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The Calorimetry of Combustions and Related Reactions:
 Inorganic Reactions *

by

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Charles E. Holley, Jr.

University of California, Los Alamos Scientific Laboratory,
 Los Alamos, New Mexico, U. S. A.

MASTER

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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%. This is commonly done in standards laboratories where certified benzoic acid is prepared. A precision of 0.03% has been attained by many experimenters, and a precision of 0.1% is common. However, when the heats of combustion of the elements ** are considered, see

** 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.

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Table 1, it is found that only for carbon has the heat of combustion been measured with a precision close to 0.01%. If the precision is lowered to 0.03% then sulfur 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%. 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%.

Of these 18 elements whose heats of combustion have been measured with a precision of 0.1% or better, only for aluminum, carbon, magnesium, molybdenum, sulfur, and tantalum are there measurements from at least two laboratories, each with a precision of 0.1% or better, agreeing within 0.1%. 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 the paper by Mackle and O'Hare contributed to this Session.² 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 noncombustible 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 analyzed 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 everpresent 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 ThO_2 or PuO_2 , where the difference is less than 1%³ and scandium burned on Al_2O_3 ⁴ or Sc_2O_3 ⁵ where the difference is about 2%. 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 vanadium.⁶ Or the stoichiometry may be off from the desired value, as is sometimes the case for uranium.⁷ 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.

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 done.⁸ 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 Fe_3O_4 within 0.15%. (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% or better and the value been confirmed to within 0.1% by a different method, solution calorimetry, having a precision of 0.1% or better. Even in this case there are other precise measurements of the heats of solution of Mg and MgO which lead to a value of the heat of formation of MgO differing from the combustion value by more than 0.1%.^{9,10,11,12} For 30 of the elements the measurements and confirmation are both better than 0.5%. For 19 elements the measurements are better than 0.5% but they have not been confirmed to 0.5%. For 5 elements the measurement is uncertain by more than 0.5%. Of these 5, for at least one of them, arsenic, the heat of combustion will probably be accurately measured in the near future.¹³

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 terbium.³ The fourth, promethium, is scarce. Of the remaining elements it seems

probable that results can be gotten 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 microcalorimeter 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 years,¹⁵ 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 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 V_2O_5 , Siemonsen and Ulich were able to 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.

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 Scott.²¹ In recent years the rotating bomb calorimeter has been applied to the

combustion of silicon,²² boron,²³ and sulfur.^{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 phosphorus,²⁷ chlorine, used for the combustion of titanium²⁸ zirconium,²⁹ tantalum,³⁰ vanadium,³¹ and hafnium,³¹ bromine, used and for the combustion of niobium,³² tantalum,³² 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 Hubbard.³⁴ There were many problems to be overcome, they have been overcome, and it is now well established. It was, of 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 thermochemistry.³⁵

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 Roth.³⁸ 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 combustions.⁴⁰

These bombs with windows or glass walls are not calorimeters. The microcalorimeter 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.^{40,41} 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, sulfides, borides, etc.

Table 1. Heats of Formation of Oxides Determined by Oxygen Bomb Calorimetry of the Elements.

Oxide	Selected Value		Confirmatory Experiments			
	ΔH_f^{298} kcal/ mole	Preci- sion %	Method	ΔH_f^{298} kcal/ mole	Preci- sion %	Differ- ence %
Al ₂ O ₃	400.48 ⁴³	.06	Combustion	400.29 ⁴⁴	.08	.05
Sb ₂ O ₃	169.4 ⁴⁵	.41	Dissoc. of oxide	167.4 ⁴⁶		1.2
Sb ₂ O ₄	216.9 ⁴⁵	.51				
As ₂ O ₃	154.7 ⁴⁷		Emf	157.0 ⁴⁸		1.5
BaO	139.06 ⁴⁹	.50	Solution	134.0 ⁵⁰		3.7
BeO	143.1 ⁵¹	.07	Combustion	145.3 ⁵²	.12	1.5
			Emf	140.9 ⁵³		1.6
			Solution	140.15 ⁵⁴		2.1
Bi ₂ O ₃	137.16 ⁵⁵	.22	Solution	137.8 ⁵⁶		.47
B ₂ O ₃ (amorph)	299.74 ²³	.13	Combustion	298.7 ⁵⁷	.60	.35
			Diborane reactions	300.98 ⁵⁸	.24	.41
CdO	61.2 ⁵⁹	.33	Solution	61.04 ⁶⁰		.26
			Emf	62.15 ⁶¹		1.4
			Combustion	62.36 ⁶⁰	.40	1.9
CaO	151.79 ⁶²	.13	Solution	151.9 ⁶³		.07
			Combustion	153 ⁶⁴	1.	.8
CO ₂	94.052 ⁶⁵	.011	Combustion	94.065 ⁶⁶	.014	.014
			Combustion	94.040 ⁶⁷	.013	.013
			Combustion	94.029 ⁶⁸	.028	.025
CeO ₂	260.18 ⁶⁹	.13				
Cr ₂ O ₃	272.7 ⁵⁹	.15	Combustion	271 ⁷⁰	.67	.63
			C-CO Equil.	270.7 ⁷¹		.74
CoO	57.1 ⁷²	.52	Combustion	57.18 ⁷³	.25	.14
			H ₂ -H ₂ O Equil.	57.23 ⁷⁴		.23
			Combustion	57.5 ⁷⁵	.35	.71
Dy ₂ O ₃	445.84 ⁷⁶	.21				

Table 1 continued - 2

Er_2O_3	453.59 ⁷⁷	.10				
Gd_2O_3	433.94 ⁷⁸	.19				
Ga_2O_3	258.6 ⁷⁹	.15	Combustion	259 ⁸⁰	.39	.15
			Combustion	261.05 ⁴	.12	.97
GeO_2	129.08 ⁸¹	.10	Solution	129.2 ⁸²	1.6	.10
			Combustion	128.6 ⁸³	.39	.39
HfO_2	266.06 ⁸⁴	.10	Combustion	271.5 ⁸⁵	1.0	2.0
Ho_2O_3	449.55 ⁸⁶	.26				
In_2O_3	221.27 ⁸⁷	.18	Combustion	222.5 ⁸⁸	.27	.54
			Combustion	220 ⁸⁹		.58
			$\text{H}_2\text{-H}_2\text{O}$ Equil.	216.8 ⁹⁰		2.0
Fe_3O_4	267.1 ⁹¹	.19	CO-CO ₂ Equil.	267.2 ⁹²		.04
			Solution	266.76 ⁹³	.08	.13
			$\text{H}_2\text{-H}_2\text{O}$ Equil.	267.47 ⁹⁴		.14
La_2O_3	428.57 ⁹⁵	.04	Solution	428.03 ^{96,97}	.15	.13
Lu_2O_3	449.8 ⁹⁸	.40				
MgO	143.70 ⁴⁴	.08	Solution	143.84 ⁹⁹	.03	.10
			Combustion	143.9 ¹⁰⁰	.83	.14
Mn_3O_4	329.0 ¹⁰¹	.22	Solution	331.65 ¹⁰²	.08	.81
			Combustion	336.5 ¹⁹	.06	2.2
MoO_3	178.16 ⁴³	.06	Combustion	178.01 ¹⁰³	.06	.10
Nd_2O_3	432.15 ¹⁰⁴	.06				
NiO	57.3 ⁷²	.18	Combustion	57.0 ⁷³		.53
Nb_2O_5	455.2 ¹⁰⁵	.13	Combustion	455.1 ¹⁰⁶		.02
			Combustion	454.8 ¹⁰⁷		.09
P_4O_{10}	713.2 ¹⁰⁸	.14	Combustion	710 ²⁷		.45
			in NO ₂			
PuO_2	252.80 ¹⁰⁹	.15	Combustion	252.4 ¹¹⁰	.40	.15
Re_2O_7	295.9 ¹⁴	.68	Combustion	295 ¹¹²	1.0	.30
RuO_2	73 ¹¹³	1.4	Dissoc. of	71 ¹¹⁴		2.8
			oxide			
Sm_2O_3	433.89 ¹¹⁵	.11	Combustion	457 ¹¹⁶		.2
Sc_2O_3	456.16 ⁵	.11				

Table 1 continued - 3

SeO ₂	53.35 ¹¹⁷	.06	Combustion	53.9 ¹¹⁸	0.6	1.0
SiO ₂	217.5 ²²	.23	Combustion in F ₂	217.75 ¹¹⁹	.15	.11
			Combustion	219 ¹²⁰	.47	.70
			Combustion	216.3 ¹²¹		.66
SrO	144.44 ⁴⁹	.28	Solution	141.8 ⁵⁰		1.8
H ₂ SO ₄	212.17 ²⁴	.03	Combustion	212.24 ²⁵	.03	.03
Ta ₂ O ₅	489.0 ¹⁰⁵	.06	Combustion	489.3 ¹²²	.08	.06
Tc ₂ O ₇	266.1 ¹²³	1.0				
TeO ₂	76.9 ¹²⁴	1.6	Emf	77.7 ¹²⁵		1.0
ThO ₂	293.2 ⁷	.14	Combustion	292.6 ⁸⁵	.48	.20
			Emf	294.1 ¹²⁶		.31
Tm ₂ O ₃	451.4 ¹²⁷	.07				
SnO ₂	138.82 ¹²⁸	.06	CO-CO ₂ Equil.	138.7 ¹²⁹	.14	.09
			Combustion	138.2 ¹³⁰		.43
TiO ₂	225.8 ¹³¹	.04	Combustion	225.52 ¹³²	.10	.13
			Combustion	226 ¹²⁰	.44	.10
W ₂ O ₃	201.46 ¹³³	.10	Combustion	200.16 ¹³⁴	.05	.64
			H ₂ -H ₂ O Equil.	202.8 ¹³⁵	.69	.64
U ₃ O ₈	852.7 ^{7,136}	.19	Combustion	856.5 ¹¹⁰	.36	.44
V ₂ O ₅	370.6 ⁸	.13	Combustion	370 ¹³⁷	.27	.16
			Solution	373 ¹³⁸		.65
V ₂ O ₄	341.16 ⁸	.10	Combustion	342 ¹⁶	.58	.25
Yb ₂ O ₃	433.68 ⁷⁶	.12				
Y ₂ O ₃	455.45 ¹³⁹	.12				
ZnO	83.36 ⁸⁰	.25	Solution	83.27 ¹⁴⁰	.06	.11
			CO-CO ₂ Equil.	82.83 ¹⁴¹		.64
			Emf	82.6 ¹⁴²		.91
ZrO ₂	258.2 ⁵²	.12	Combustion	258.1 ⁸⁵	.23	.04
			Combustion	258.8 ¹⁴³		.23
			Combustion	261.5 ¹⁰⁵	.08	1.3

Table 2. Oxides whose Heats of Combustion have been Measured

Oxide	Selected Value		- - - Confirmatory Experiments - - -			
	$-\Delta H_f^{298}$ kcal/ mole	Preci- sion %	Method	$-\Delta H_f^{298}$ kcal/ mole	Preci- sion %	Differ- ence %
<chem>Ce2O3</chem>	434.93 ¹⁴⁴	.23	Emf Combustion	435 ¹⁴⁵ 427.01 ⁵⁵	.16	.02 1.8
<chem>Ga2O</chem>	84 ⁸⁰	2.4				
<chem>FeO</chem>	64.0 ⁹¹		Solution Combustion Solution CO-CO ₂ Equil. H ₂ -H ₂ O Equil.	64.2 ¹⁴⁶ 64.3 ¹⁴⁷ 63.3 ⁹¹ 63.4 ¹⁴⁸ 63.4 ¹⁴⁹	.16 .7 1.1 .94 1.1	.31 .47 1.1 .94 1.1
<chem>MnO</chem>	91.6 ¹⁹	.33	Solution	92.0 ⁴¹⁵⁰	.11	.48
<chem>MoO2</chem>	140.88 ¹⁰³	.09	Combustion CO-CO ₂ Equil.	140.64 ⁴³ 141.5 ¹⁵¹	.09	.17 .43
<chem>NbO</chem>	96.0 ¹⁵²	2.7	Combustion	100.1 ¹⁰⁷		4.1
<chem>NbO2</chem>	190.6 ¹⁰⁷		Combustion Combustion	190.9 ¹⁵³ 190.0 ¹⁵²	.21 1.4	.16 .31
<chem>ReO3</chem>	146.0 ¹¹¹	2.1	Emf	146.1 ¹⁵⁴	.55	.07
<chem>SnO</chem>	68.35 ¹²⁸	.23				
<chem>TiO</chem>	123.91 ¹³²	.23	Combustion	125.16 ¹⁵⁵	.03	1.0
<chem>Ti2O3</chem>	362.93 ¹³²	.13	Combustion	362.85 ¹⁵⁵	.08	.02
<chem>Ti3O5</chem>	586.69 ¹³²	.12	Combustion	587.1 ¹⁵⁶		.07
<chem>WO2</chem>	140.94 ¹³³	.15	Combustion Emf	137 ¹⁵⁷ 136.6 ¹⁵⁸	.73	2.8 3.1
<chem>UO2</chem>	258.9 ^{7,136}	.23	Combustion	259.1 ¹⁵⁹		.08
<chem>VO</chem>	103.2 ⁶	.29	Combustion Combustion	103.4 ¹⁶⁰ 102 ¹⁶¹		.19 1.2
<chem>V2O3</chem>	291.3 ⁶	.14	Combustion	296 ¹⁶	.67	1.9

Table 3. Some kinds of Inorganic Compounds whose Heats of Combustion have been Measured by Oxygen Bomb Calorimetry.

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

Table 4. Heats of Formation of Nitrides Determined by Nitrogen Bomb Calorimetry of the Elements.

Nitride	Selected Value		- - - Confirmatory Experiments - - -			
	$-\Delta H_f^{298}$ kcal/ mole	Preci- sion %	Method	$-\Delta H_f^{298}$ kcal/ mole	Preci- sion %	Differ- ence %
AlN	76.47 ¹⁶²	.26	Equil.	74.7 ¹⁶³		2.3
Be ₃ N ₂	133.7 ¹⁶⁴	.49				
BN	60.7 ¹⁶⁵	.56	F ₂ Comb.	60 ^{166*}		1.2
			O ₂ Comb.	59.7 ^{165**}	.67	1.7
			O ₂ Comb.	59.7 ^{167**}		1.7
Ca ₃ N ₂	102.6 ¹⁶⁸	.97				
CrN	29.5 ¹⁶⁹	1.7				
LaN	71.06 ¹⁷⁰					
Li ₃ N	47.17 ¹⁶⁴					
Mg ₃ N ₂	116.0 ¹⁶⁴	1.7	Solution	119.7 ¹⁷¹		3.2
Mn ₅ N ₂	57.2 ¹⁶⁸	.70	Dissoc.	57.0 ¹⁷²		.35
			O ₂ Comb.	48.2 ¹⁷³		16.
Th ₃ N ₄	308.4 ¹⁷⁰		O ₂ Comb.	312.3 ⁵²		1.3
UN	69.6 ¹⁷⁴	.57	N ₂ Comb.	68.5 ¹⁷⁰		1.6
U ₂ N ₃	168.4 ¹⁷⁴	.6				

*Preliminary value

**Recalculated using value for ΔH_f^{298} (B₂O₃, amorphous) given in Table 1.

Table 5. Heats of Formation of Compounds Determined by Fluorine Bomb Calorimetry

Compound	$-\Delta H_f^{\circ}$ kcal/mole	Precision %
AlF ₃	356.0 ^{166*} 358.3 ¹⁷⁵	.17
BF ₃	269.5 ¹⁷⁶ 271.2 ¹⁷⁷	.19 .15
BN	60 ^{166*}	
CdF ₂	167.39 ¹⁶⁶	.14
HfF ₄	461.40 ¹⁷⁸	.18
MgF ₂	264.9 ^{166*}	
MoF ₆	372.35 ¹⁷⁹	.06
PF ₅	381.4 ¹⁷⁷	.10
RuF ₅	213 ^{166*}	
SiF ₄	386.02 ¹¹⁹	.06
SiO ₂ - α -quartz	217.75 ¹¹⁹	.16
TiF ₄	394.19 ¹⁷⁸	.09
UF ₆	522.57 ¹⁶⁶	.08
ZnF ₂	182.7 ^{166*}	
ZrF ₄	456.80 ⁹⁶	
ZrB ₂	71.47 ^{166*}	.05

*Preliminary or tentative values

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