Fluorine combustion calorimetry: progress in recent years and possibilities of further development

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Abstract - The present state of fluorine bomb calorimetry is discussed. A survey and analysis of the results obtained by this method in the past decade are given. Combustion of some substances in fluorine (e.g. dense modifications of BN) is a very difficult task. Questions dealing with the determination of the $\Delta_f H°$ values of dense modifications of boron nitride are considered. On the basis of the thermochemical data for these compounds a more precise pressure/temperature phase diagram of BN was obtained. Apparatus and procedures permitting measurements of the enthalpies of fluorination reactions with XeF_2(cr) have been developed. This is a new approach to fluorine bomb calorimetry.
The problem of the selection of test substances for fluorine combustion calorimetry is discussed. Germanium and boron appear to be the best new candidates for such substances. Ways to further develop fluorine combustion calorimetry are considered. This method is useful especially for determination of the $\Delta_f H°$-values of lower fluorides and some refractory compounds having variable compositions (mainly borides, silicides,chalcogenides, and so on).

INTRODUCTION

Fluorine bomb calorimetry (FBC) occupies a special place among modern thermochemical methods. This is so not only because it opens a new, independent way of determining enthalpies of formation of various compounds. A much more essential implication is that, owing to the exceptionally high reactivity of fluorine, this method permits the inclusion in the sphere of research compounds that could not formerly be studied by any of the conventional methods. Today, we have at our disposal extensive experimental data on calorimetric studies of fluorination reactions wherein elemental fluorine is mainly used as the oxidant. The first reviews in this area (ref. 1,2) were published about 13 years ago. The present work deals with the progress in fluorine bomb calorimetry since the publication of those reviews. A survey and analysis of the results obtained by the FBC-method beginning with 1978-1979 are given. Details of the determination of the $\Delta_f H°$-values for dense modifications of boron nitride are discussed as an example of the solution of difficult problems as a results the development of FBC-experimental techniques.

The search for new effective fluorinating agents for calorimetry is an urgent task. Leonidov et al. (ref. 3-5) have described a technique where fluorination is achieved by using crystalline xenon difluoride as oxidant.

The need for test substances for FBC was discussed in ref. 1. At the present time, new recommendations can be made for such substances. The direction of further development of FBC and new materials that could be studied by this method are considered.

The laboratory abbreviations used in this work are as follows:
ANL- Argonne National Laboratory, Argonne, Illinois, U.S.A. ;
IHT- Institute for High Temperatures, Academy of Sciences of the USSR, Moscow, USSR ;
IGIC-N.S.Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, USSR ;
KU -Kyoto University, Kyoto, Japan ;
LF -Laboratorium für Festkörperphysik ETH, Zürich, Switzerland ;
NERF-Netherlands Energy Research Foundation ECN, Petten, Netherlands.

SURVEY OF RESULTS OBTAINED BY THE FLUORINE BOMB CALORIMETRIC METHOD IN RECENT YEARS

Values for enthalpies of formation that have been determined by combustions in fluorine in the past decade have been listed in Tables 1 and 2. Listed in Table 1 are values that have been determined by combustion of some elements in fluorine. Listed in Table 2 are other values determined by the FBC method. Apart from the data and references included in Table 2, there is further work (ref. 43) devoted to the determination of enthalpies of formation of UF_3 (cr) and UF_4 (cr) by the FBC method; however measured values are not given in the text.

TABLE 1. Enthalpies of formation at 298.15 K of binary fluorides determined in the past decade by direct combination of the elements

Element reacted	Fluoride formed	$\Delta_f H°$, kJ/mol	Laboratory (Note a), reference
La(cr)	LaF_3(cr)	-1699.5±2.0	ANL (ref. 6)
Pr(cr)	PrF_3(cr)	-1689.1±2.6	ANL (ref. 6)
Nd(cr)	NdF_3(cr)	-1660.6±4.9	KU (ref. 7)
Sm(cr)	SmF_3(cr)	-1679.4±1.9 -1669.0±4.6	ANL (ref. 6) KU (ref. 8)
Gd(cr)	GdF_3(cr)	-1699 ± 7	KU (ref. 9)
Dy(cr)	DyF_3(cr)	-1699.3±2.3 -1678 ± 8	ANL (ref. 6) KU (ref. 10)
Ho(cr)	HoF_3(cr)	-1692.0±1.9 -1698 ± 6	ANL (ref. 6) KU (ref. 11)
Er(cr)	ErF_3(cr)	-1697.8±2.3 -1669 ± 6	ANL (ref. 6) KU (ref. 12)
Tm(cr)	TmF_3(cr)	-1693,6±1.9 -1656 ± 7	ANL (ref. 6) KU (ref. 13)
Yb(cr)	YbF_3(cr)	-1570 ± 7	KU (ref. 9)
U(cr)	UF_6(cr)	-2197.7±1.8	ANL (ref. 14)
Si(cr)	SiF_4(g)	-1615.8±0.5	ANL (ref. 15)
Sb(cr)	SbF_5(l)	-1328.0±0.9	ANL (ref. 16)
S (cr)	SF_6(g)	-1221.2±0.4	ANL (ref. 17)
Fe(cr)	FeF_3(cr)	-990.8 ±2.1	IGIC(ref. 18)
Ni(cr)	NiF_2(cr)	-989.6 ±2.2 -656.9 ±2.5	ANL (ref. 19) IHT,IGIC(ref.20)

Note a: The key to laboratory abbreviations is given in the introduction.

TABLE 2. Enthalpies of formation at 298.15 K of compounds
other than binary fluorides determined in the
past decade by fluorine combustion calorimetry

Compound	$\Delta_f H°$, kJ/mol	Laboratory (see footnote of the Table 1), reference
$UO_{2.000}$ (cr)	-1085.1±2.5	ANL (ref. 21)
$UO_{2.023}$ (cr)	-1090.2±2.8	ANL (ref. 21)
K_2S (cr)	- 406.2±2.9	ANL (ref. 22)
$CuFeS_2$ (cr)	- 173.1±8.7	ANL (ref. 23)
TmS (cr)	- 460 ± 13	LF (ref. 24)
YbS (cr)	- 427 ± 13	LF (ref. 24)
$US_{1.992}$ (cr)	- 519.7± 8.0	ANL (ref. 25)
GeS_2 (cr)	- 124.7± 2.6	ANL (ref. 26)
TiS_2 (cr)	- 410.3± 2.4	ANL (ref. 27)
As_2S_3 (glass)	- 69.6± 4.2	ANL (ref. 28)
As_4S_4 (cr,β)	- 134.6± 6.7	ANL (ref. 28)
Sb_2S_3 (cr)	- 141.8± 4.1	ANL (ref. 16)
$VS_{1.043}$ (cr)	- 230.3± 2.2	ANL (ref. 29)
WS_2 (cr)	- 240.8± 3.1	ANL (ref. 30)
TmSe (cr)	- 351 ± 13	LF (ref. 24)
YbSe (cr)	- 343 ± 17	LF (ref. 24)
GeSe (cr)	- 51.4± 1.5	ANL (ref. 31)
$GeSe_2$ (cr)	- 102.2± 2.6	ANL (ref. 32)
$MoSe_2$ (cr)	- 234.2± 3.3	ANL (ref. 33)
Mo_6Se_6 (cr)	- 477.8±10	ANL (ref. 33)
WSe_2 (cr)	- 185.3± 5.5	ANL (ref. 34)
TmTe (cr)	- 318 ± 17	LF (ref. 24)
YbTe (cr)	- 310 ± 17	LF (ref. 24)
$ZrTe_2$ (cr)	- 294.1 ± 6.7	ANL (ref. 35)
$MoTe_2$ (cr)	- 84.2 ± 4.6	ANL (ref. 36)
$UN_{0.997}$ (cr)	- 290.3 ± 2.2	ANL,NERF (ref.37)
$UN_{1.466}$ (cr,β)	- 362.9 ± 2.3	ANL,NERF (ref.37)
$UN_{1.606}$ (cr,α)	- 382.2 ± 2.3	ANL,NERF (ref.37)
$UN_{1.674}$ (cr,α)	- 391.5 ± 2.3	ANL,NERF (ref.37)
BN (cr,α,hex.)	- 250.6 ± 2.1	IHT (ref. 38)
BN (cr,β,cub.)	- 266.8 ± 2.2	IHT (ref. 39)
BN (cr,γ,wurz.)	- 263.2 ± 2.3	IHT (ref. 40)
MoF_3 (cr)	- 957.3 ± 3.5	IHT,IGIC (see text)
$UPd_{3.099}$ (cr)	- 536.7 ±30.8	ANL (ref. 41)
$S_2N^+AsF_6^-$ (cr)	-1413.8 ± 1.9	ANL (ref. 42)

The use of fluorine in calorimetry has provided a direct way of
measuring enthalpies of formation of the inorganic fluorides. In
recent years, the data for the higher fluorides of fourteen metals and
two non-metals were obtained. This information (together with the
$\Delta_f H°$-values for fluorides of other elements previously determined by
the same method) has created a sufficient base for determining by FBC
the enthalpies of formation of different inorganic compounds. Below,
the classes and number (in brackets) of the compounds are listed which
have been investigated by the FBC-method in the past 12-13 years:
higher fluorides (16), oxides (2), sulfides (12), selenides (7), tel-
lurides (4), nitrides (7),lower fluorides (3),and other compounds (2).
Many of these compounds are rather hard to investigate by conventional
thermochemical methods. Combustion of some substances in fluorine
(such as rare-earth metals, U, Fe, Ni, $UO_{2.000}$, K_2S, $US_{1.992}$, $VS_{1.043}$,
and dense modifications of BN) was a very difficult task for investi-
gators. Separate substances (Fe, Ni, dense modifications of BN,

$UPd_{3.099}$) are very fluorine-resistant; their combustion caused parti-
cular difficulties. Proper selection of the optimum conditions has
ensured a high degree of combustion of these compounds. Specific prob-
lems attending the use of fluorine in calorimetry require that distor-
tion of the experimental results be avoided due to thermal side
effects. Special precautions have been taken to eliminate or to mini-
mize these effects in each case. Some of the compounds investigated
were nonstoichiometric (some chalcogenides of metals, uranium compo-
unds). Problems of the investigation of such substances by the FBC -
method and the relationship between «x» and $\Delta_f H°(AB_x)$ were discussed
in ref. 44. Values of the enthalpies of formation of rare-earth metal
trifluorides determined by investigators at ANL are more reliable than
the values of the same quantities obtained by Kim et al. (KU) (see
Table 1). Their result for $\Delta_f H°(ErF_3$, cr, 298.15 K) (ref. 12) is 25
kJ/mol more positive than the ANL result. We feel that their value for
ErF_3 must be too positive when one considers that the usual difference
between enthalpies of formation of halides of adjacent members of the
isostructural rare-earth series is less than 10 kJ/mol.

For a number of years the thermochemical group at ANL has been using
the FBC-method to determine the $\Delta_f H°$-values of high-temperature and
refractory materials. In resent times, these studies have tended to
concentrate on chalcogenides of metals and non-metals, many of which
are important in the new technologies (see Table 2). Soviet investiga-
tors at IHT and IGIC have carried out the determination of the enthal-
py of formation of MoF_3(c) by the FBC method. This result will be pub-
lished in Technical papers of the International Symposium on Calori-
metry and Chemical Thermodynamics (Moscow, 23-28 June, 1991). O'Hare
et al. (ref. 42) carried out for the first time the determination of
the enthalpy of the formation of a quaternary compound (S_2NAsF_6) by
the FBC-method. The results obtained by investigators at LF have, as a
rule, comparatively low accuracy.

DETERMINATION OF THE ENTHALPIES OF FORMATION OF DENSE MODIFICATIONS OF BORON NITRIDE

Three modifications of boron nitride are known: 1) α-BN with a hexa-
gonal graphitic structure; 2) β-BN with a cubic, dense-packed structu-
re of the sphalerite type; 3) γ-BN with a hexagonal dense-packed
structure of the würzite type. Since no experimental data on enthal-
pies of formation of dense modifications of BN had been published
previously, Leonidov et al. (IHT) attempted to use fluorine bomb calo-
rimery to determine these values (refs. 39, 40). It was shown that the
dense modifications of BN didn't react with fluorine at normal tempe-
rature, even at rather high pressures of oxidant. Success was achieved
in initiation of the studied reactions in a calorimetric bomb by
adding a small amount of sulfur to the sample being burned. The degree
of combustion of the β-BN and γ-BN samples in fluorine was greatly
increased by compacting the samples. Special attention was given to
the precise determination of free and bonded carbon impurities in the
BN samples, since these impurities (in particular carbon in the form
of B_4C) exert the most noticeable effect on the determined energies of
fluorination of the BN samples. The procedure for precise determina-
tion of C_{free} and C_{bond} in the BN samples was based on successive
removal of C and B_4C from the samples in flowing oxygen (at 1173 and
1473 K, respectively) and determining the amount of CO_2 thus formed.

At the same time, a technique was developed with the help of which
the α-BN and β-BN samples were completely freed from such impurities
as C_{free}, C_{bond} , and B_2O_3: after removal of carbon impurities from
the samples, diboron trioxide was removed by heating the sample in
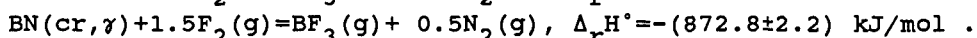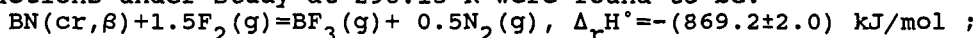vacuum at 1573 K.

The purified β-BN contained (in mass per cent): Si,0.03; Al,0.09; Mg,$6 \cdot 10^{-3}$; Ca,0.01; Fe,$2 \cdot 10^{-3}$; and O < 0.01. According to X-ray analysis, the content of α-BN in the sample was about 2.4 per cent. The sample of γ-BN contained the following impurities (in mass per cent): C,0.14; C_{bond},0.15; B_2O_3,0.1; Si,$3 \cdot 10^{-3}$; Cu,$1 \cdot 10^{-3}$; Mg,$5 \cdot 10^{-2}$; Al,$2 \cdot 10^{-3}$; Ti,$1 \cdot 10^{-2}$; Mn,$1 \cdot 10^{-3}$; Fe,$1 \cdot 10^{-2}$; α-BN < 0.05. The sample had a hexagonal crystal lattice with constants a=0.255 nm and c=0.420 nm; the density of the sample was 3.49 g/cm^3.

Initial fluorine was of a high purity grade and contained (in vol. per cent): F_2,99.6; N_2,0.2; O_2,0.1; and CO_2,0.1. As an auxiliary substance, high purity grade (99.97 mass per sent) sulfur was used.
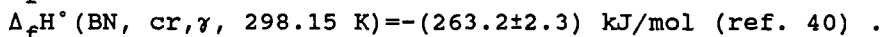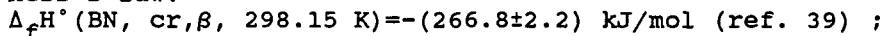
In these works (refs. 39,40) a two-compartment Monel bomb was used. The following experimental procedure was worked out. A pellet-shaped sample of boron nitride (0.15-0.20 g) was placed on a nickel disc of special construction in the bomb. An optimum amount of sulfur required for firing the sample (20-35 mg) was determined experimentally. The initial fluorine pressure was 350 kPa. This procedure made it possible to attain a high degree of combustion of the BN samples (99.0-99.8 per cent). Spectroscopic analysis of solid combustion products showed that after the experiments there was only a residue of the initial boron nitride on the nickel disc and in the case of γ-BN a small amount of NiF_2 was also detected which had been formed as a side product due to fluorination of the surface of the nickel disc. The total amounts of unburned boron nitride and NiF_2 were determined as the difference between the masses of the disc with the residue and the empty disc. The mass of nickel reacted with fluorine did not exceed 0.2 mg and was determined as the difference between the initial mass of the disc and its mass after the removal of the solid residue. The amount of boron nitride participating in the reaction was deduced from the mass of the unburned sample.

Spectroscopic analysis of the gaseous combustion products in the experiments with β-BN separated from excess fluorine revealed the presence of BF_3 and SF_6 only. Gas-chromatographic analysis of the products of fluorination of γ-BN showed that neither NF_3 nor any gaseous boron compounds (except BF_3) were present.

After application of the necessary corrections, the enthalpies of the reactions under study at 298.15 K were found to be:

$$BN(cr,\beta)+1.5F_2(g)=BF_3(g)+ 0.5N_2(g), \quad \Delta_r H^\circ=-(869.2 \pm 2.0) \text{ kJ/mol} ;$$

$$BN(cr,\gamma)+1.5F_2(g)=BF_3(g)+ 0.5N_2(g), \quad \Delta_r H^\circ=-(872.8 \pm 2.2) \text{ kJ/mol} .$$

On the basis of these values, the enthalpies of formation were calculated by Hess's law:

$$\Delta_f H^\circ (BN, cr,\beta, 298.15 \text{ K})=-(266.8 \pm 2.2) \text{ kJ/mol (ref. 39)} ;$$

$$\Delta_f H^\circ (BN, cr,\gamma, 298.15 \text{ K})=-(263.2 \pm 2.3) \text{ kJ/mol (ref. 40)} .$$
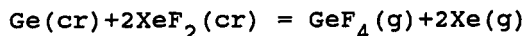
The calculated $\Delta_f H^\circ$ (298.15K) values for the different BN modifications can be used to delineate the P,T-phase diagram of boron nitride. Leonidov et al. (refs. 38,45) have calculated the temperature dependence of the Gibbs energy $(\Delta_r G_T^\circ=f(T))$ for the reaction BN (cr,α) = =BN (cr,β). It has been shown that at P=101.3 kPa, within the temperature range from 0 to 1570 K, cubic boron nitride is the stable modification rather than graphitic BN as was assumed earlier. This fact changes traditional ideas about the polymorphism of boron nitride.

CRYSTALLINE XENON DIFLUORIDE — A NEW OXIDANT FOR CALORIMETRY

A group of Soviet investigators at IHT has developed apparatus and procedures permitting measurements (in a one-compartment bomb) of

enthalpy of fluorination reactions with the participation of crystal-
line xenon difluoride. It is a new variety of FBC-method. The bomb,
made of Monel, contained a special device which permitted, at a given
moment, contact of xenon difluoride and the substance under study,held
in different containers (upper and lower Monel crucibles) before the
reaction.Initially the xenon difluoride was kept in the upper crucible
and the substance under study in the lower crucible. A thin platinum
wire kept the upper crucible in an upright position. To initiate spon-
taneous reaction, the platinum wire was burned through, whereby the
upper crucible toppled over, spilling the xenon difluoride into the
lower crucible . The reaction studied with the help of this technique
was:

$$Ge(cr)+2XeF_2(cr) = GeF_4(g)+2Xe(g)$$

yielding -(163.2±1.3) kJ/mol for the enthalpy of formation of cristal-
line xenon difluoride (ref. 3).

For combustion of holmium (ref. 4) and dysprosium (ref. 5) in XeF_2(cr)
a new approach was used. A cylindrical Monel vessel filled with the
XeF_2 powder served as reactor. A rare-earth metal sample (in the form
of a thin plate) was placed on the XeF_2 layer.An additional XeF_2 layer
was spread on the metal sample surface. The method used to initiate
the fluorination reactions consisted in passing an electrical current
through the same metal strip being in contact with the rare-earth
metal sample under study.The enthalpy of formation values,at 298.15 K,
for crystalline holmium and dysprosium trifluorides calculated from
these experimental results are -(1700.4±4.2) kJ/mol (ref. 4) and
-(1685.7±3.6) kJ/mol (ref. 5), respectively.

Crystalline xenon difluoride is recommended as a new effective
fluorine-containing oxidant for calorimetric investigations.

TEST SUBSTANCES FOR FLUORINE BOMB CALORIMETRY

To confirm the reliability of the data obtained and the absence of
systematic errors in measurements performed by the fluorine calorimet-
ric technique one has to use test substances. Earlier (see (refs 1,2))
tungsten and sulfur were proposed as the first test substances for
fluorine calorimetry. Tungsten can be used in either one- or two- com-
partment calorimetric bombs; sulfur can be used only in a two-compart-
ment bomb. Today, we have at our disposal some other substances whose
energies of combustion in fluorine have been measured rather accurate-
ly in various laboratories.As for their properties germanium and boron
appear to be the best new candidates for such substances. There are
three and four consistent values of the standard energies of combus-
tion in fluorine for germanium and boron respectively(refs 1,2). Since
Ge spontaneously reacts with fluorine,it can serve as a test substance
when conducting experiments in a two-compartment bomb. Boron is a
suitable test substance for studying the reaction with fluorine both
in one-compartment and two-compartment calorimetric bombs.

DISCUSSION

The enthalpies of formation of over 50 compounds belonging to diffe-
rent classes have been determined by the FBC-method in the past 12-13
years. This method has been developed to a high degree of perfection
such that the accuracy of results (which in a many cases is from 0,03
to 0,2 per cent) is now comparable with that of the results obtained
by the oxygen bomb calorimetric method. The extreme reactivity of flu-
orine makes it possible to study compounds not amenable to oxygen com-
bustion calorimetry or any of the conventional calorimetric methods.
Examples of such compounds are dense modifications of boron nitride,
uranium nitrides, $UPd_{3.099}$, some chalcogenides,fluorides of rare-earth
metals, iron, and nickel.In many cases, when the overall uncertainties
of the results are large compared with the usual uncertainties, it is

due to uncertainties in analyses performed to define the initial samples, the products of reaction under study, or the state of combination of impurities, rather than uncertainties in the calorimetric method.

It is useful to discuss further developments of fluorine combustion calorimetry. A group of Soviet investigators at IHT is going in the future to continue the determination of $\Delta_f H°$-values of lower fluorides and some variable-composition compounds, mainly borides and silicides of transitional metals, by the FBC method. This method is useful especially for the investigation of such compounds because one of the products of the fluorination reactions is a gaseous substance (boron trifluoride or silicon tetrafluoride). In the U.S.A., the thermochemical investigations of chalcogenides of metals and non-metals having many technical applications will be continued. There is the programme of the determination of the enthalpies of formation of some vitreous chalcogenides begun recently at the National Institute of Standards and Technology (U.S.A.). The FBC-method will be used for this purpose. It is expected that the new data obtained will provide bench-mark information for the study of the amorphous state and for characterization of the interatomic forces which have been postulated to govern the enthalpy changes associated with vitreous-to-crystal transitions. It is proposed also to use the FBC-method for the determination of the enthalpies of formation of compounds of more than three elements.

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