

THE CALORIMETRY OF COMBUSTIONS AND RELATED REACTIONS: INORGANIC REACTIONS†

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INTRODUCTION

The modern combustion calorimeter is an instrument capable of precise measurements. In the combustion of organic compounds it is possible to achieve a precision of 1 part in 10,000 or 0.01 per cent. This is commonly done in standards laboratories where certified benzoic acid is prepared. A precision of 0.03 per cent has been attained by many experimenters, and a precision of 0.1 per cent is common. However, when the heats of combustion of the elements§ are considered, see *Table 1*, it is found that only for carbon has the heat of combustion been measured with a precision close to 0.01 per cent. If the precision is lowered to 0.03 per cent then sulphur may be added to the list. There are 16 additional elements whose heats of combustion have been measured with a precision between 0.03 and 0.1 per cent. Since the heats of combustion of 54 of the elements under consideration have been measured, this means that for 36 of them the precision is poorer than 0.1 per cent.

Of these 18 elements whose heats of combustion have been measured with a precision of 0.1 per cent or better, only for aluminium, carbon, magnesium, molybdenum, sulphur, and tantalum are there measurements from at least two laboratories, each with a precision of 0.1 per cent or better, agreeing within 0.1 per cent. This seems to be a rather poor showing in view of the capability of the method. Therefore, a consideration of the sources of error in a combustion calorimetry experiment seems appropriate.

SOURCES OF ERROR IN COMBUSTION CALORIMETRY

There are, of course, the errors involved in determining the corrected temperature rise and in determining the energy equivalent. These have been thoroughly discussed¹ and are mentioned here only for completeness. However, it is worth remarking that the use of certified benzoic acid as a standard substance for the determination of the energy equivalent has provided a means for tying together the results from combustion calorimeters all over the world. This has been of great benefit to combustion calorimetry.

The determination of the ignition energy has been given considerable attention in recent years. A method using a current integrator is discussed in

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§ The heat of formation of the oxide formed in the combustion is used as a measure of the heat of combustion. This allows comparison of results between combustion calorimetry and other methods of determining heats of formation. The heats of formation of the oxides of hydrogen, nitrogen, and the halogens are not considered because they are not measured in a bomb calorimeter.

the paper by Mackle and O'Hare contributed to this Session². The use of proper methods should make any error from this source negligible.

The oxygen must be purified to remove any combustible contaminants. Its pressure should be measured and the presence of any non-combustible contaminants, such as argon, should be known so that its initial state will be known. The bomb should be flushed to remove nitrogen unless nitrogen oxides can be tolerated.

There is no satisfactory substitute for high purity in the sample. In actual practice, however, the calorimetrist is usually dependent on someone else for his source of supply. Even if he purifies his materials himself, he has to strike a compromise between the highest possible purity and the time available for doing the purification. The presence of impurities is probably the source of most of the uncertainty in the majority of these experiments.

The sample should be analysed for everything that could be present. The impurities in the starting materials from which the sample was made, and the method used in making it, can serve as guides. In addition it should be remembered that oxygen, carbon, hydrogen, and nitrogen are ever present contaminants. The uncertainties in the analyses will, of course, show up as uncertainties in the correction for impurities, so they should be determined or estimated.

The presence of impurities causes uncertainties in the results of a combustion experiment in many ways besides the uncertainty in the correction for the heat evolved by their combustion. They may not be uniformly distributed, thus causing scatter in the results. Their chemical state may not be known, or, if it is known, the heat of formation of that chemical state may not be known. They also give rise to side reactions if the oxide formed by combustion of the impurity reacts with the main oxide or dissolves in it.

There are other sources of side reactions. If the fuse is not of the same material as the sample, then its oxide may react with the main oxide. Wires of most metals are now available and the best fuse is a wire of the same material as the sample, if the sample is a metal. The oxide formed from the combustion is very hot, usually molten. It must be contained on a material with which it will not react. Usually the best material is some more of the same oxide. If a different kind of container is used the effect may be small or large. Examples are plutonium burned on thorium oxide or plutonium oxide, where the difference is less than 1 per cent³ and scandium burned on aluminium oxide⁴ or scandium oxide⁵ where the difference is about 2 per cent. High precision is not evidence for lack of reaction with the container^{4, 5}.

Account must be taken of the possibility of a mixture of oxides being formed, as for vanadium⁶. Or the stoichiometry may be off from the desired value, as is sometimes the case for uranium⁷. The stoichiometry of the refractory oxides which have been quenched from the melting point has not been sufficiently studied and it is quite possible that significant errors can arise from this cause in the determination of the heats of formation of such oxides. Therefore, the products of the reaction must be characterized.

After the reaction is over a determination must be made of the amount of reaction. This may simply involve collecting the combustion products and weighing them, or it may involve more complicated methods of analysis depending on the substance in question.

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Some substances are reactive with oxygen at 25°. It is, therefore, necessary to make a preliminary test to see if reaction with oxygen occurs under the bomb conditions before ignition.

Finally, the energy having been measured and the reaction to which it applies having been determined, everything must be referred to standard states so that a thermodynamically meaningful statement can be made about what has been done⁸. For solid materials, account should be taken of strains, defects, and other imperfections. For the starting material such imperfections can probably be eliminated. For the combustion product it may not be possible. If the combustion product is a smoke or otherwise finely divided so that it has a large surface area, surface energy may be important. In this case, also, significant quantities of gas may be adsorbed and the heat of adsorption might be significant.

CONFIRMATION OF RESULTS

The question of confirmation of results has been mentioned briefly. There are two fundamentally different kinds of confirmation. The heat of combustion may be confirmed by another investigator using a different calorimeter and a different sample. This is a necessary kind of confirmation. However, it does not eliminate the possibility of systematic errors which may exist in the nature of the experiment itself such as, for example, deviations of the combustion products from the expected stoichiometry. A more fundamental kind of confirmation is that in which the heat of formation obtained by combustion calorimetry is found to be in agreement with the heat of formation as determined by a different type of experiment, *e.g.*, solution calorimetry or equilibrium measurements. This type of confirmation is well illustrated for iron where four kinds of measurements give agreement as to the heat of formation of ferric oxide within 0.15 per cent (see *Table 1*).

THE COMBUSTION OF THE ELEMENTS

The foregoing remarks serve as an introduction to *Table 1* which is an attempt to show what has been done in the combustion calorimetry of the elements and the confirmation experiments where they are available. The columns on the left give, in order, the oxide, a selected value for its heat of formation as determined by combustion calorimetry, and the precision of the determination expressed in per cent. The columns on the right give similar information for the confirmation experiments. The combustion references are believed to be nearly complete. The solution references are not quite as complete as the combustion references. The references to equilibrium methods are not complete. Attention is called to the following points. For only one element, magnesium, has the heat of combustion been measured with a precision of 0.1 per cent or better and the value been confirmed to within 0.1 per cent by a different method, solution calorimetry, having a precision of 0.1 per cent or better. Even in this case there are other precise measurements of the heats of solution of magnesium and magnesium oxide which lead to a value of the heat of formation of magnesium oxide differing from the combustion value by more than 0.1 per cent⁹⁻¹². For 30 of the elements the measurements and confirmation are both better than 0.5 per cent. For 19 elements the

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Table 1. Heats of formation of oxides determined by oxygen bomb calorimetry of the elements

Selected value			Confirmatory experiments			
Oxide	$-\Delta H^\circ_{f298}$ (kcal/mole)	Precision (%)	Method	$-\Delta H^\circ_{f298}$ (kcal/mole)	Precision (%)	Difference (%)
Al ₂ O ₃	400.48 ⁴³	0.06	Combustion	400.29 ⁴⁴	0.08	0.05
Sb ₂ O ₃	169.4 ⁴⁵	0.41	Dissociation of oxide	167.4 ⁴⁶		1.2
Sb ₂ O ₄	216.9 ⁴⁵	0.51				
As ₂ O ₃	154.7 ⁴⁷		e.m.f.	157.0 ⁴⁸		1.5
BaO	139.06 ⁴⁹	0.50	Solution	134.0 ⁵⁰		3.7
BeO	143.1 ⁵¹	0.07	Combustion	145.3 ⁵²	0.12	1.5
			e.m.f.	140.9 ⁵³		1.6
			Solution	140.15 ⁵⁴		2.1
Bi ₂ O ₃	137.16 ⁵⁵	0.22	Solution	137.8 ⁵⁶		0.47
B ₂ O ₃ (amorph)	299.74 ²³	0.13	Combustion	298.7 ⁵⁷	0.60	0.35
			Diborane reactions	300.98 ⁵⁸	0.24	0.41
CdO	61.2 ⁵⁹	0.33	Solution	61.04 ⁶⁰		0.26
			e.m.f.	62.15 ⁶¹		1.4
CaO	151.79 ⁶²	0.13	Combustion	62.36 ⁶⁰	0.40	1.9
			Solution	151.9 ⁶³		0.07
CO ₂	94.052 ⁶⁵	0.011	Combustion	153 ⁶⁴	1.0	0.8
			Combustion	94.065 ⁶⁶	0.014	0.014
			Combustion	94.040 ⁶⁷	0.013	0.013
			Combustion	94.029 ⁶⁸	0.028	0.025
CeO ₂	260.18 ⁶⁹	0.13				
Cr ₂ O ₃	272.7 ⁵⁹	0.15	Combustion	271.7 ⁷⁰	0.67	0.63
			C-CO equilibrium	270.7 ⁷¹		0.74
CoO	57.1 ⁷²	0.52	Combustion	57.18 ⁷³	0.25	0.14
			H ₂ -H ₂ O equilibrium	57.23 ⁷⁴		0.23
			Combustion	57.5 ⁷⁵	0.35	0.71
Dy ₂ O ₃	445.84 ⁷⁶	0.21				
Er ₂ O ₃	453.59 ⁷⁷	0.10				
Gd ₂ O ₃	433.94 ⁷⁸	0.19				
Ga ₂ O ₃	258.6 ⁷⁹	0.15	Combustion	259 ⁸⁰	0.39	0.15
			Combustion	261.05 ⁴	0.12	0.97
GeO ₂	129.08 ⁸¹	0.10	Solution	129.2 ⁸²	1.6	0.10
			Combustion	128.6 ⁸³	0.39	0.39
			Combustion	271.5 ⁸⁵	1.0	2.0
HfO ₂	266.06 ⁸⁴	0.10				
Ho ₂ O ₃	449.55 ⁸⁶	0.26				
In ₂ O ₃	221.27 ⁸⁷	0.18	Combustion	222.5 ⁸⁸	0.27	0.54
			Combustion	220 ⁸⁹		0.58
			H ₂ -H ₂ O equilibrium	216.8 ⁹⁰		2.0
Fe ₃ O ₄	267.1 ⁹¹	0.19	CO-CO ₂ equilibrium	267.2 ⁹²		0.04
			Solution	266.76 ⁹³	0.08	0.13
			H ₂ -H ₂ O equilibrium	267.47 ⁹⁴		0.14
			Solution	428.03 ^{96, 97}	0.15	0.13
La ₂ O ₃	428.57 ⁹⁵	0.04				
Lu ₂ O ₃	449.8 ⁹⁸	0.40	Solution	143.84 ⁹⁹	0.03	0.10
MgO	143.70 ⁴⁴	0.08	Combustion	143.9 ¹⁰⁰	0.83	0.14
Mn ₃ O ₄	329.0 ¹⁰¹	0.22	Solution	331.65 ¹⁰²	0.08	0.81
			Combustion	336.5 ¹⁹	0.06	2.2
			Combustion	178.01 ¹⁰³	0.06	0.10
MoO ₃	178.16 ⁴³	0.06				
Nd ₂ O ₃	432.15 ¹⁰⁴	0.06				
NiO	57.3 ⁷²	0.18	Combustion	57.0 ⁷³		0.53
Nb ₂ O ₅	455.2 ¹⁰⁵	0.13	Combustion	455.1 ¹⁰⁶		0.02
			Combustion	454.8 ¹⁰⁷		0.09
P ₄ O ₁₀	713.2 ¹⁰⁸	0.14	Combustion in NO ₂	710 ²⁷		0.45
PuO ₂	252.80 ¹⁰⁹	0.15	Combustion	252.4 ¹¹⁰	0.40	0.15
Re ₂ O ₇	295.9 ¹⁴	0.68	Combustion	295 ¹¹²	1.0	0.30
RuO ₂	73 ¹¹³	1.4	Dissociation of oxide	71 ¹¹⁴		2.8
Sm ₂ O ₃	433.89 ¹¹⁵	0.11				

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Table 1—continued

Selected value			Confirmatory experiments			
Oxide	$-\Delta H_{f298}^{\circ}$ (kcal/mole)	Precision (%)	Method	$-\Delta H_{f298}^{\circ}$ (kcal/mole)	Precision (%)	Difference (%)
Sc ₂ O ₃	456.16 ⁵	0.11	Combustion	457.11 ⁶		0.2
SeO ₂	53.35 ¹¹⁷	0.06	Combustion	53.9 ¹¹⁸	0.6	1.0
SiO ₂	217.5 ²²	0.23	Combustion in F ₂	217.75 ¹¹⁹	0.15	0.11
			Combustion	219 ¹²⁰	0.47	0.70
			Combustion	216.3 ¹²¹		0.66
SrO	144.44 ⁴⁹	0.28	Solution	141.8 ⁵⁰		1.8
H ₂ SO ₄	212.17 ²⁴	0.03	Combustion	212.24 ²⁵	0.03	0.03
Ta ₂ O ₅	489.0 ¹⁰⁵	0.06	Combustion	489.3 ¹²²	0.08	0.06
Tc ₂ O ₇	266.1 ¹²³	1.0				
TeO ₂	76.9 ¹²⁴	1.6	e.m.f.	77.7 ¹²⁵		1.0
ThO ₂	293.2 ⁷	0.14	Combustion	292.6 ⁸⁵	0.48	0.20
			e.m.f.	294.1 ¹²⁶		0.31
Tm ₂ O ₃	451.4 ¹²⁷	0.07				
SnO ₂	138.82 ¹²⁸	0.06	CO-CO ₂ equilibrium	138.7 ¹²⁹	0.14	0.09
			Combustion	138.2 ¹³⁰		0.43
TiO ₂	225.8 ¹³¹	0.04	Combustion	225.52 ¹³²	0.10	0.13
			Combustion	226 ¹²⁰	0.44	0.10
WO ₃	201.46 ¹³³	0.10	Combustion	200.16 ¹³⁴	0.05	0.64
			H ₂ -H ₂ O equilibrium	202.8 ¹³⁵	0.69	0.64
U ₃ O ₈	852.77, ¹³⁶	0.19	Combustion	856.5 ¹¹⁰	0.36	0.44
V ₂ O ₅	370.6 ⁶	0.13	Combustion	370 ¹³⁷	0.27	0.16
			Solution	373 ¹³⁸		0.65
V ₂ O ₄	341.16 ⁶	0.10	Combustion	342 ¹⁶	0.58	0.25
Yb ₂ O ₃	433.68 ⁷⁶	0.12				
Y ₂ O ₃	455.45 ¹³⁹	0.12				
ZnO	83.36 ⁶⁰	0.25	Solution	83.27 ¹⁴⁰	0.06	0.11
			CO-CO ₂ equilibrium	82.83 ¹⁴¹		0.64
			e.m.f.	82.6 ¹⁴²		0.91
ZrO ₂	258.2 ⁵²	0.12	Combustion	258.1 ⁸⁵	0.23	0.04
			Combustion	258.8 ¹⁴³		0.23
			Combustion	261.5 ¹⁰⁵	0.08	1.3

measurements are better than 0.5 per cent but they have not been confirmed to 0.5 per cent. For 5 elements the measurement is uncertain by more than 0.5 per cent. Of these 5, for at least one of them, arsenic, the heat of combustion will probably be accurately measured in the near future¹³.

The heats of combustion of many elements have not yet been measured. Included among these are the alkali metals. There are problems involved with them because they react spontaneously with oxygen and they tend to form higher oxides. These problems will probably be solved by protecting the sample from the oxygen before ignition and by rotating bomb calorimetry, respectively, so that measurements on these elements should be possible. There are also four rare earth elements yet to be done. Preliminary work has been done on three of these, praseodymium, europium, and terbium³. The fourth, promethium, is scarce. Of the remaining elements it seems probable that results can be obtained on lead, osmium, thallium, neptunium, and perhaps copper. The others are either quite unreactive, scarce, or very radioactive. Protactinium has an isotope of half-life comparable to that of plutonium, so the problem with it is to obtain the element in sufficient quantity. Perhaps the use of a micro-calorimeter would make possible the determination of the heats of combustion

of protactinium, and even americium, curium, and radium. The design of microcalorimeters is an active field as is attested by the fact that two papers have been contributed to the Symposium on this subject^{2, 14}. Since appreciable amounts of berkelium and californium are expected to be available in a few years¹⁵, it does not seem impossible that combustion measurements will be made on them eventually.

HEATS OF COMBUSTION OF INORGANIC COMPOUNDS

In order to interpret the results from experiments on the heat of combustion of an inorganic compound it is necessary that the heats of formation of the oxides obtained in the combustion be known. This emphasizes the importance of knowing the heats of formation of the oxides.

The discussion given above about the sources of error in a combustion experiment applies, with appropriate modifications, to the combustion of compounds. Practically no complications are introduced if the compound is a lower oxide being oxidized to a higher oxide. *Table 2* gives a list of several oxides whose

Table 2. Oxides whose heats of combustion have been measured

<i>Selected value</i>			<i>Confirmatory experiments</i>			
<i>Oxide</i>	$-\Delta H^\circ_{1298}$ (kcal/mole)	<i>Precision</i> (%)	<i>Method</i>	$-\Delta H^\circ_{1298}$ (kcal/mole)	<i>Precision</i> (%)	<i>Difference</i> (%)
Ce ₂ O ₃	434.93 ¹⁴⁴	0.23	e.m.f.	435 ¹⁴⁵		0.02
			Combustion	427.01 ⁵⁵	0.16	1.8
Ga ₂ O	84 ⁸⁰	2.4				
FeO	64.0 ⁹¹		Solution	64.2 ¹⁴⁶	0.16	0.31
			Combustion	64.3 ¹⁴⁷	0.7	0.47
			Solution	63.3 ⁹¹		1.1
			CO-CO ₂ equilibrium	63.4 ¹⁴⁸		0.94
			H ₂ -H ₂ O equilibrium	63.4 ¹⁴⁹		1.1
MnO	91.6 ¹⁹	0.33	Solution	92.04 ¹⁵⁰	0.11	0.48
MoO ₂	140.88 ¹⁰³	0.09	Combustion	140.64 ⁴³	0.09	0.17
			CO-CO ₂ equilibrium	141.5 ¹⁵¹		0.43
NbO	96.0 ¹⁵²	2.7	Combustion	100.1 ¹⁰⁷		4.1
NbO ₂	190.6 ¹⁰⁷		Combustion	190.9 ¹⁵³	0.21	0.16
			Combustion	190.0 ¹⁵²	1.4	0.31
ReO ₃	146.0 ¹¹¹	2.1	e.m.f.	146.1 ¹⁵⁴	0.55	0.07
SnO	68.35 ¹²⁸	0.23				
TiO	123.91 ¹³²	0.23	Combustion	125.16 ¹⁵⁵	0.03	1.0
Ti ₂ O ₃	362.93 ¹³²	0.13	Combustion	362.85 ¹⁵⁵	0.08	0.02
Ti ₃ O ₅	586.69 ¹³²	0.12	Combustion	587.1 ¹⁵⁶		0.07
WO ₂	140.94 ¹³³	0.15	Combustion	137 ¹⁵⁷	0.73	2.8
			e.m.f.	136.6 ¹⁵⁸		3.1
UO ₂	258.97, ¹³⁶	0.23	Combustion	259.1 ¹⁵⁹		0.08
VO	103.2 ⁵	0.29	Combustion	103.4 ¹⁶⁰		0.19
			Combustion	102 ¹⁶¹		1.2
V ₂ O ₃	291.3 ⁵	0.14	Combustion	296 ¹⁶	0.67	1.9

heats of combustion have been measured. There are many other oxides which can be burned and this field has not been exploited.

In addition to oxidizing lower oxides to higher oxides, it is also possible to use the heat of a combustion to reduce a higher oxide to a lower oxide. Thus, by burning paraffin oil mixed with V₂O₅, Siemonsen and Ulich were able to

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get V_2O_4 , and from the heat absorbed by the dissociation plus their other experiments on the combustion of vanadium to V_2O_5 , they were able to arrive at the heat of formation of V_2O_4 ¹⁶. Similar kinds of experiments have been done with CrO_3 ^{17, 18}, MnO_2 ¹⁹ and Mn_2O_7 ²⁰.

If compounds other than oxides are burned, there will be more than one oxide in the combustion products and the possibility of reaction between them must be considered. Also, if one or more of the oxides is a gas, the fugacities of the various components of the gas phase must be used in converting to standard states. Including alloys, the number of compounds which can be burned is enormous. Some of them whose heats of combustion have been measured are given in *Table 3*. This list is not intended to be complete.

Table 3. Some kinds of inorganic compounds whose heats of combustion have been measured by oxygen bomb calorimetry

<i>Nitrides</i>	<i>Carbides</i>	<i>Hydrides</i>
Al	Fe	Ti
Be	Mn	Th
B	Ni	Zr
Hf	Nb	
Mn	Si	
Nb	Ta	<i>Sulphides</i>
P	U	Mo
Ta	V	W
Th	W	
Ti	Zr	
U		<i>Borides</i>
V		Zr
Zr		

ROTATING BOMB CALORIMETER

The problem of defining the final state can be made easier, in some cases at least, by the use of the rotating bomb calorimeter. The application of rotating bomb calorimetry to the combustion of organometallic compounds has been discussed by Good and Scott²¹. In recent years the rotating bomb calorimeter has been applied to the combustion of silicon²², boron²³ and sulphur^{24, 25}. The application of the rotating bomb calorimeter to inorganic combustion calorimetry is in its initial stages

THE USE OF GASES OTHER THAN OXYGEN

Gases other than oxygen may be used in the combustion bomb. Many metals react readily with nitrogen. Some of them can be ignited with a fuse wire. Others require an electric heater to get the reaction started. The heats of formation of at least twelve nitrides have been determined by direct combination of the elements as listed in *Table 4*. There may be others. The method should have the advantage that the quantity of interest is measured directly instead of being derived from the difference of two large numbers. However, the precision of the actual measurements is not high for most of the experiments to date.

Other gases which have been used include hydrogen, used for the reduction of CrO_2 ²⁶, nitrogen dioxide, used for the combustion of phosphorus²⁷, chlorine, used for the combustion of titanium²⁸, zirconium²⁹, tantalum³⁰, vanadium³¹,

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Table 4. Heats of formation of nitrides determined by nitrogen bomb calorimetry of the elements

Selected value			Confirmatory experiments			
Nitride	$-\Delta H^\circ_{f298}$ (kcal/mole)	Precision (%)	Method	$-\Delta H^\circ_{f298}$ (kcal/mole)	Precision (%)	Difference (%)
AlN	76.47 ¹⁶²	0.26	Equilibrium	74.7 ¹⁶³		2.3
Be ₃ N ₂	133.7 ¹⁶⁴	0.49	F ₂ combustion O ₂ combustion O ₂ combustion	60 ^{166†}	0.67	1.2
BN	60.7 ¹⁶⁵	0.56		59.7 ^{165‡}		1.7
				59.7 ^{167‡}		1.7
Ca ₃ N ₂	102.6 ¹⁶⁸	0.97	Solution Dissociation O ₂ combustion O ₂ combustion N ₂ combustion	119.7 ¹⁷¹		3.2
CrN	29.5 ¹⁶⁹	1.7		57.0 ¹⁷²		0.35
LaN	71.06 ¹⁷⁰			48.2 ¹⁷³		16.0
Li ₃ N	47.17 ¹⁶⁴			312.3 ³²		1.3
Mg ₃ N ₂	116.0 ¹⁶⁴	1.7		68.5 ¹⁷⁰		1.6
Mn ₅ N ₂	57.2 ¹⁶⁹	0.70				
Th ₃ N ₄	308.4 ¹⁷⁰					
UN	69.6 ¹⁷⁴	0.57				
U ₂ N ₃	168.4 ¹⁷⁴	0.6				

† Preliminary value

‡ Recalculated using value for ΔH°_{f298} (B₂O₃ amorph) given in Table 1.

and hafnium³¹, bromine, used for the combustion of niobium³², and titanium³³, tantalum³², and fluorine (see below).

It would seem that with a little development, the direct measurement of the heat of hydride formation could be done in a hydrogen bomb calorimeter.

FLUORINE BOMB CALORIMETRY

The use of fluorine is a particularly significant development. The technique has been described by Hubbard³⁴. There were many problems to be overcome, they have been overcome, and it is now well established. It was, of

Table 5. Heats of formation of compounds determined by fluorine bomb calorimetry

Compound	$-\Delta H^\circ_{f298}$ (kcal/mole)	Precision (%)
AlF ₃	356.0 ^{166†}	
	358.3 ¹⁷⁵	0.17
BF ₃	269.5 ¹⁷⁶	0.19
	271.2 ¹⁷⁷	0.15
BN	60 ^{166†}	
CdF ₂	167.39 ¹⁶⁶	0.14
HfF ₄	461.40 ¹⁷⁸	0.18
MgF ₂	264.9 ^{166†}	
MoF ₆	372.35 ¹⁷⁹	0.06
PF ₅	381.4 ¹⁷⁷	0.10
RuF ₅	213 ^{163†}	
SiF ₄	386.02 ¹¹⁹	0.06
SiO ₂ -α-quartz	217.75 ¹¹⁹	0.16
TiF ₄	394.19 ¹⁷⁸	0.09
UF ₆	522.57 ¹⁶⁶	0.08
ZnF ₂	182.7 ^{166†}	
ZrF ₄	456.80 ⁹⁶	0.05
ZrB ₂	71.47 ^{166†}	

† Preliminary or tentative values.

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course, necessary to determine the heats of formation of the fluorides before other compounds could be attacked. A list of some of the compounds whose heats of formation have been determined is shown in *Table 5*. The method of fluorine bomb calorimetry has led to the solution of several persistent problems in thermochemistry³⁵.

Some of the techniques developed for fluorine bomb calorimetry will undoubtedly also be useful in oxygen bomb calorimetry. Particular reference is made to the various ways of supporting the sample^{34, 36}, and the techniques for isolating spontaneously ignitable samples from the fluorine until it is desired for the reaction to start^{34, 37}.

COMBUSTION BOMB WITH WINDOW

The design of a combustion bomb with a window was reported in 1948 by Ziehl and Roth³⁸. However, apparently the first extensive use of such an apparatus to study combustions has been in fluorine bomb calorimetry^{34, 39}. Several laboratories have now built such pieces of apparatus and for some of them there are provisions for taking moving pictures of the combustions⁴⁰.

These bombs with windows or glass walls are not calorimeters. The micro-calorimeter described by Calvet and Tachoire¹⁴ is made of glass and they have studied the combustion of zirconium and have measured the energy given off by the reaction as light as well as the energy given off as heat. This promises to be a very interesting technique.

OTHER DIRECT REACTION CALORIMETERS

If the heat of formation of a compound can be measured by a reaction involving direct combination of the elements the result is likely to be more accurate than if an indirect method is employed. Thus oxides are best measured by oxygen calorimetry, fluorides by fluorine calorimetry, *etc.* Kubaschewski and co-workers have developed some calorimeters for the direct determination of the heat of alloy formation^{41, 42}. It seems that these types of calorimeters would be useful in the determination of the heats of formation of compounds other than alloys, such as carbides, sulphides, borides, *etc.*

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