

# FLUORINE BOMB CALORIMETRY\*

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## INTRODUCTION

There are many inorganic compounds for which heat of formation values have not been measured, often because of the lack of suitable experimental methods. Exploratory experiments in this laboratory in oxygen bomb and aqueous solution calorimetry on various transition metal borides, sulphides and silicides re-emphasized the need for a general method for determining the heat of formation of compounds not amenable to conventional thermochemical calorimetry. With the aim of developing such a method, attention was directed towards the use of fluorine as an oxidant in calorimetry.

The use of fluorine in calorimetry is not a new idea. However, in previous work it was used when necessary in the investigation of the heat of a particular reaction, rather than as a general tool.

As early as 1926, Wartenberg and his co-workers used fluorine flow calorimetry in some of their studies, synthesizing  $\text{HF}$ <sup>1</sup>,  $\text{F}_2\text{O}$ <sup>2</sup> and  $\text{AgF}_2$ <sup>3</sup> in a calorimeter. Wartenberg<sup>4</sup> has also treated silicon, carbon and silicon carbide and more recently, at the National Bureau of Standards, Jessup and Armstrong<sup>5-7</sup> have treated  $\text{CoF}_2$ <sup>5</sup>,  $\text{CH}_4$ <sup>6</sup> and  $\text{NH}_3$ <sup>7</sup> with fluorine in a flow-type calorimeter. P. Gross<sup>8</sup> has treated titanium and sulphur with fluorine in a constant volume glass vessel in a calorimeter. Various fluorine-containing compounds have also been made to react with other compounds in a calorimeter, *e.g.*,  $\text{NF}_3$  with  $\text{H}_2$ <sup>9</sup>,  $\text{CrF}_3$  with  $\text{Mg}$ <sup>10</sup>,  $\text{CrF}_4$  with  $\text{H}_2$ <sup>10</sup>,  $\text{CoF}_2$  with  $\text{KOH}$ <sup>11</sup>,  $\text{CoF}_3$  with  $\text{C}_6\text{H}_4(\text{CF}_3)_2$  and  $\text{H}_2$ <sup>5</sup>,  $\text{K}$  with  $\text{CF}_4$ <sup>12</sup> and  $\text{ClF}_3$  with  $\text{NaCl}$ .

In solution calorimetry the use of aqueous hydrofluoric acid as the solvent is well documented. The use of  $\text{BrF}_3$  as a non-aqueous solvent in solution calorimetry has been suggested by Woolf<sup>14-16</sup>. Woolf<sup>16</sup> also suggested the possibility of fluorine bomb calorimetry, but expressed a preference for  $\text{BrF}_3$  solution calorimetry.

It was decided in this laboratory to develop fluorine bomb calorimetry as a general tool for studying compounds not easily studied with conventional calorimetric methods. Information on the chemistry of bromine trifluoride and fluorine reactions indicates that the reactions in fluorine bomb calorimetry appear to be more easily characterized and adapted to calorimetric study than the reactions in bromine trifluoride solution calorimetry.

\* Work performed under the auspices of the U.S. Atomic Energy Commission.

## CONSTRUCTION MATERIALS AND SAFETY FEATURES

Although fluorine is recognized as a very dangerous material, it can be handled without undue hazards if proper materials of construction are used and reasonable safety precautions are taken.

Nickel and Monel are by far the best general-purpose materials to use in the construction of apparatus for handling fluorine. However, where use of nickel and Monel is not possible, copper, brass, stainless steel or aluminium may be substituted. For gaskets, aluminium, tin, copper or lead may be used. For valve packing or gasketing, poly(tetrafluoroethylene) (Teflon) may be used, if well protected.

Lines and components permanently joined should be welded. Silver solder may be used on temporary apparatus or where its use is unavoidable. For permanent joints, where welding is impossible, threaded or flanged pipe fittings should be used. For frequently disconnected joints standard flare- or ferrule-type tubing fittings may be used.

Various commercially available valves have been tried in the fluorine bomb calorimetric work and found to be satisfactory. All of them had Monel bodies and nickel stems. For higher pressures valves packed with poly(tetrafluoroethylene) were employed. For lower pressures (up to 5000 mm) a diaphragm type of valve was used in which the diaphragm was sealed with an aluminium gasket. Another type of valve used where weight or space was limited and brass and silver solder could be tolerated was a small packless Monel valve with a nickel stem and brass bellows. The bomb valves were specially made. These valves, except for the K-Monel stems, were made mostly of nickel and were packed with a washer of poly(tetrafluoroethylene).

The pressure gauges used were all Bourdon tube gauges with welded Monel tubes.

The resistance of nickel and the other metals of construction to fluorine depends upon the formation of a protective fluoride film. Before any equipment, lines or components were put into service they were thoroughly cleansed of all foreign matter and prefluorinated cautiously until conditions were reached under which the system was to be operated. Prefluorination of the interior surfaces of the bomb was carried out under increasingly severe conditions until the bomb containing fluorine was held at 200°C for ten hours. A very adherent and coherent protective film of nickel fluoride was thus produced, sufficient to prevent significant further reaction of the nickel with fluorine.

An important precaution which has become standard practice in our laboratory is to expose the prefluorinated bomb only to dry atmospheres. This is done by handling the open bomb only in a dry box. In this way adsorption of moisture by the bomb or its contents is avoided.

The following safety precautions were used during bomb charging and discharging operations. Valves were operated by manually activated extensions passing through a 0.25 in. plastic or safety glass barricade. The entire apparatus was enclosed in a well-ventilated hood. The high pressure fluorine supply tank and bomb charging system were enclosed in 0.25 in. steel plate. To facilitate smoother and less hazardous reduction of pressure double valves and a ballast tank were employed.

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While manipulating the equipment the operator always wore a leather coat, leather gloves and a face shield.

After the bomb is placed in the calorimeter a hazard may arise from possible leakage of fluorine into the surrounding water bath. Experiments were carried out with deliberate leaks of up to 500 cm<sup>3</sup>/min through a small hole, which showed that the reaction occurred without sufficient violence to present a hazard to the operator.

### THE BOMB AND FLUORINE HANDLING APPARATUS

The bomb used for the calorimetric experiments is dimensionally identical with the bombs used in this laboratory for oxygen bomb calorimetry<sup>17</sup>. The body and cap of the bomb are fabricated of pure nickel and are sealed with a 0.06 in.-thick soft aluminium gasket. The valve housings of the bomb are made of nickel and screwed into the bomb cap, the seal being effected with a lead gasket. The stem of the valve is made of K-Monel and sealed with a washer of poly(tetrafluoroethylene).

To contain the sample in the bomb before and during the combustion reaction is one of the more formidable problems of fluorine bomb calorimetry. Various arrangements of sample supports and electrodes within the bomb have been employed.

The samples to be studied can be classified according to the type of container or support that is required as follows:

- (1) those that do not undergo significant spontaneous reaction with fluorine and can be fabricated into a shape that can be suspended in the bomb;
- (2) those that do not undergo significant spontaneous reaction but require a support such as a crucible;
- (3) those that react spontaneously with fluorine and require isolation from the fluorine before the main period.

The easiest substances to handle are those of the first class, in which the sample is in the form of a wire or sheet suspended in the bomb. For combustions of molybdenum, an example of this type, the sample was 0.005 in. thick sheet and was suspended from an insulated rod by a short length of molybdenum wire 0.005 in. in diameter. Two nickel electrodes were also provided between which was attached a molybdenum ignition wire which had been threaded through holes at the bottom of the sample. Other experiments were carried out in which the sample was in the form of a suspended coiled wire.

Samples of the second class require a crucible or disc support. For these samples the most promising technique that has been tried is a nickel crucible lined with a stable fluoride, preferably the fluoride of the metal involved in the reaction. Nickel crucibles are attacked in combustions of many substances, but may be useful for a limited number of reactions.

Samples of the third class require isolation of the sample from fluorine before intentional ignition. One technique for this, on which some experimentation has been done, is the enclosing of the sample in a thin weighed metal foil of cadmium, indium, lead, tin or zinc. The foil is sealed by either welding or crimping. Another possible technique is the

use of quartz ampoules in much the same way as they are used for various organic compounds.

With whatever sample support method is used, ignition of the sample is accomplished by the passage of an electric current through an ignition wire close to or touching the sample. When metal fluorinations are being studied the same metal is generally used for the ignition wire. Because of the reactivity of fluorine most ignition wires, regardless of the metal used, will ignite and break the circuit. Consequently, a current integrating device, similar to that described by Pilcher and Sutton<sup>18</sup>, is used to measure the ignition energy.

The bomb charging equipment consists of a fluorine supply tank, a sodium fluoride trap to remove traces of hydrogen fluoride, a ballast tank, and appropriate valves, gauges, and lines with connections to the bomb, an inert gas supply and a vacuum system. The sodium fluoride trap is easily regenerated by heating *in situ* at 250–300°C while purging with dry nitrogen.

The bomb discharging equipment consists of a series of cold traps with appropriate connections to the bomb, a Booth–Cromer pressure gauge<sup>19</sup>, an infra-red spectrum cell, an inert-gas supply, and the vacuum system. The vacuum pump is protected from fluorine by a large, dry soda-lime trap. The cold traps are provided to permit trap-to-trap distillation of the product gases to aid in their identification by vapour pressure measurements or by spectral analysis. The infra-red cells were made of nickel with windows of barium fluoride, calcium fluoride, silver chloride, or polyethylene.

### THE CALORIMETER AND ITS CALIBRATION

A bomb calorimetric system similar to that described by Hubbard, Katz and Waddington<sup>17</sup> was employed, the calorimetric observations being taken in the usual manner. The calibration of the system was carried out by combustions of benzoic acid in the bomb according to standard practice. However, since the electrodes, sample supports and other internal fixtures are different in the calibration and combustion experiments, the "contents of the bomb" for which heat capacity corrections are made include all such internal components.

#### Fluorine

Three grades of fluorine have been used in our work:

- (1) a high-purity (99–99.5 per cent) commercial grade, no longer available;
- (2) commercially available fluorine of modest purity (97.5–98.5 per cent); and
- (3) fluorine fractionated at liquid nitrogen temperatures, of which the best fraction has an impurity content of less than 0.1 per cent.

### EXPERIMENTAL PROCEDURE

The experimental procedure used in carrying out an experiment in fluorine bomb calorimetry involves very little that has not been either inferred or discussed previously. After the sample is placed in the bomb in one of the various sample-support arrangements, the bomb is closed,

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connected to the charging apparatus and evacuated. Fluorine from the storage tank is allowed to enter the ballast tank until a pressure somewhat greater than the desired charging pressure is reached. The valves to the storage tank are then closed, the bomb charged to pressure, the connecting lines are broken, and the bomb is placed in the calorimeter where the calorimetric measurements are carried out in the usual manner.

After the experiment the bomb is connected to the discharging apparatus and, from this point on, the procedure varies with the particular reaction carried out and the analytical tests necessary. For gaseous reaction products tests are carried out in the apparatus previously discussed. For solid reaction products the usual identification by X-ray diffraction techniques and chemical analyses may be carried out on the bomb residue.

The standard state corrections are made according to the procedure of Hubbard, Scott and Waddington<sup>20</sup>. However, the calculations are far less complicated for combustions in fluorine since no water is added to the bomb. The equation of state<sup>21</sup>,  $PV = RT - 0.0196 P l. atm.$ , applies to fluorine gas;  $(\partial E/\partial P)_T$  for fluorine at 25°C is  $-1.78 \text{ cal mole}^{-1} \text{ atm}^{-1}$ .

## CONCLUSION

The fluorine bomb calorimetric techniques which have been presented in this paper were developed from many exploratory experiments with approximately 25 metallic or metalloid elements and 15 inorganic compounds representing their combinations. The reactions of three-quarters of these substances with fluorine immediately appeared to be suitable for calorimetric study, being rapid, complete, and well defined. With the remaining substances the reactions, under the conditions used in these brief explorations, were not self-sustaining or led to a mixture of products.

Although fluorine bomb calorimetry is still in its infancy and many of the techniques used have yet to stand the test of time, it can be concluded with confidence that (1) fluorine bomb calorimetry can be carried out without undue hazard to the investigator; (2) suitable materials of construction can be found for the bomb and auxiliary apparatus, and (3) fluorine bomb calorimetry will be very useful in the determination of heats of formation of many fluorides, practically the entire measured energy being due to the heat of formation of the compound.

It is quite apparent that the formation of fluorides by the fluorine bomb combustion of many elements and inorganic compounds will rapidly become a useful tool for thermochemical studies of modern calorimetric precision.

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