work with fluorine, and with combustion methods for various substances. Since the measurement procedure, the design of the calorimeter, and the calculation of the calorimetric results do not differ in any way from those used, for example, in calorimetric combustions in oxygen[74], we shall not dwell on these problems in the present review§.

## III. FLUORINE ANALYSIS

The mercury method, consisting in chemically absorbing the fluorine in metallic mercury and measuring the volume of residual gases, is generally used for fluorine analysis in calorimetric work. Klyuev[81] has given a full review of all the published work on the mercury method. This is undoubtedly the most accurate chemical method of analysis of high-purity fluorine. It is relatively simple and convenient under laboratory conditions. The method is applied in a variety of forms, differing in the method of measuring the volume of residual gas, in the design of the apparatus, and in the attainable precision. We shall briefly outline the published work on the application of this method to fluorine calorimetry.

Armstrong and Jessup[4] analysed fluorine of 97–99 vol.% purity by the following procedure. A quartz vessel 50 $cm^3$ in volume containing 1–2 $cm^3$ of pure mercury was evacuated to a pressure of 0.01 mmHg, and filled with fluorine at atmospheric pressure through a special micro-valve. The valve was shut, the vessel was disconnected from the gas lines, and it was manually shaken for 10–15 min.

§Most of the calorimetric measurements of fluorine bomb calorimetry (see Table) were carried out in standard water calorimeters with an isothermal enclosure (with the exception of the work of Gross and coworkers[2,13,15,35,36,41], Hayman[17], and Schröder[6]). The only non-standard component of the calorimetric system was the bomb itself.

Complete absorption of the fluorine was judged from the cooling of the vessel and from the change in colour of the mercury surface. The residual pressure was measured with a U-tube manometer filled with fluorocarbon oil. The manometer reading was corrected for the expansion of the gases into the auxiliary volumes (manometer limb, connecting tube) and the volume of the residual, non-absorbed gas was calculated. A reproducibility of 0.05% in a short series of measurements is claimed[4]. A similar procedure was used in calorimetric experiments by Stein and coworkers[69], Armstrong and coworkers[67,70], and Hubbard and coworkers[3]. Stein[69] describes an i.r. spectral method of estimating HF, $OF_2$, $CF_4$, $C_2F_6$, $C_3F_8$, $NF_3$, and $CO_2$ impurities in the residual gas. Domalski and Armstrong[70] reported some measurements of the impurity content of commercial fluorine samples (see above) by a mass spectrometric identification of the residual gas components. The same method was used to analyse fluorine of 99.95% purity, purified by low-temperature distillation[3]. Subsequently King and Armstrong[67], and also Pervov and coworkers[75], used gas chromatography to determine oxygen and nitrogen impurities in the gas which was not absorbed by mercury.

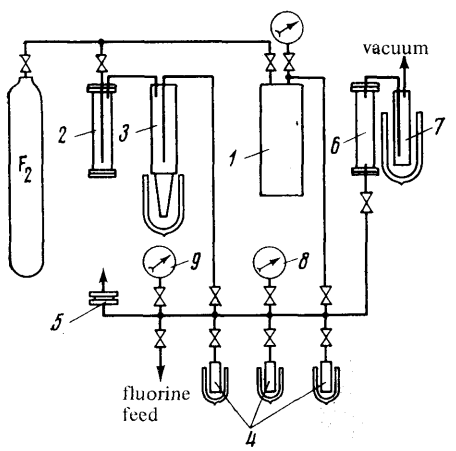



**Figure 1.** Apparatus for fluorine purification: *1*) storage vessel, *2*) granulated NaF absorber for removing HF, *3*) low-temperature condenser with nickel packing, *4*) receivers for fluorine condensation, *5*) pressure relieving valve, *6*) tube packed with metallic silicon for fluorine absorption, *7*) trap for $SiF_4$, *8*) manometer, *9*) vacuum gauge.

However, in spite of their good reproducibility (0.05–0.10%), many of the reported analytical results for fluorine[3,67,69,70] have doubtful precision. Most of the early work on the mercury method includes several sources of systematic error which affect the results of the fluorine analysis. For example, later workers[71,76] have identified the reaction between some impurities (HF, $OF_2$) and mercury as the main source of systematic error. According to Miller and Bigellow[77] the main contribution to the lack of precision comes from the pressure measurements (both the initial pressure of fluorine and the final pressure of the residual gases). A recent paper[75] suggests that the analytical results can be affected by the adsorption of impurities on the mercury fluoride, by temperature changes during the reaction between fluorine and mercury, and by the mixing conditions.

Pervov and coworkers[75] have made a thorough study of the effect of all these factors on the precision of the analysis of fluorine containing only oxygen and nitrogen impurities. They found that, because of the variability of the impurities in ordinary fluorine and of their chemical behaviour under the conditions of analysis by the mercury method, results of adequate precision can be obtained only if the analytical problem is simplified by a preliminary purification of the fluorine. They suggest a relatively simple method of purification, consisting in freezing out most of the impurities (except oxygen and nitrogen) in a flow-through trap at −170°. This procedure achieves two desirable ends: the reliability of the calorimetric results is improved by the use of purer fluorine, and the analytical data are more precise.

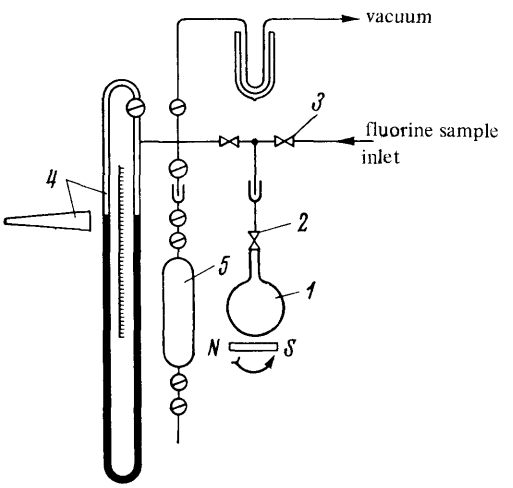



**Figure 2.** Fluorine analysis apparatus: *1*) flask, *2*) needle valve, *3*) tap, *4*) mercury manometer with cathetometer, *5*) gas burette for sampling residual gas.

The apparatus for removing impurities from the fluorine[75] except oxygen and nitrogen is shown in Fig. 1.

Fig. 2 shows an improved apparatus[75] for the analysis of the purified fluorine (>99.5 vol. % $F_2$) by the mercury method with a guaranteed precision. The total concentration of impurities is measured with a precision of 0.05 to 0.10 vol.%; identification is by mass spectrometric or gas chromatographic analysis of the residual gas. This form of the mercury method is ideally suited[4,75] to the analysis of high-purity fluorine (~99.9%), since in this case also the main impurities are oxygen and nitrogen[9], and there are no systematic errors from side reaction or adsorption of impurities. In either case the fluorine used in the calorimetric experiment can be analysed with a precision sufficient to give a reliable correction for the heat of the reaction with the oxygen and nitrogen impurities in the bomb, or alternatively to prove that the correction is unnecessary.

## IV. APPARATUS

The equipment needed for fluorine bomb calorimetry includes the special calorimetric bombs¶ and apparatus for the preliminary purification and anslysis of the fluorine, for filling the bomb, and for sampling and separating the gaseous combustion products. Careful commissioning and operation of this specialised equipment is an essential prerequisite to the achievement of high precision in the measurement of heats of combustion in fluorine. A glass bomb for preliminary experiments on the optimisation of the conditions of combustion in fluorine should also be available because visual observations can be very valuable in this type of work†.

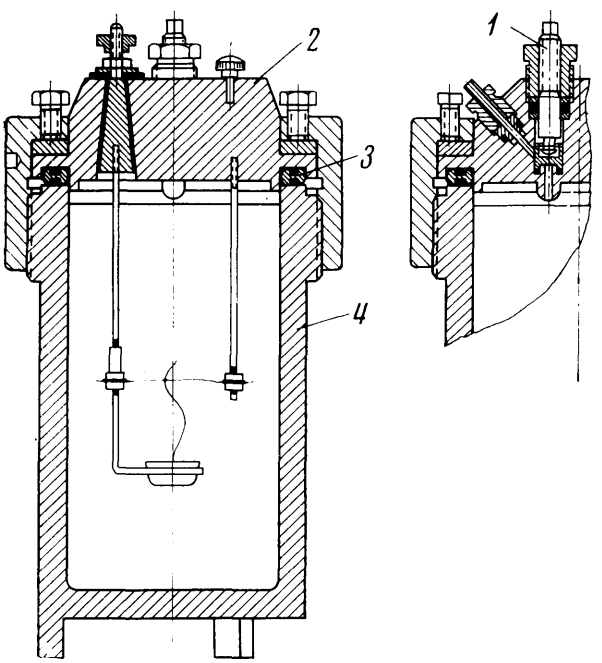



**Figure 3.** Single-chamber bomb calorimeter: *1*) valve, *2*) lid, *3*) seal, *4*) body.

The design of the calorimetric bomb must take account of a number of special requirements which are common to all fluorine-handling equipment. First and foremost, the bombs must be made of fluorine-resistant materials such as pure nickel, Monel metal, some high-alloy carbon-free steels of the Fe–Cr–Ni type, aluminium, gold, and Teflon (used to make sealing gaskets and partitions). Some types of ceramic can also be used (fluorite, fused alumina, and in some cases fused quartz[3,67]). Mechanical properties, operating conditions, and passivation regimes all have to be considered before finalising the choice of materials. For example, Teflon and quartz can ignite spontaneously in compressed fluorine at moderately high temperatures (50–100°). A reliable and simple operating procedure is another important requirement for equipment (including calorimeters) designed to handle fluorine under pressure.

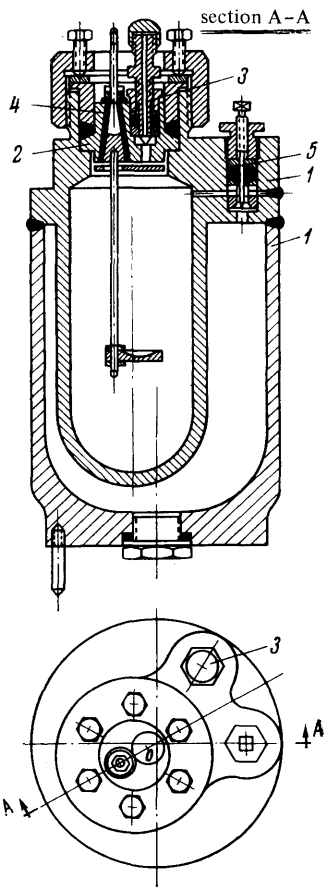



**Figure 4.** Double-chamber bomb calorimeter: *1*) body, *2*) lid, *3*) valve, *4*) electrical lead, *5*) mixing device with break seal.

The most critical elements of fluorine bomb calorimeters are the seals and the locking devices. Hubbard and coworkers used simple gold[9] and aluminium[10] gaskets, or gold–Teflon gaskets[8], to seal the lids of their single-chamber bombs; Armstrong and coworkers[67] used Teflon seals. A single-chamber calorimetric bomb of 350 cm³ capacity[32,33], made of Monel metal, is shown in Fig. 3. It relies on aluminium seals with Teflon-filled channels. We have also used Teflon seals designed on the self-tightening principle[78,79]. Various other effective sealing arrangements for fluorine bomb calorimeters have been described[78–81].

¶The calorimetric bombs are designed to be used in conjunction with the most widely used type of calorimetric system: the water calorimeter with an isothermal enclosure.

†We shall not attempt to describe the glass apparatus for fluorine calorimetry used by Gross and coworkers[2,13,15,35,36,41] because of its limited pressure range, difficult operating procedure, and liability to attack on the glass. Some other unusual approaches[17,63] will also be ignored.

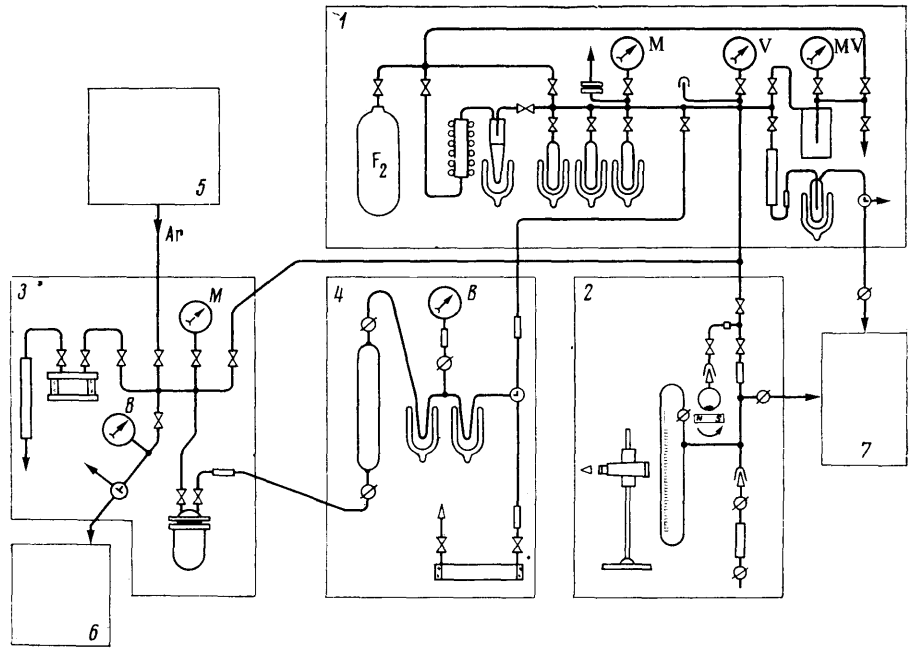



Figure 5. Fluorine handling apparatus for calorimetric work: *1*) purification and storage train, *2*) fluorine analysis, *3*) bomb filling assembly, *4*) assembly for collecting and separating the gaseous combustion products, *5*) argon purification, *6*) and *7*) backing pump and vacuum pump, M) manometer, V) vacuum gauge, MV) combined manometer and vacuum gauge.

As stated above, the possibility of spontaneous reaction can be a serious problem in calorimetric work with fluorine in a bomb. It may be necessary to prevent contact between the reactants until the beginning of the main period of the calorimetric experiment. The commonest solution of this problem is to use a two-chamber bomb. A widely used type of two-chamber bomb was designed by Hubbard and coworkers [82,83]; our own design (Fig. 4) is described in Ref. 79. The two-chamber bomb described by Barberi and coworkers [63] was not so successful. Alternative means of isolating the sample from the fluorine in a single-chamber bomb have also been proposed. Thus, Schröder and Sieben [6] measured the heats of combustion of tungsten pentafluoride and of elemental sulphur, which ignite spontaneously in fluorine, in a single-chamber bomb fitted with a nickel vessel and external means for opening and shutting the lid of this vessel. The weighed sample was placed in the nickel vessel, which remained filled with argon until the beginning of the main period. A similar device was used by Bisbee and coworkers [61,64] to measure the heat of the reaction between $ClF_5$ and hydrogen. A thin-walled Monel metal bulb, previously filled with $ClF_5$, was placed in the bomb and punctured with a special device, thus allowing the $ClF_5$ to react with the hydrogen filling of the main chamber.

Other methods, described in the following Section, use an auxiliary material (which does not react spontaneously with fluorine) to isolate the sample from the fluorine in a single-chamber bomb. The partition is ignited when contact between the sample and the fluorine is required.

Fig. 5 shows a typical assembly for handling fluorine in calorimetric work. It is more complicated than some other designs [3,68] because it includes all the necessary subsidiary facilities such as apparatus for purifying and storing the fluorine (*1*), for analysing the fluorine by the mercury method (*2*) including provisions for sampling the residual gases, for filling the bomb (*3*), and for sampling and separating the gaseous combustion products including provisions for duplicate analysis of the excess fluorine and for sampling gaseous fluorides (*4*). Facilities for purifying the argon used to purge the apparatus (*5*), and for producing a rough vacuum (*6*) and a high vacuum (*7*), are also shown. Items *1* and *3* are made of nickel, with stainless steel valves and taps. Items *2* and *4* are made of quartz and Pyrex glass. The glass vacuum joints are lubricated with a special perfluorinated grease.

We have already pointed out that corrosion of the apparatus and (particularly of the bomb) in fluorine can lead to major difficulties in high-precision measurements. The following precautions are taken to ensure that the results are not affected by side reaction of the construction materials with the fluorine or with the fluorides produced by the combustion. First, all the metal vessels and connecting tubes are tested under pressure, under vacuum, and they are then exposed for several days to fluorine at its working pressure‡. Furthermore, a number of "blank" combustions of the sample are carried out in the calorimetric bomb [31-34]. The products of these combustions are tested for the presence of products of any reactions between the fluorine and the bomb materials, the sample supports, and the passivating fluoride films which are formed on

‡Wise and coworkers [11] describe a method of passivating the calorimetric apparatus by heating it for several hours at 110° in the presence of fluorine at 1 atm pressure.

their surface[32,34]. The success of the passivating treatment is checked by separately weighing the internal components of the bomb[32].

Secondly, all operations (loading and unloading) with the passivated bomb are carried out in a "dry" box§ to avoid the danger of hydrolysis of the passivating fluoride film. The other parts of the apparatus are kept filled with dry argon after passivation[32]. Additional tests include check measurements of the water equivalent of the calorimetric system by calibration[85] before and after each series of experiments. Electrical calibration is preferred, but the combustion in oxygen of calorimetric standards such as benzoic acid is also acceptable[3,32,33].

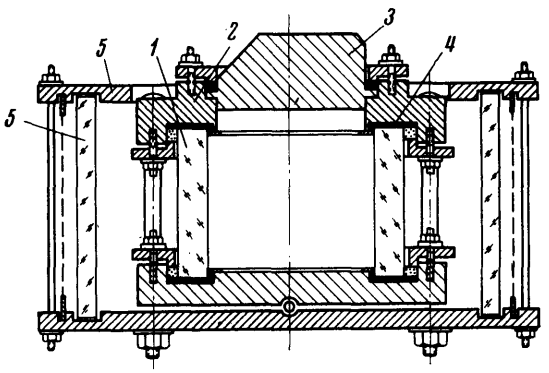



**Figure 6.** Glass bomb for experiments on the optimum conditions for fluorine combustion: *1*) glass body, *2* nickel flange, *3*) lid, *4*) seal, *5*) explosion guard.

A glass bomb for test combustions in fluorine is a valuable facility for auxiliary experiments aimed at selecting the best combustion conditions for the calorimetric bomb. The bomb (Fig. 6) has transparent walls through which the reactions in the chamber can be visually observed at fluorine pressures up to 10 atm. The apparatus was first used by Hubbard and coworkers[84]; our modification, shown in Fig. 6, was described in Ref. 78.

Special safety precautions are essential in all laboratory work involving liquid fluorine and gaseous fluorine under pressure. The danger of explosions and the high toxicity of fluorine and fluorides must be carefully considered in the design of the apparatus, the layout of the accommodation, and the choice of operating procedure[3,68,71,74,85].

## V. COMBUSTION METHODS

The main consideration in the search for the optimum combustion conditions is the nature of the reaction between the sample and the fluorine. The geometry of the sample (assuming, of course that the sample is not gaseous) is of crucial importance. Hubbard[3] has made a special study of this problem, and has even suggested a classification of combustion methods based on sample geometry¶.

It can be seen from the Table that metals account for a significant proportion of the materials which have been investigated by this method. When metallic samples are burned in fluorine under bomb conditions the temperature can be high enough to melt the sample, at least partially. The effect depends markedly on the rate of reaction of the metal with fluorine. If the rate is high, and the resulting fluoride has a low boiling point (e.g. tungsten[6,31-33]), there is little danger of side reactions leading to analytical complications. On the other hand if the rate is relatively low, the thermal conductivity of the sample is high, and the resulting fluoride is involatile, the molten metal tends to break up into drops and to spatter, together with some of the fluoride formed by the reaction. This effect can have various undesirable consequences, particularly at the contact between the metal and the support. It can be avoided by diluting the fluoride with an inert gas so as to lower the temperature and the reaction rate.

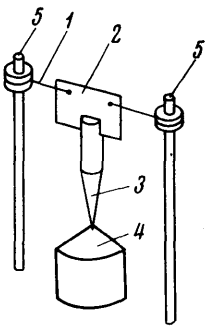



**Figure 7.** Combustion of metallic zirconium in fluorine: *1*) zirconium igniting wire, *2*) zirconium foil, *3*) pointed zirconium rod, *4*) massive nickel block.

Thus, in the first investigation by fluorine bomb calorimetry described by Hubbard and coworkers[8] the sample of zirconium metal (of the shape shown in Fig. 7) was burned from the top towards the bottom. The reaction stopped after ~75% of the sample had been burned, owing to the loss of heat to the massive nickel heat sink. Fusion of the zirconium was avoided by diluting the fluorine with helium (fluorine pressure 2000 mmHg, total pressure 12 atm). A similar method was used by Hubbard and coworkers in their calorimetric work with metallic uranium[16].

§However, it has been pointed out[11,37] that the water equivalent of the calorimetric system is practically unaffected by storing the passivated nickel bomb in ordinary air and by washing it in water.

¶There are, of course, other classifications, e.g. classifications according to the phase composition of the products (gaseous, fused, or solid), or according to the number of products (only the higher fluoride if the reactant is an element or a lower fluoride, but if the sample is more complex several products may be formed, and may have to be separated for analysis). Alternative methods of classification could be based on the use of auxiliary materials, on the ignition procedure, on the propensity to spontaneous reaction with fluorine, etc.

When metallic copper[33], zinc[21], cadmium[19], magnesium[22], or nickel[37] are burned in fluorine an acceptable rate of combustion is obtained only at temperatures in excess of the melting point of the metal. Several workers[19,21,22,24,26,37] have therefore been compelled to line the inner surface of the bomb and to use a substrate made from a fused fluoride of the metal under test. It was assumed that under these conditions no undesirable reactions can occur between the metal and the substrate in a fluorine atmosphere. However, oxygen evolution was observed in the bomb during the combustion of metallic nickel[37] in the presence of high pressures of fluorine (15–25 atm). Evidently the $NiF_2$ substrate still contained some nickel oxide in spite of having been carefully prepared by lengthy baking in HF and $ClF_3$. Side reactions with formation of copper monofluoride between molten copper and the $CuF_2$ substrate could not always be avoided in calorimetric combustions of metallic copper[33,86].

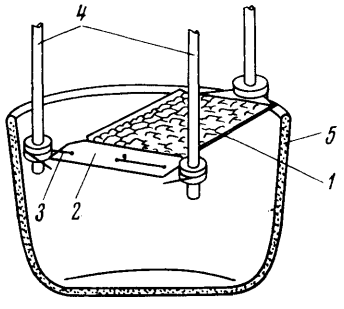



**Figure 8.** Combustion in fluorine of a copper sample with tungsten: *1*) copper sample (gauze), *2*) tungsten sheet, *3*) tungsten igniting wire, *4*) electrodes, *5*) fused alumina heat screen.

The possibility of forming lower fluorides and the difficulty of separating and analysing the combustion products can preclude the use of "inert" fluoride substrates. In these circumstances it is better to use an auxiliary material whose combustion can raise the temperature in the reaction zone. In this way the rate of the main reaction is increased, and the resulting fluorides are volatilised and condense on the cold walls of the bomb. Drop formation and spattering of the molten metal can be avoided by keeping the rate of fluorination high and the thermal conductivity of the sample low. Analysis and identification of the combustion products becomes much simpler if the conditions are chosen so that only gaseous products are formed in the combustion zone. Another important consideration is the possibility of working at much lower initial pressures of fluorine if an auxiliary material is introduced as an igniter.

We have used this procedure to measure the enthalpy of formation of $CuF_2$ by burning metallic copper in fluorine[33], and also in seeking the best conditions for the combustion of metallic nickel in fluorine. The type of copper sample[33] is illustrated in Fig. 8. The auxiliary material was metallic tungsten. The geometry of the sample ensures the maximum concentration of heat at the combustion front. Domalski and Armstrong used a similar method in their calorimetric combustions in fluorine of metallic aluminium[23], one of the boron carbides[52], and aluminium boride[48]. Their samples consisted of pressed disks of the powdered material (aluminium, aluminium borides, or boron carbide) mixed with powdered Teflon which they found to be a suitable igniter for these reactions[23,48,52].

Ill-defined reaction products, including lower fluorides, are occasionally obtained when some metals are burned in fluorine. As was pointed out above, this difficulty was encountered in our work on the combustion of copper[33]. In the determination of $\Delta H_f^\circ(UF_6, g)$ by the combustion of metallic uranium in fluoride[16] small amounts (~1%) of lower uranium fluorides were invariably produced in the bomb, requiring very accurate chemical analyses to enable the appropriate corrections to be calculated. Careful analyses of the solid "residues" of lower fluorides had to be made also in other investigations[10,29].

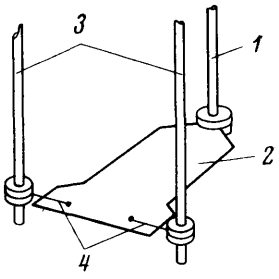



**Figure 9.** Combustion of a metallic tungsten sample in a fluorine bomb: *1*) holder, *2*) tungsten foil, *3*) electrodes, *4*) tungsten igniter wire.

In spite of these difficulties, it is often possible to choose a type of metal sample for combustion (foil, wire, or rod) which avoids or minimises the substrate problem. The geometry of the sample and the method of clamping the sample in the bomb are usually determined by the need to avoid direct contact between the combustion zone and the constructional materials (substrate, bomb fixtures). The design of tungsten foil sample shown in Fig. 9, used for calorimetric combustions at fluorine pressures up to 3 atm [32], satisfies all these requirements. The tungsten foil, 0.06 mm thick, can be burned completely without undesirable effects such as spattering or contamination of the combustion zone by falling fragments of the sample support.

When powdered samples are used for calorimetric combustion in a fluorine bomb they are usually contained in a simple nickel capsule or crucible. Contact between hot particles and the container material leads to local overheating and enhanced corrosion of the nickel. Various practical steps can be taken to minimise this effect. The burning rate of the particles can be decreased by diluting the fluorine with helium or argon, and by choosing the most appropriate particle size for the sample[11]. Alternatively, massive containers can be used to conduct the heat away from the reaction zone[50]. Occasionally it is possible to use a container material which avoids the danger of side reactions between the combustion products of the main sample and the passivating fluoride film of the constructional material. For example, Hubbard and coworkers[50]

used a container of metallic zirconium in their study of zirconium diboride. Often the container material is chosen empirically. Containers of fused alumina or nickel had been found[11] to react with fluorine at the points of contact with a charge of crystalline boron powder. They were successfully replaced by a $CaF_2$ crucible. Combustible containers, which fulfil the role of igniter, have also been used[33,48,52].

A test for the absence of "premature" reaction between the sample and the fluorine is an essential part of the search for the optimum combustion conditions (unless of course the design of the bomb allows physical isolation of the two reactants). The test usually takes the form of repeated weighings of the sample after exposure to fluorine in the bomb at the working pressure. If the premature reaction is significant the simple test is followed by analytical determinations. Hubbard and coworkers burned metallic uranium[16], and niobium and tantalum[25], in a single-chamber bomb after determining the extent of the preliminary reaction with fluorine. They showed that this reaction (between uranium and fluorine) produces uranium tetrafluoride[16], and they were able to correct their calorimetric measurements accordingly.

We have already pointed out that the most effective and generally applicable precaution in the study of materials which ignite spontaneously in fluorine is to use a two-chamber bomb. The other methods of isolating the reactants mentioned in the previous Section are attempts at designing a "universal" bomb[6,64]. It is appropriate at this point to review the methods of isolating the reactants by using auxiliary materials as combustible partitions in one-chamber bombs. Thus, Margrave and coworkers[43,55] used a nickel vessel with a pressure-tight lid including a tungsten foil diaphragm. The vessel, containing a weighed amount of the sample, was filled with helium and inserted into the calorimetric bomb, which was filled with fluorine. At the beginning of the main period of the calorimetric experiment the foil was kindled with an igniter wire, thus allowing the fluorine to reach the sample. The review articles by Hubbard[3] and Armstrong[68] suggest the use of quartz bulbs[3] sealed by a small stopper of thin Teflon[68] or metal foil[3].

A number of conditions must be satisfied when auxiliary materials are used in calorimetric combustions in fluorine. The main condition is an appropriate choice of the auxiliary material itself. As well as being compatible with the chosen method of combustion, it must have an accurately known heat of combustion in fluorine. Also, its fluorination products should be inert towards the fluorination products of the main sample. The presence of an auxiliary material introduces additional measurement difficulties. In order to obtain accurate results the heat of combustion in fluorine of the auxiliary material must be determined in a separate series of experiments, using the same sample geometry and identical bomb conditions (initial fluorine pressure, amount of material, method of supporting the sample). These precautions ensure that the result is unaffected by impurities and by uncontrolled combustion conditions[23,33].

Preliminary measurements of the heat of combustion in fluorine of the auxiliary material were made in all the thermodynamic investigations listed in the Table which relied on an auxiliary material. Thus, Hubbard and coworkers measured the heat of combustion of sulphur in fluorine[5], and subsequently used this material to initiate the combustion of molybdenum and vanadium sulphides[44,56] and of niobium and tantalum borides[51] in a two-chamber bomb. Precise measurements of the heat of combustion of silicon in fluorine[18] enabled Hubbard and coworkers to use silicon as an initiator for graphite[39] and silica[18]. Armstrong and coworkers repeatedly measured the heat of combustion of Teflon in fluorine[23,38], and they used Teflon as the auxiliary material in their studies of the heat of combustion of aluminium, graphite, aluminium borides, etc.[23,38,48] Tests for possible interactions between the fluoride of the main sample and that of the auxiliary material are made by various methods, described below.

Other workers have used tungsten[33,43,55], sulphur[44,51,56,58], silicon[18,39], Teflon[23,38,48,55], phosphorus trifluoride[59], titanium[11], and molybdenum[12] as the auxiliary material. Tungsten, titanium, and molybdenum in the form of thin wires can be used to ignite samples by the electrical discharge method[11,12,33,43].

It is evident from the above discussion that the combustion of samples in fluorine in a calorimetric bomb can be carried out by very different procedures. The most important criterion for choosing the best combustion conditions is freedom from side reactions. Equally important is the provision of simple, reliable, and accurate methods of analysis of the bomb products.

It may be useful to dwell in some detail on some differences in the analytical techniques used to identify the products of combustion in fluorine. These differences arise mainly from the need to estimate the excess of fluorine and the gaseous products of the combustion in fluorine, as well as identifying any interactions with the bomb materials.

Analysis of the excess of fluorine involves the separation of the gaseous fluorides by low-temperature vacuum condensation. It has been shown[18,41,47,60,66] that the combustion of many oxides in a fluorine bomb produces the corresponding fluoride and oxygen; nitrogen is formed when nitrides[49,57] and some other nitrogenous compounds are burned (e.g. thiazyl trifluoride[59]). Most of the other elements burn with formation of higher fluorides. Thus the excess of fluorine may contain amounts of oxygen, nitrogen, and some fluorides ($CF_4$, $BF_3$, $SF_6$, etc.) corresponding to the stoichiometry of the reactions under study. Because the boiling points of these materials are not very different from that of fluorine we cannot expect complete separation by the low-temperature vacuum condensation method. The excess of fluorine may contain also additional amounts of oxygen, nitrogen, carbon tetrafluoride, etc. produced by the combustion in fluorine of impurities in the main sample. Hence a study of the composition of the residual gas after absorption of the fluorine in mercury is an essential analytical operation. For example, King and Armstrong[66] showed, by chromatographic separation of the components of the gaseous residue, that free oxygen is formed by the reaction between oxygen difluoride and hydrogen. I.r. and gas-chromatographic analyses of the residual gases enabled O'Hara and Hubbard to show[34] that phosphorus pentafluoride is the only product of the reaction between phosphorus and fluorine under calorimetric bomb conditions. Hubbard and coworkers[49] proved, by mass-spectrometric analysis of the gaseous residue, that free nitrogen and boron trifluoride are formed in the reaction between boron nitride and fluorine.

If the reaction under study gives rise to a mixture of volatile fluorides, which is invariably the case when auxiliary materials are used, the possibility of side reactions between the fluorides must be examined. This problem can also be solved by the analytical procedures described above. Special experiments are sometimes needed. Thus, the absence of interactions between boron

trifluoride and tungsten hexafluoride during the combustion of tungsten borides in fluorine[58] was demonstrated by volumetric experiments with mixtures of these gases. Gross and coworkers[36] tested for interactions between phosphorus pentafluoride and boron trifluoride, in their work on the heat of formation of boron phosphide, by a series of calorimetric experiments in which equimolar mixtures of boron and phosphorus (and separate samples of boron and phosphorus) were burned in fluorine.

Gas chromatography is perhaps the most convenient method of analysis of the gaseous products of combustion in a calorimetric fluorine bomb (including the excess of fluorine)†.

The solid products of the reaction between the sample and fluorine can be analysed by chemical and X-ray diffraction methods[33,37]. Solid reaction products are separated from the unburned part of the sample by appropriate choice of combustion conditions. The extent of side reactions with the sample support materials is checked at the same time. If necessary, the results of these analyses are used to calculate corrections to be applied to the calorimetric measurement. The correction for attack on a nickel support has been specially discussed[34,58].

## VI. CONCLUSIONS

The above discussion of the special features of reaction calorimetry in a fluorine bomb gives some insight into the aspects which must be considered before deciding to use this method in specific instances. The method is relatively complex and laborious, since it requires special experimental procedures and a large number of analytical checks. We have tried to make clear the extent to which thermochemically well defined conditions can be achieved in fluorine bomb calorimetry.

After applying the corrections for side reactions the calorimetric result is calculated by normal procedures[74]. However, there are some differences of detail in the calculation of the correction for standard conditions. Thus the determination of the Washburn corrections (for the change in internal energy of the system when converted to the standard conditions) can present some difficulty due to the lack of necessary data. A method of calculating the Washburn correction from the coefficient $(\partial E/\partial p)_g$ for fluorine and gas mixtures containing fluorine, measured in a separate experiment by Hirschfelder's method, has been described by Hubbard in detail[3]. Calculations of the correction for reactions with impurities in the sample usually assume that oxygen and nitrogen are evolved in the free state during combustion in fluorine. All other impurities are assumed to form higher fluorides[32,33,57].

When a double-chamber calorimetric bomb is used, the heat associated with the transfer of the fluorine into the combustion chamber has to be measured by a series of "blank" calorimetric experiments with a bomb containing the fluorine but not the main sample. The results are used to apply a correction to the calorimetric results of the main experiment[5,7,44,46].

One fundamental problem in the adoption of fluorine bomb calorimetry is the lack of a really satisfactory standard material. Calibration standards for combustion in fluorine should meet the following requirements[3]: their heat of combustion in fluorine should be reliably and accurately known, the combustion and analysis procedures should be simple and the reaction should be thermochemically well defined, there should be no side reactions with fluorine or with impurities in the fluorine, and lastly the material should be available in a high state of purity. We believe[33] that metallic tungsten satisfies all these requirements. The value $\Delta H^\circ_{f\,298\cdot15}(WF_6, g) = 411.4 \pm 0.2$ kcal mole$^{-1}$ appears to be well established[32,33]. It agrees well with the results obtained in two other laboratories[6,31]. The procedure for burning tungsten in fluorine[32,33] is relatively simple (see Fig. 9): the only combustion product is gaseous tungsten hexafluoride, which can easily be separated from the excess of fluorine for subsequent analysis by vacuum condensation[31-33].

Standardisation of some of the auxiliary procedures (in particular, the fluorine analysis) would be desirable. Our procedure and apparatus[75], described in Section III, give accurate analytical results after a relatively simple purification of the fluorine, and can be recommended as the preferred method of fluorine analysis in calorimetric work. Our method of passivating the calorimetric bomb, and the operating conditions, can also be recommended. We also believe that the initial pressure of fluorine in the bomb should be as low as possible. We have shown that the maximum pressure of fluorine can be limited to 8–10 kg cm$^{-2}$ even with samples of metallic copper and nickel, which can be classified as "difficult" because of their inertness towards fluorine. The tendency to use lower fluorine pressures is justified by the lower corrosion rate of the bomb materials in low-pressure fluorine.

This brief review suggests that the experimental problems encountered in the use of a fluorine bomb in reaction calorimetry have been solved to a large extent. More accurate and better standardised experimental approaches are needed to extend the range of applications of the method, which is still considered to be a laborious and specialised procedure, and to allow its advantages to be fully realised. It is clear from the results listed in the Table that although the stage of determining the heats of formation of simple fluorides is far from complete, there are already indications that the method can be applied to complex materials. Examples of the successful application of fluorine calorimetry in the study of compounds include the fluorine combustion of $SiO_2$, $B_2O_3$, and $GeO_2$, which provided the first reliable values of the enthalpy of formation of these compounds. The reaction with fluorine is the most convenient method of measuring $\Delta H^\circ_{f\,298}$ of several refractory compounds, especially borides and silicides, as well as the lower fluorides. We can expect the range of applications of fluorine calorimetry to continue to expand, and in future the method is likely to become one of the most widely used thermochemical procedures.

## REFERENCES

1. H. von Wartenberg and O. Fitzner, Z. anorg. Chem., 151, 313 (1926).
2. P. Gross, C. Hayman, and D. L. Levi, XVII Intern. Kongress für reine und angewandte Chemie, Münich 1959, Band 1, 1959, p. 90.
3. W. N. Hubbard in "Experimental Thermochemistry", Vol. 2, New York–London, 1965, p. 95.
4. G. T. Armstrong and R. S. Jessup, J. Res. Nat. Bur. Standards, **64A**, 49 (1960).

†A gas chromatograph for the analysis of aggressive and easily hydrolysable materials (KhG2302) has recently been developed by the Analytical Instrumentation Division of the USSR Academy of Sciences. This apparatus can be used for the analysis of gas mixtures containing fluorine.

5. P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, Trans. Faraday Soc., 62, 558 (1966).
6. J. Schröder and F. J. Sieben, Chem. Ber., 103, 76 (1970).
7. V. Ya. Leonidov, V. S. Pervov, O. M. Gaisinskaya, and L. I. Klyuev, Dokl. Akad. Nauk SSSR, 211, 901 (1973).
8. E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem., 66, 1345 (1962).
9. E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem., 65, 1168 (1961).
10. J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 65, 1337 (1961).
11. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 65, 2157 (1961).
12. G. K. Johnson, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 70, 1 (1966).
13. P. Gross, C. Hayman, and M. S. Stuart, Trans. Faraday Soc., 62, 2716 (1966).
14. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Standards, 71A, 195 (1967).
15. P. Gross, C. Hayman, and M. S. Stuart, Proc. Brit. Ceramic Soc., 8, 39 (1967).
16. J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 67, 1892 (1963).
17. C. Hayman, "Thermodynamik simposium", Heidelberg, 1967, Paper 1/7.
18. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 67, 815 (1963).
19. E. Rudsitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 67, 2388 (1963).
20. E. Greenberg and W. N. Hubbard, "24th Annual Calorimetry Conference", Portsmouth (New Hampshire), 1969, Abstracts of Papers, p. 33.
21. E. Rudsitis, R. Terry, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 68, 617 (1964).
22. E. Rudsitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 68, 2978 (1964).
23. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Standards, 69A, 137 (1965).
24. E. Rudsitis, H. M. Feder, and W. N. Hubbard, Inorg. Chem., 6, 1716 (1967).
25. W. N. Hubbard, E. Greenberg, and C. A. Natke, J. Phys. Chem., 69, 2089 (1965).
26. E. Rudsitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 69, 2305 (1965).
27. G. T. Armstrong, Sci. Technol. Aerospace Reports, 3, 3389 (1965).
28. K. L. Churney and G. T. Armstrong, J. Res. Nat. Bur. Standards, 73A, 281 (1969).
29. H. A. Porte, E. Greenberg, and W. N. Hubbard, J. Phys. Chem., 69, 2308 (1965).
30. P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem., 69, 4358 (1965).
31. P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem., 70, 3353 (1966).
32. V. Ya. Leonidov, V. S. Pervov, L. I. Klyuev, O. M. Gaisinskaya, V. A. Medvedev, and N. S. Nikolaev, Dokl. Akad. Nauk SSSR, 205, 349 (1972).
33. V. S. Pervov, V. Ya. Leonidov, L. I. Klyuev, and A. G. Muravina, Dokl. Akad. Nauk SSSR, 214, 1088 (1974).
34. P. A. G. O'Hare and W. N. Hubbard, Trans. Faraday Soc., 62, 2709 (1966).
35. P. Gross, C. Hayman, and M. S. Stuart, Trans. Faraday Soc., 62, 2716 (1966).
36. P. Gross, C. Hayman, and M. S. Stuart, Trans. Faraday Soc., 65, 2628 (1969).
37. E. Rudsitis, E. H. Van Devenier, and W. N. Hubbard, J. Chem. Eng. Data, 12, 133 (1967).
38. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Standards, 71A, 105 (1967).
39. E. Greenberg and W. N. Hubbard, J. Phys. Chem., 72, 222 (1968).
40. J. L. Wood, R. J. Lagow, and J. L. Margrave, J. Chem. Eng. Data, 12, 255 (1967).
41. P. Gross, C. Hayman, and I. T. Bingham, Trans. Faraday Soc., 62, 2388 (1966).
42. P. A. G. O'Hare, J. Johnson, B. Klamecki, M. Mulvihill, and W. N. Hubbard, J. Chem. Thermodynamics, 2, 177 (1969).
43. G. P. Adams, T. V. Charly, and J. L. Margrave, J. Chem. Eng. Data, 15, 42 (1970).
44. G. K. Johnson and W. N. Hubbard, J. Chem. Thermodynamics, 6, 59 (1974).
45. G. P. Adams, J. L. Margrave, and R. W. Wilson, J. Chem. Thermodynamics, 2, 741 (1970).
46. E. Rudsitis, E. H. Van Deventer, and W. N. Hubbard, J. Chem. Thermodynamics, 2, 221 (1970).
47. G. K. Johnson and W. N. Hubbard, J. Chem. Thermodynamics, 1, 459 (1969).
48. E. S. Domalski and G. T. Armstrong, "19th Annual Calorimetry Conference", Washington, 1964, Abstracts of Papers, VIb.
49. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 70, 7 (1966).
50. G. K. Johnson, E. Greenberg, J. L. Margrave, and W. N. Hubbard, J. Chem. Eng. Data, 12, 137 (1967).
51. G. K. Johnson, E. Greenberg, J. L. Margrave, and W. N. Hubbard, J. Chem. Eng. Data, 12, 597 (1967).
52. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Standards, 72A, 133 (1968).
53. H. E. Flotow, D. W. Osborne, P. A. G. O'Hare, J. L. Settle, F. D. Mracek, and W. N. Hubbard, J. Chem. Phys., 51, 583 (1969).
54. E. Greenberg, C. A. Natke, and W. N. Hubbard, J. Chem. Thermodynamics, 2, 193 (1970).
55. G. P. Adams, J. L. Margrave, and P. W. Wilson, J. Chem. Thermodynamics, 2, 591 (1970).
56. P. A. G. O'Hare, E. Benn, F. Yu. Cheng, and G. Kuzmycz, J. Chem. Thermodynamics, 2, 797 (1970).
57. I. L. Wood, G. P. Adams, I. Mukereyi, and J. L. Margrave, "Third International Conference on Chemical Thermodynamics", Baden (Austria), 1973, Abstracts of Papers, Vol. 1, p. 115.
58. V. Ya. Leonidov, O. M. Gaisinskaya, V. S. Pervov, and S. S. Ordan'yan, Zhur. Fiz. Khim. (in press).
59. P. A. G. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, J. Chem. Thermodynamics, 2, 71 (1970).
60. W. R. Bisbee, J. V. Hamilton, R. Rushworth, J. M. Gerhauser, and T. J. Houser, AIAA Bull., 2, n3, 114 (1965).
61. W. R. Bisbee, J. V. Hamilton, R. Rushworth, T. J. Houser, and J. M. Gerhauser, Adv. Chem. Series, 54, 215 (1965).
62. I. C. Walker, J. Phys. Chem., 71, 361 (1967).
63. P. Barberi, J. Caton, J. Gruillen, and O. Hartmanshen, Rapport CEA-R-3761 (1969).
64. W. R. Bisbee, J. V. Hamilton, J. M. Gerhauser, and R. Rushworth, J. Chem. Eng. Data, 13, 382 (1968).
65. G. K. Johnson, J. G. Malm, and W. N. Hubbard, J. Chem. Thermodynamics, 4, 879 (1972).
66. R. C. King and G. T. Armstrong, J. Res. Nat. Bur. Standards, 72A, 113 (1968).
67. R. C. King and G. T. Armstrong, J. Res. Nat. Bur. Standards, 74A, 769 (1970).

68. G. T. Armstrong, Paper presented to the Fifth All-Union Conference on Calorimetry, Tbilisi, 1973.
69. L. Stein, E. Rudsitis, and J. T. Settle, US Atomic Energy Commission ANL-6364, 1961.
70. E. S. Domalski and G. L. Armstrong, Technical Report AFAPL-TR-65-110, Oct., 1965, USA.
71. N. P. Galkin and A. B. Krutikov, "Tekhnologiya Ftora" (Fluorine Technology), Atomizdat, Moscow, 1968.
72. G. Müller and G. Grauk, "Reinste Gase", Berlin, 1965.
73. J. Gillardean, L. Vincent, and J. Oudar, Compt. rend., C263, 1469 (1966).
74. S. M. Skuratov, V. P. Kolesov, and A. F. Vorob'ev, "Termokhimiya" (Thermochemistry), Pt. 1, No. 2, Izd. Moskov. Univ., 1966.
75. V. S. Pervov, L. I. Klyuev, V. Ya. Leonidov, and N. S. Nikolaev, Zhur. Analit. Khim., 26, 2196 (1970).
76. H. Schmitz and M. J. Schumacher, Z. anorg. Chem., 245 (1940).
77. W. T. Miller and L. A. Bigellow, J. Amer. Chem. Soc., 58, 1585 (1936).
78. Ya. A. Gurevich, V. S. Pervov, V. Ya. Leonidov, and I. M. Ievleva, Zavod. Lab., 35, 1510 (1969).
79. L. I. Klyuev, V. Ya. Leonidov, G. N. Gaisinskaya, and V. S. Pervov, Zhur. Fiz. Khim., 48, 212 (1974) [Russ. J. Phys. Chem., No. 1 (1974)].
80. L. I. Klyuev, V. Ya. Leonidov, V. S. Pervov, O. M. Gaisinskaya, V. A. Medvedev, and N. S. Nikolaev, "Tret'ii Vsesoyuznyi Simpozium po Khimii Neorganicheskikh Ftoridov" (Third All-Union Symposium on the Chemistry of Inorganic Fluorides), Collected Papers, Odessa, 1972, p. 92.
81. L. I. Klyuev, Thesis, Moscow, 1974.
82. R. L. Nutall, S. S. Wise, and W. N. Hubbard, Rev. Sci. Instr., 32, 1402 (1961).
83. J. L. Settle, E. Greenberg, and W. N. Hubbard, Rev. Sci. Instr., 38, 1805 (1967).
84. R. L. Nutall, M. A. Frisch, and W. N. Hubbard, Rev. Sci. Instr., 4, 461 (1960).
85. J. F. Froning, H. K. Richards, T. W. Stricklin, and S. G. Turnbull, Ind. Eng. Chem., 39, 3 (1947).
86. H. von Wartenberg, Z. anorg. Chem., 241, 381 (1939).

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