

KEY HEAT OF FORMATION DATA

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INTRODUCTION

Key heat of formation data might be defined as those which are important not only in themselves, but also because they serve as stepping-stones in the determination of the heats of formation of numerous other compounds. Such "key data" exist because the thermochemist is usually obliged to determine the heat of formation of a given compound *indirectly*: the direct measurement of the heat of synthesis of a compound from its constituent elements is only occasionally a practicable proposition. Typical indirect methods include those in which the compound is chemically transformed into "simpler" substances, or alternatively is synthesized from "simpler" starting substances; in either event, these "simpler" substances become of key importance thermochemically.

The most widely used indirect method, especially for organic compounds, is that of combustion in oxygen, whereby the compound is transformed into the oxides or oxyacids of its constituent elements: the first large group of "key substances" thus includes the oxides of the common elements and the common oxyacids—*e.g.* HNO_3 , H_2SO_4 , H_3PO_4 , H_3BO_3 . The halogen acids, HF and HCl, as combustion products of organic fluorine- and chlorine-containing compounds, also belong to this group. Combustion in *fluorine* gas now presents itself as a major thermochemical method for inorganic substances, thus elevating the fluorides of the common elements into the "key substance" category.

Reactions of thermochemical importance *other* than combustion include hydrolysis, oxidation and reduction, double decomposition and replacement reactions in solution, complex formation, and addition reactions of various types. The reagents required for these investigations include acids, alkalis, oxidizing and reducing agents, donor solvents and other specific reagents: accurate heat of formation data for all these are clearly of key importance in reaction calorimetry.

The publication in 1952 of the extensive compilation of thermochemical data entitled "Selected Values of Chemical Thermodynamic Properties" (Circular 500 of the National Bureau of Standards, Washington D.C.) represents the most complete effort so far to prepare a self-consistent table of heats of formation of chemical substances. It is, of course, recognized that this task is a continuing one, and that revision will be required constantly, as new and more accurate data come into being. Evidently the *first* requirement for stability and self-consistency in master tables is the existence of a set of accurate "key data" upon which many of the rest ultimately depend. It now seems that several "key data" adopted in Circular 500 should be revised, in some cases by substantial amounts. These are examined in this

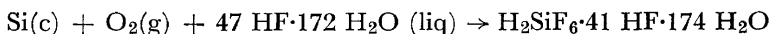
paper, together with other data that do not inspire confidence and which require further experimental investigation.

OXIDES

The heats of formation of the oxides of the majority of the elements have been obtained mainly from measurements of their heats of combustion in a bomb calorimeter. Certain metals and metalloids do not burn completely under these conditions, making the experimental results difficult to interpret correctly. For this reason, despite careful experimentation, the "best" available heat of formation data for several metal oxides still retain possibilities of error in excess of the published experimental "uncertainty intervals". A case in point is provided by the investigation of Humphrey and King¹ in 1952 of the combustion of silicon in a conventional bomb calorimeter: these authors accepted the manufacturer's statement of purity (99.9 per cent) and analysis of the sample, and corrected for impurities present, and for traces of incomplete combustion by igniting the solid product removed from the bomb to constant weight. Despite these precautions, their measure value, ΔH_c° (Si \rightarrow SiO₂, α -cristobalite) = -209.33 ± 0.25 kcal/mole, is now believed to be in error by some 8 kcal/mole. Evidence has since been presented by Golutvin² that the analytical method of estimating unburned silicon used by Humphrey and King was misleading and incorrect. Furthermore, it has now transpired that the combustion sample was less pure than claimed by the suppliers.

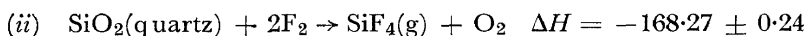
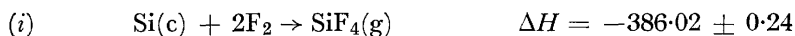
Chipman³ subsequently pointed out that experimental data obtained from equilibrium studies on certain high temperature metallurgical reactions involving silica are inconsistent with Humphrey and King's heat of formation for quartz, and that the correct value should be *ca.* 5 kcal/mole more negative. Decisive evidence is now available from two completely new and independent measurements of ΔH_f° (SiO₂, quartz), by Good⁴, and by Wise, Margrave, Feder and Hubbard⁵.

Good measured the heat of combustion in oxygen of pure silicon admixed with vinylidene fluoride polymer, using a rotating bomb calorimeter containing aqueous HF as solvent. Under these conditions, all the silicon was converted to fluorosilicic acid dissolved in aqueous HF solution. If SiO₂ was formed as a reaction intermediate, it was totally dissolved by the aqueous HF on rotation of the bomb. These experiments gave $\Delta H = -250.3 \pm 0.3$ kcal/mole for the reaction:



On combining this result with King's measurements⁶ of the heat of solution of pure quartz in aqueous HF, the value ΔH_f° (SiO₂ quartz) = -217.5 ± 0.5 kcal/mole was derived.

Wise *et al.* made use of the technique of fluorine bomb calorimetry to measure the heats of combustion in fluorine gas of silicon and of quartz,



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finding whence ΔH_f° (SiO₂, quartz) = -217.75 ± 0.34 kcal/mole, in very satisfactory agreement with Good's result.

The determination of the heat of combustion of boron in oxygen meets similar difficulties to those encountered with silicon, reflected by the published values for ΔH_c° of elemental boron which range from -270 to -368 kcal/g-mole B₂O₃. The recent measurements by Gal'chenko, Kornilov and Skuratov⁷ emphasized the difficulty of attaining complete combustion of boron, and drew attention to the inadequacies of simple analytical methods of estimating the extent of combustion. Gal'chenko *et al.* preheated the boron sample electrically to 1000° in the bomb to assist the combustion process. This investigation, leading to ΔH_f° (B₂O₃, amorph) = -299.1 ± 1.8 kcal/mole (from amorphous boron) is perhaps the most convincing effort so far to measure the heat of formation directly.

The most decisive measurement, however, by Good, Månsson and McCullough⁸, has been achieved by application of the rotating bomb technique to the combustion of boron in essentially similar manner to that used by Good with silicon. Crystalline boron powder, admixed with vinylidene fluoride polymer, was burned in oxygen in a rotating bomb, which contained

 Table 1. ΔH_f° values of oxides

Oxide	ΔH_f° (kcal/mole)		Ref.	Method
	Circ. 500	New value		
BeO (c)	-146.0	-143.1 ± 0.1	9	BC
B ₂ O ₃ (c)	-302.0	-304.10 ± 0.41 ^a	8	RBC
B ₂ O ₃ (amorph)	-297.6	-299.74 ± 0.40 ^a	8	RBC
Al ₂ O ₃ (corundum)	-399.09	-400.48 ± 0.25	10	BC
SiO ₂ (quartz)	-205.4	-217.5 ± 0.5	4	RBC
		-217.75 ± 0.34	5	FBC
P ₄ O ₁₀ (c, hex)	-720	-713.2 ± 1.0 ^b	11	BC
TiO ₂ (rutile)	-218	-225.5 ± 0.23	12	BC
Cr ₂ O ₃ (c, hex)	-269.7	-272.7 ± 0.4	13	BC
NiO (c)	-57.8	-57.3 ± 0.1	14	BC
Ga ₂ O ₃ (c, β)	-258	-261.05 ± 0.3	15	BC
GeO ₂ (c, hex)		-129.08 ± 0.13 ^c	16	BC
GeO ₂ (glass)	-128.3	-125.8 ± 0.15 ^c	16	BC
SeO ₂ (c)	-55.0	-57.5 ± 1.0 ^d	17	BC
ZrO ₂ (c, monoclinic)	-258.2	-261.5 ± 0.2	18	BC
Nb ₂ O ₅ (c, β)	-463.2	-455.2 ± 0.6	18	BC
MoO ₃ (c)	-180.33	-178.16 ± 0.11	10	BC
In ₂ O ₃ (c)	-222.5	-221.27 ± 0.4	19	BC
Sb ₂ O ₃ (c, orthorh)	-168.4	-169.4 ± 0.7	20	BC
Sb ₂ O ₄ (c)	-214	-216.9 ± 1.1	20	BC
TeO ₂ (c)	-77.69	-76.9 ± 1.2	21	BC
Ta ₂ O ₅ (c)	-499.9	-488.8 ± 0.5	18	BC
WO ₃ (c)	-200.84	-201.46 ± 0.20	22	BC
Bi ₂ O ₃ (c)	-137.9	-137.16 ± 0.3	23	BC
ThO ₂ (c)	-292	-293.2 ± 0.4	24	BC
U ₃ O ₈ (c)	-898	-853.5 ± 1.6	24	BC

BC: Combustion in a conventional bomb calorimeter in O₂ under pressure (30 ± 15 atm)

RBC: Combustion in rotating bomb calorimeter, containing aq. HF solvent

FBC: Combustion in fluorine bomb-calorimeter

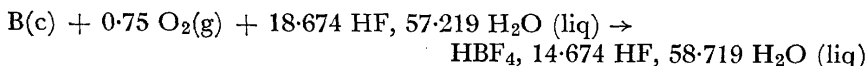
a: From crystalline B

b: From white P

c: From crystalline Ge

d: From amorphous Se

aqueous HF as solvent for the combustion products. Solid oxidation products were not found, the boric oxide and/or boron fluorides initially formed dissolving completely in the HF solution to form aqueous HBF_4 . Combustion of boron was *complete* under these conditions (30 atm O_2 initial pressure). The measurements gave $\Delta H_c^\circ = -173.41 \pm 0.20$ kcal/g-atom for the combustion reaction:



which, in conjunction with separate measurements on the heat of solution of crystalline boric acid in aqueous HF solution, and the heat of hydration of boric oxide, lead finally to $\Delta H_f^\circ (\text{B}_2\text{O}_3 \text{ amorph}) = -299.74 \pm 0.40$ kcal/mole, and $\Delta H_f^\circ (\text{B}_2\text{O}_3 \text{ cryst}) = -304.10 \pm 0.41$ kcal/mole, both these values being with reference to *crystalline* boron.

Table 1 lists heat of formation data obtained during the past decade for a number of oxides, each of which differs from the recommended value in Circular 500. The quoted error limits attached to the new values are those given by the authors themselves.

The oxides of the metals listed in *Table 1* are solids, and it is pertinent to ask if the extent of combustion of the metals concerned was accurately determined in each case. The published reports state:

Be \rightarrow BeO:	“Suitable analysis showed combustion was complete”
Al \rightarrow Al_2O_3 :	Combustion 99.14–99.66 per cent complete, determined from the weight of alumina formed
Cr \rightarrow Cr_2O_3 :	95.3–98.9 per cent complete, determined from the weight of product formed
Ni \rightarrow NiO:	87.3–92.9 per cent complete, determined from the weight of product formed
Ge \rightarrow GeO_2 :	Combustion 97.8–98.8 per cent complete, from weight increase; paraffin was required as kindling agent
Ga \rightarrow Ga_2O_3 :	Combustion complete—no weight increase on igniting the product
Se \rightarrow SeO_2 :	Unburnt Se estimated by dissolving the product in water, and separating insoluble Se residue
Zr \rightarrow ZrO_2 :	Combustion complete—no weight increase on ignition
Nb \rightarrow Nb_2O_5 :	97.6–99.4 per cent complete, from weight increase on igniting the products in O_2
Mo \rightarrow MoO_3 :	84.2–93.4 per cent from weight increase on ignition
In \rightarrow In_2O_3 :	97.6–98.6 per cent, from H_2 volume produced on treatment of products with 6N HCl
Sb \rightarrow $\text{Sb}_2\text{O}_3 + \text{Sb}_2\text{O}_4$:	Composition of product determined from mass of product formed

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Te \rightarrow TeO ₂ :	Combustion aid, graphite; analysis used to determine unburnt C and Te; combustion of Te nearly complete
Ta \rightarrow Ta ₂ O ₅ :	97.23–99.99 per cent complete, from increase in weight of products on ignition at 700°
Th \rightarrow ThO ₂ :	99.74–99.99 per cent complete, from volume of H ₂ evolved on dissolving products in 6N HCl
U + UO ₂ \rightarrow U ₃ O ₈ :	Combustion complete if the U metal admixed with UO ₂

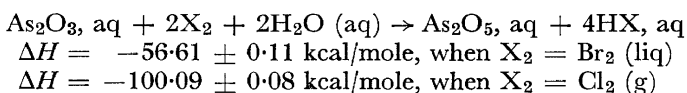
Thus complete combustion was attained only with Be, Ti, Ga, and Zr; Sb gave a mixture of oxides, and U needed UO₂ as an aid to complete combustion. Otherwise combustions were incomplete, and corrections to allow for this had to be made. There is no reason to suspect inaccuracy in the combustion analyses, but the need for corrections detracts from the certainty of the results. More decisive ΔH_f° values for several of these oxides should become available with the application of fluorine bomb calorimetry and rotating bomb methods.

The redetermination of the heat of combustion of phosphorus by Holmes¹¹ is welcome, the early measurements of Giran²⁵ lacking conviction. The new value, ΔH_f° (P₄O₁₀, c) = -713.2 ± 1.0 kcal/mole, was obtained from the heat of combustion in O₂ of α -white phosphorus, coated with a film of Perspex (polymethylmethacrylate). Corrections were made for the partial hydration of the P₄O₁₀ by the water formed on combustion of the protective Perspex coating, and for traces of unburnt phosphorus remaining in the crucible (estimated by oxidation with I₂, or by HNO₃). These studies ought now to be followed up by investigations of the heat of combustion of phosphorus using rotating bomb calorimetry: there is every reason to expect that a sharper value could be obtained.

The value quoted in Circular 500 for ΔH_f° (GeO₂, amorph) is based on heats of combustion measured by Becker and Roth²⁶ and Hahn and Juza²⁷. Although these investigators agreed well with one another, in both cases corrections for incomplete combustion of the order 1–2 per cent were necessary. Recently, Jolly and Latimer²⁸ measured the heat of solution of germanium in hypochlorite, leading to $\Delta H = -160.2 \pm 1.8$ kcal/mole for the reaction: $\text{Ge}(c) + 2\text{ClO}^-(\text{aq}) \rightarrow \text{GeO}_2(\text{amorph}) + 2\text{Cl}^-(\text{aq})$. Combination of this with ΔH_f° (ClO⁻, aq) = -26.2 ± 0.1 kcal/mole²⁹, gives ΔH_f° (GeO₂, amorph) = -132.6 ± 2 kcal/mole.

New measurements by Mah and Adami¹⁶ of the heat of combustion of germanium have provided a value for the heat of formation which differs from earlier results, and although seemingly satisfactory the new value needs confirmation before doubt is removed in this case.

Re-investigation of the heats of formation of both As₂O₃ and As₂O₅ is needed in view of measurements by Bjellerup, Sunner and Wadsö³⁰, and by Sunner and Thorén^{30a}, of the heat of oxidation of aqueous As₂O₃ by bromine and by chlorine



Combination of these data with the heats of formation of HBr and HCl (infinite dilution) gives -76.89 and -76.65 kcal/mole respectively for the difference $\Delta H_f^\circ [\text{As}_2\text{O}_5, \text{aq}] - \Delta H_f^\circ [\text{As}_2\text{O}_3, \text{aq}]$: the value from Circular 500 for this same difference is -74.9 kcal/mole. Whether the error lies in the recommended value for As_2O_3 or for As_2O_5 , or both, is difficult to decide, since neither is convincing in itself.

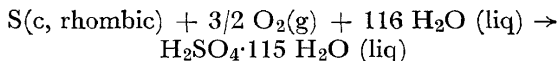
ACIDS

New investigations since 1952 have led to revised values for the heats of formation of H_2SO_4 , H_3BO_3 , H_3PO_4 , H_3PO_3 , and HBr: the value for HCl has been confirmed, and that for HF shown to be doubtful and in need of further investigation. The revised values are briefly discussed below.

Sulphuric acid

The rotating bomb technique has been applied at Bartlesville and at Lund to measure the heat of formation of dilute sulphuric acid by direct combustion of rhombic sulphur.

For the reaction



Good, Lacina and McCullough³¹ obtained $\Delta H_c^\circ = -143.85 \pm 0.06$ kcal/mole, corresponding to $\Delta H_f^\circ (\text{H}_2\text{SO}_4 \cdot 115 \text{H}_2\text{O}) = -212.17 \pm 0.06$ kcal/mole.

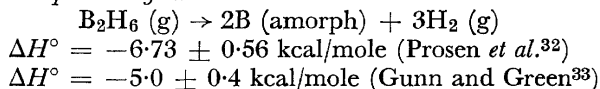
The results of Månsson and Sunner^{31a} are in close agreement. The mean value from the two independent investigations, $\Delta H_f^\circ = -212.20 \pm 0.05$ kcal/mole differs by *ca.* $\frac{1}{2}$ kcal/mole from that given in Circular 500 ($\Delta H_f^\circ = -212.63$ kcal/mole).

Boric acid

Reference has already been made (p. 115) to the measurement by Good *et al.*⁸ of the heat of combustion of crystalline boron by the rotating bomb method: combination of this with the heat of solution of boric acid in aqueous HF yields the value $\Delta H_f^\circ (\text{H}_3\text{BO}_3, \text{c}) = -261.47 \pm 0.20$ kcal/mole. This relates to formation from crystalline boron, and is to be preferred to earlier values obtained by reaction calorimetric studies, which refer ultimately to the rather ill-defined "amorphous" boron.

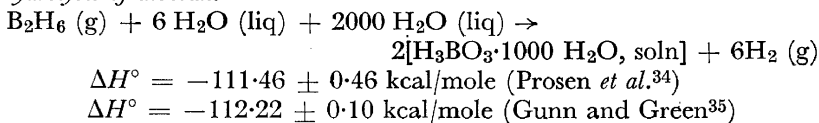
The earlier values derive from measurements of the heats of hydrolysis and thermal decomposition of gaseous diborane, and of the heats of hydrolysis and synthesis of boron trichloride. The relevant data are listed below:

(a) Thermal decomposition of diborane

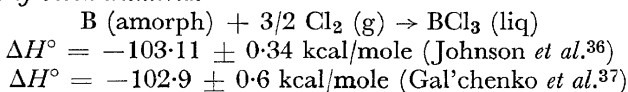


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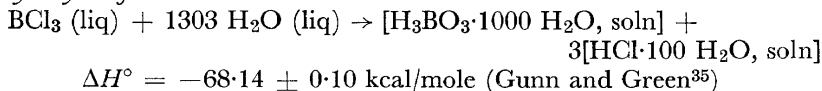
(b) *Hydrolysis of diborane*



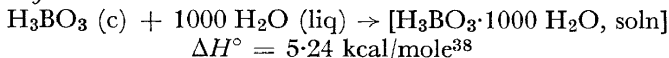
(c) *Synthesis of boron trichloride*



(d) *Hydrolysis of boron trichloride*



(e) *Solution of boric acid*



Combination of (a) and (b) with (e), choosing Prosen's ΔH° for (a) and Gunn's ΔH° for (b), gives

$$\Delta H_f^\circ (\text{H}_3\text{BO}_3, \text{c}) = -262.94 \pm 0.30 \text{ kcal/mole;}$$

combination of (c) and (d) with (e), choosing Johnson's value of ΔH° for (c), gives $\Delta H_f^\circ (\text{H}_3\text{BO}_3, \text{c}) = -262.30 \pm 0.4 \text{ kcal/mole}$. Both these determinations relate to formation from *amorphous* boron.

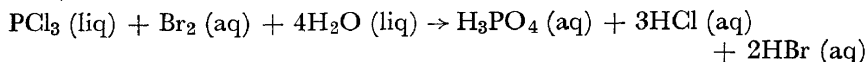
The heat of transition from crystalline to amorphous boron has not been measured accurately as yet, so that strict comparison between the reaction calorimetric values and Good's value for boric acid cannot be made. Gross *et al.*³⁹ measured the heat of fluorination of two samples of boron, one of these being a high purity zone-refined crystalline form, the other the amorphous powder obtained by thermal decomposition of diborane: the difference between the measured heats of reaction was 0.8 kcal/mole. Accepting this figure, provisionally, for the difference between amorphous and crystalline boron, the value $\Delta H_f^\circ (\text{H}_3\text{BO}_3, \text{c}) = -261.50 \pm 0.4 \text{ kcal/mole}$ (with respect to *crystalline* boron) is derived from the hydrolysis of BCl_3 , and $-262.14 \pm 0.3 \text{ kcal/mole}$ from the hydrolysis of B_2H_6 ; the former is in excellent agreement with Good's value of -261.47 ± 0.2 , from combustion measurements.

Phosphoric acid

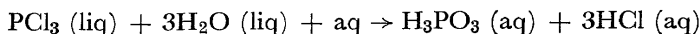
New measurements of the heats of solution of P_4O_{10} and of H_3PO_4 by Holmes¹¹, in conjunction with the redetermination of $\Delta H_f^\circ (\text{P}_4\text{O}_{10}, \text{c})$ already mentioned, yield the value $\Delta H_f^\circ (\text{H}_3\text{PO}_4, \text{c}) = -305.7 \pm 0.3 \text{ kcal/mole}$. The value given in Circular 500 is -306.2 kcal/mole .

Phosphorous acid

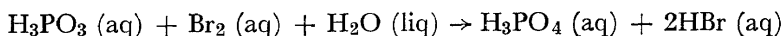
Neale and Williams⁴⁰ measured the heat of the reaction



finding $\Delta H^\circ = -137.9 \pm 0.4$ kcal/mole: Charnley and Skinner⁴¹ obtained $\Delta H^\circ = -67.7 \pm 0.4$ kcal/mole for the heat of hydrolysis



Combining these together gives $\Delta H^\circ = -70.2 \pm 0.6$ kcal/mole for the heat of the reaction



Whence, accepting Holmes'¹¹ $\Delta H_f^\circ (\text{H}_3\text{PO}_4, \text{aq}) = -308.1 \pm 0.5$ kcal/mole, and $\Delta H_f^\circ (\text{HBr}, \text{aq}) = -29.0$ kcal/mole (*v.i.*), one obtains $\Delta H_f^\circ (\text{H}_3\text{PO}_3, \text{aq}) = -226.5 \pm 0.8$ kcal/mole. Neale and Williams state that ΔH_{soln} of crystalline H_3PO_3 in aq. HCl is *ca.* 1 kcal/mole; hence, $\Delta H_f^\circ (\text{H}_3\text{PO}_3, \text{c}) = -227.5$ kcal/mole. This determination cannot be classified as "final", but the new value is more firmly based than the Circular 500 figure of -232.2 kcal/mole.

Hydrobromic acid

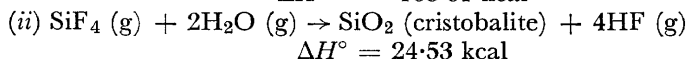
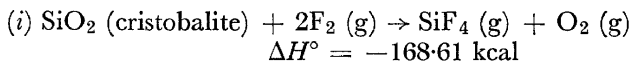
Measurements by Lacher, Casali and Park⁴² of the direct heat of combination of the elements indicated that the Circular 500 value for HBr (g) is correct within limits of ± 0.2 kcal/mole. Measurements by Johnson and Sunner⁴³ of the heat of reaction of bromine with SO_2 to form H_2SO_4 (aq) and HBr (aq) gave $\Delta H_f^\circ (\text{HBr}, 1250 \text{H}_2\text{O}) = -29.00$ kcal/mole, as compared with -28.81 of Circ. 500. The new value is based on the revised ΔH_f° for sulphuric acid. Similar studies by Sunner and Thoren^{30a} support a change of *ca.* 0.2 kcal/mole in the heat of formation of HBr. Johnson and Ambrose⁴⁴ from measurements of the heat of reaction of chlorine with SO_2 to form H_2SO_4 (aq) and HCl (aq) have confirmed the value in Circular 500 for $\Delta H_f^\circ (\text{HCl}, \text{aq})$.

Hydrofluoric acid

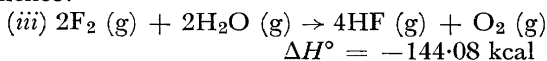
Measurements of the heat of combustion of ammonia in the constant-pressure fluorine flame calorimeter by Armstrong and Jessup⁴⁵ gave $\Delta H_f^\circ (\text{HF}, \text{g}) = -64.63$ kcal/mole (± 0.07): the non-ideality corrections for HF gas were based on the *PVT* data of Strohmeier and Briegleb⁴⁶. The measurements by von Wartenberg and Schütza⁴⁷ of the heat of reaction of fluorine with excess hydrogen were made at 100° to avoid the non-ideality corrections, and gave -64.45 ± 0.1 kcal/mole for $\Delta H_f^\circ (\text{HF}, \text{g})$. Further evidence that the heat of formation is more negative than the Circular 500 value of -64.2 kcal/mole has been presented by Feder, Hubbard, Wise and Margrave⁴⁸: these authors obtained $\Delta H_f^\circ (\text{HF}, \text{g}) = -64.92 \pm 0.12$ kcal/mole by combining the

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measured heat of combustion in fluorine of silica⁵ with the heat of hydrolysis of SiF₄, as determined from the equilibrium studies of Lenfesty *et al.*⁴⁹, thus



whence:



If the calorimetrically measured heat of hydrolysis of SiF₄⁵⁰ is used in the above scheme in place of step (ii), the value derived for ΔH_f° (HF, g) is even more negative: this raises an additional query concerning the accepted heat of solution HF in water.

Evidently further investigations are needed, but meanwhile the choice $\Delta H_f^\circ = -64.7 = 0.5 \text{ kcal/mole}$ seems preferable to that recommended in Circular 500.

Fluorides

Table 2 summarizes recent heat of formation measurements on inorganic fluorides, several of which were obtained by fluorine bomb calorimetry. It is noticeable that the new values are generally more negative than found in earlier studies.

Table 2. ΔH_f° values of fluorides

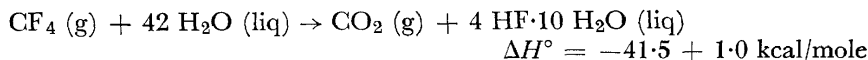
Fluoride	ΔH_f° (kcal/mole)		Ref.	Method
	Circ. 500	New value		
HF (g)	-64.2	-64.7 ± 0.5		See Above
BeF ₂ (c)	—	-241.2 ± 2	51	RC; BeO in HF aq
BF ₃ (g)	-265.2	-270.1 ± 0.24	52	FBC
CF ₄ (g)	-162.5	-219.9 ± 2	53, 54	FFC; CH ₄ + F ₂
		-218.3 ± 1	55	RBC; Teflon/oil
		-219.2 ± 2.3	56	RC; CF ₄ + Na
NF ₃ (g)	-27.2	-30.7 ± 3.4	57	RC; NF ₃ + H ₂
		-29.4 ± 2.1		RC; NF ₃ + NH ₃
		-265.0 ± 0.7	57a	FBC
MgF ₂ (c)		-356.2 ± 2	58	RC; PbF ₂ + Al
AlF ₃ (c)	-311	-356.6 ± 0.8	57a	FBC
		-386.0 ± 0.24	5	FBC
		-218.3	59	RC; PCl ₃ + $\frac{3}{2}$ CaF ₂
PF ₃ (g)	—	-381.4 ± 0.38	39	RC; white P + F ₂
PF ₅ (g)	—	-288.5 ± 0.7	60	RC; S + F ₂
SF ₆ (g)	-262	-171.7 ± 2.5	61	RC; SF ₄ + H ₂
SF ₄ (g)	—	-394.2 ± 0.25	62	FBC
TiF ₄ (c)	-370	-102.5 ± 0.2	63	RC; Br ₂ + F ₂
BrF ₅ (g)	—	-456.8 ± 0.25	64	FBC;
ZrF ₄ (c, β)	-445	(-432 ± 10)	65	RC; hydrolysis
NbF ₅ (c)	—	-372.35 ± 0.22	66	FBC
MoF ₆ (g)	—	-205.0 ± 1.5	67	RC; hydrolysis
IF ₅ (liq)	—	-461.40 ± 0.85	62	FBC
HfF ₄ (c)	—	-422 ± 4	65	RC; hydrolysis
WF ₆ (liq)	—			

FBC: Fluorine bomb calorimetry
 FFC: Fluorine flame calorimetry
 RBC: Rotating bomb calorimetry
 RC: Reaction calorimetry

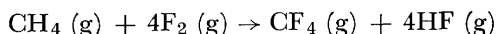
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The ΔH_f° values for BeF_2 , CF_4 , NF_3 , SF_4 , NbF_5 , IF_5 and WF_6 were derived from heats of reactions in which hydrofluoric acid was involved as reactant or product of reaction; the values may thus be due for revision should the doubts associated with ΔH_f° (HF) prove to be well-founded. In this connexion, Armstrong⁵³ has already pointed out that the present situation in respect of ΔH_f° (CF_4) and ΔH_f° (HF) is far from satisfactory: both these are "key" data vital to the correct interpretation of heats of combustion of organic fluorine compounds, and ought to be known with an accuracy comparable to that attained for ΔH_f° (CO_2) and ΔH_f° (H_2O).

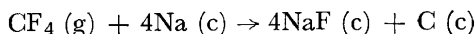
However, the measurements so far reported for ΔH_f° (CF_4) depend directly on the value accepted for ΔH_f° (HF). The combustion studies of Good, Scott and Waddington⁵⁵, on polytetrafluoroethylene-hydrocarbon oil mixtures using rotating bomb calorimetry, provided an indirect measure of the heat of hydrolysis of CF_4 *viz.*



from which ΔH_f° (CF_4 , g) was derived; the derivation involves ΔH_f° ($\text{HF} \cdot 10 \text{H}_2\text{O}$) *four times*, so that an error of $\pm x$ in the latter introduces error $\pm 4x$ in ΔH_f° (CF_4 , g). The same is true of the measurements by Jessup *et al.*⁵⁴ on the reaction



and of Vorobiev and Skuratov⁵⁶ on the reaction



(since ΔH_f° (NaF, c) was determined from the heat of neutralization of hydrofluoric acid by caustic soda). It would help to have a more *direct* determination of the heat of formation of CF_4 either by combustion of graphite, or possibly of polytetrafluoroethylene, in fluorine.

ALKALIS

New measurements by Gunn and Green⁶⁸ of the heats of reaction of the alkali metals (Li, Na, and K) with water, using their "rocking bomb" reaction calorimeter, have provided improved heat of formation data for the aqueous hydroxides, *viz.*

	ΔH_f° (kcal/mole)	
	<i>G. & G.</i>	<i>Circ. 500</i>
LiOH, $\infty \text{H}_2\text{O}$	-121.572 ± 0.02	-121.511
NaOH, $\infty \text{H}_2\text{O}$	-112.483 ± 0.006	-112.236
KOH, $\infty \text{H}_2\text{O}$	-115.323 ± 0.01	-115.0

The new values agree fairly well with other recent measurements by Ketchen and Wallace⁶⁹, and by Messer, Fasolani and Thalmayer⁷⁰. The changes from the Circular 500 values are slight, but significant in the field of solution calorimetry.

KEY HEAT OF FORMATION DATA

OXIDIZING AND REDUCING AGENTS

Heat of formation data have been reported recently for several commonly used oxidizing and reducing agents; these are summarized in *Table 3*, and discussed individually below.

Diborane

The "best" value is chosen by combining the heat of hydrolysis of diborane gas, measured by Gunn and Green³⁵, with the heat of formation of boric acid obtained by Good *et al.*⁸ The chosen value is more negative than indicated by measurements of the heat of thermal decomposition^{32, 33}, and the reason for the divergence is not yet fully explained.

Borohydrides of Li, Na and K

Measurements of the heats of hydrolysis in hydrochloric acid of LiBH_4 , NaBH_4 and KBH_4 have been reported by Davis, Mason and Stegeman⁷¹ and by Johnson, Schumm, Wilson and Prosen⁷²: the derived ΔH_f° values listed in *Table 3* are based on Good's value for the heat of formation of boric acid.

Lithium aluminium hydride

Davis *et al.*⁷¹ measured the heat of reaction with aqueous hydrochloric acid; the derived ΔH_f° in *Table 3* assumes Coughlin's value⁷³ for the heat of formation of aluminium chloride (*Table 4*).

Lithium hydride

Gunn and Green⁶⁸ measured the heat of hydrolysis of LiH .

Titanous chloride

Clifton and MacWood⁷⁴ measured the heat of solution of TiCl_3 (c) and of TiCl_4 (liq) in HCl/FeCl_3 solution. The derived ΔH_f° for TiCl_3 depends on the value accepted for ΔH_f° of TiCl_4 (see *Table 4*).

Benzoquinone-quinol

The heats of combustion in O_2 were measured by Pilcher and Sutton⁷⁵.

Hydrogen peroxide

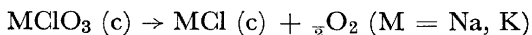
Giguère *et al.*⁷⁶ measured the heat of decomposition, $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$, catalysed by colloidal platinum.

Sodium peroxide

Gilles and Margrave⁷⁷ measured the heat of hydrolysis in the presence of MnO_2 as catalyst.

Potassium and sodium chlorates

Vorobiev *et al.*⁷⁸ measured the heat of thermal decomposition



Potassium and sodium perchlorates

Skuratov *et al.*⁷⁹ measured the heat of thermal decomposition of the perchlorates of Na, K, and Ba. The heat of thermal decomposition of KClO_4 has also been measured by Johnson and Galliland⁸⁰, but the agreement with Skuratov was not good: Skuratov has defended his measurements, but further work will be needed to resolve the discrepancy.

Hypochlorite

New measurements of the heat of hydrolysis of Cl_2 have been reported by McDonald *et al.*²⁹

Hypobromite

McDonald and Cobble⁸² measured the heat of hydrolysis of Br_2 in alkaline solution.

Ferric and ferrous chlorides

Kochler and Coughlin⁸³ measured the heat of solution of Fe in hydrochloric acid and the heat of oxidation of ferrous to ferric chloride.

Table 3. ΔH_f° values of oxidizing and reducing agents

Compound	ΔH_f° (kcal/mole)		Ref.	Method
	Circ. 500	New value		
B_2H_6 (g)	7.5	9.53 ± 0.42	35	Hydrolysis
LiBH_4 (c)	-44.6	-45.37 ± 0.5	71	Reaction with HCl, aq
NaBH_4 (c)	-43.82	-45.05 ± 0.4	71	Reaction with HCl, aq
KBH_4 (c)	—	-54.01 ± 0.5	72	Reaction with HCl, aq
LiAlH_4 (c)	-24.2	-26.6 ± 0.4	71	Reaction with HCl, aq
LiH (c)	-21.61	-21.67 ± 0.03	68	Hydrolysis
TiCl_3 (c)	-165	-172 ± 1	74	Soln in aq HCl/ FeCl_3
Quinol (c)	—	-87.51 ± 0.28	75	Combustion
H_2O_2 (liq)	-44.84	-44.88 ± 0.03	76	Catalysed decomposition
Na_2O_2 (c)	-120.6	-122.1 ± 1.2	77	Catalysed hydrolysis
NaClO_3 (c)	-85.73	-85.5 ± 0.3	78	Thermal decomposition
KClO_3 (c)	-93.50	-93.0 ± 0.4	78	Thermal decomposition
NaClO_4 (c)	-92.18	-90.68 ± 0.3	79	Thermal decomposition
		-91.48 ± 0.22	81	Soln calorimetry
KClO_4 (c)	-103.6	-101.9 ± 0.2	79	Thermal decomposition
		-103.22 ± 0.15	80	Thermal decomposition
ClO^- (aq)	-24.5	-26.2 ± 0.1	29	Hydrolysis of Cl_2
BrO^- (aq)	—	-23.05 ± 0.5	82	Hydrolysis of Br_2
FeCl_2 (c)	-96.8	-95.7 ± 0.2	83	Soln of Fe in HCl: oxidation with H_2O_2

In addition to the data given in Table 3 the following items are also worthy of note.

Ferrous and ferric sulphates

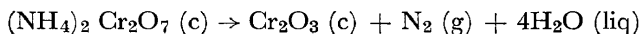
Bewley⁸⁴ measured the heat of reaction between ferrous ions and hydrogen peroxide in aqueous solution. The author pointed out that the measured heat is *not* consistent with the values quoted in Circ. 500 for ΔH_f° (FeSO_4 , aq) and ΔH_f° ($\text{Fe}_2(\text{SO}_4)_3$, aq), although in good agreement with the quoted heats of

KEY HEAT OF FORMATION DATA

formation of Fe^{2+} and Fe^{3+} ions in aqueous solution. Bewley implies that the recommended value for ΔH_f° of ferric sulphate is incorrect by a substantial amount.

Ammonium dichromate

Neugebauer and Margrave⁸⁵ measured the heat of the decomposition



from which $\Delta H_f^\circ ((\text{NH}_4)_2 \text{Cr}_2\text{O}_7, \text{c}) = -432.1$ kcal/mole is derived if one assumes Mah's value for $\Delta H_f^\circ (\text{Cr}_2\text{O}_3, \text{c})$, and that the chromic oxide formed was the same as that obtained by Mah. Muldrow and Hepler⁸⁶, from solution calorimetry, obtained -425.0 kcal/mole for the heat of formation of ammonium dichromate: the latter depends on an assumed $\Delta H_f^\circ (\text{Cr}_2\text{O}_3, \text{c}) = -138.0$ kcal/mole. The discrepancy no doubt reflects inaccuracies in the accepted heats of formation of the oxides of chromium, and until these items are better established the heat of formation data on dichromates and chromates remain rather indefinite. Similar remarks apply to the available heat of formation data on permanganates and manganates.

DONOR SOLVENTS

The heats of formation of the following donor solvents (of interest to the thermochemistry of co-ordination complexes) have recently been derived from heat of combustion measurements: dimethyl ether⁸⁷; diethyl ether⁸⁸; dibutyl ether⁸⁹; tetrahydrofuran^{90, 91}, tetrahydropyran⁹⁰⁻⁹²; 1:4-dioxan⁹²; methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, and triethylamine⁹³; pyrrolidine⁹⁴; piperidine⁹⁵; pyridine^{96, 97}; picolines⁹⁶⁻⁹⁹ and lutidines^{96, 100}.

CHLORIDES

Metallic chlorides frequently serve as the starting point for determining the heats of formation of other salts by solution calorimetric methods. In a few cases, the heats of formation of metal chlorides have been measured directly; otherwise, the heats of solution of the metals, or metallic oxides, in hydrochloric acid have been measured. The opportunity for cross-checking of the heats of formation exists in several cases, and ought to be pursued more thoroughly.

Recently determined ΔH_f° values for metallic chlorides are listed in *Table 4*, in which new data for a few metal bromides are included. Still in need of modern measurement are the heats of formation of AsCl_3 , SbCl_3 , SiCl_4 and GeCl_4 , PCl_3 and PCl_5 , in each case preferably by direct synthesis in a calorimeter.

ORGANIC COMPOUNDS

The heats of formation of organic compounds are obtained for the most part from heats of combustion, so that "key data" refer to products of combustion, already described. Reaction and solution calorimetric methods for the study of organic compounds are, however, finding increasing application, and it is

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Table 4. ΔH_f° values for chlorides and bromides

Compound	ΔH_f° (kcal/mole)		Ref.	Method
	Circ. 500	New value		
BeCl ₂ (c)	-122.3	-118.0 ± 0.6	101	Direct synthesis
		-118.3 ± 0.3	102	Soln of Be in aq HCl
BCl ₃ (liq)	-100.0	-102.3 ± 0.3	35	Hydrolysis
AlCl ₃ (c)	-166.2	-168.6 ± 0.5	73	Soln of Al in aq HCl
PCl ₃ (liq)	-81.0	-73.9 ± 1.0	40	Reaction with aq Br ₂
TiCl ₄ (liq)	-179.3	-192 ± 1	103, 104	Direct synthesis
TiCl ₃ (c)	-165	-172 ± 1	74, 105	Soln in FeCl ₃ /HCl; in I ₂ /KI
TiCl ₂ (c)	-114	-123.5 ± 1	106	Soln in FeCl ₃ /HCl
VCl ₄ (liq)	-138	-136.2 ± 0.2	107	Direct synthesis
VCl ₃ (c)	-137	-143 ± 1	108	Soln in aq KOH
VCl ₂	-108	-110 ± 1	109	Equilibrium VCl ₂ + H ₂
MnCl ₂ (c)	-115.3	-115.2 ± 0.1	83	Soln of Mn in aq HCl
FeCl ₃ (c)	-96.8	95.7 ± 0.2	83	Oxidation FeCl ₂ with H ₂ O ₂
FeCl ₂ (c)	-81.5	-81.9 ± 0.1	83	Soln of Fe in aq HCl
ZrCl ₄ (c)	-230	-234.7 ± 0.4	110	Direct synthesis
NbCl ₅ (c)	—	-190.6 ± 0.3	111	Direct synthesis
		-190.4 ± 1	112	Soln of Nb, NbCl ₅ in aq HF
NbCl ₄ (c)	—	-166.0	112	Soln in aq HF
MoCl ₅ (c)	-90.8	-126	113	Soln in aq NaOH/H ₂ O ₂
MoCl ₄ (c)	-79	-114	113	Soln in aq FeCl ₃ /HCl
MoCl ₃ (c)	-65	-94	113	Combustion in O ₂
MoCl ₂ (c)	-44	-69	113	Combustion in O ₂
RuCl ₃ (c)	-63	-60.5 ± 2	114	Equilibria involving RuCl ₃ (g)
HfCl ₄ (c)	—	-236.9 ± 0.3	107	Direct synthesis
TaCl ₅ (c)	—	-205.5 ± 0.1	111	Direct synthesis
		-205.0 ± 0.3	115	Soln of Ta, TaCl ₅ in aq HF
TaCl ₄ (c)	—	-168.8 ± 0.5	116	Soln in aq HF
WCl ₆ (α, c)	-98.7	-163	113	Soln in aq NaOH
WCl ₅ (c)	-82	-137	113	Disproportionation of vapour
WCl ₄ (c)	-71	-121	113	Disproportionation of vapour
WCl ₂ (c)	-38	-60 ± 3	113	Combustion in O ₂
ReCl ₃ (c)	—	-63 ± 0.8	117	Soln in basic OCl ⁻
UCl ₄ (c)	-215.2	-251.2 ± 0.4	118	Soln of U, UCl ₄ in aq HCl/Na ₂ SiF ₆
BBr ₃ (liq)	-52.8	-57.5 ± 1.0	119	Hydrolysis
PBr ₃ (liq)	-47.5	-41.5 ± 1.5	41	Hydrolysis
TiBr ₄ (c)	-155	-147.8 ± 1	104, 120	Direct synthesis
NbBr ₅ (c)	—	-132.9 ± 0.4	121	Direct synthesis
MoBr ₄ (c)	-45	-74.5	122	Soln in aq FeCl ₃ /HCl
MoBr ₃ (c)	-41	-64 ± 5	123	Combustion in O ₂
MoBr ₂ (c)	-29	-54 ± 5	123	Combustion in O ₂
TaBr ₅ (c)	—	-143.0 ± 0.4	121	Direct synthesis
WBr ₆ (c)	-44	-92 ± 1	124	Soln in aq NaOH
ReBr ₃ (c)	—	-39.3 ± 0.8	117	Soln in basic OCl ⁻
BiBr ₃ (c)	—	-63 ± 3	125	Equilibrium Bi + BiBr ₃

perhaps time to promote the common carboxylic acids, alcohols, phenols, amines, and alkyl and phenyl halides to the category of "key compounds".

In this connexion, it is encouraging to record new measurements of the heats of formation of several alcohols^{126, 127}, carboxylic acids^{128, 129}, phenols¹³⁰ and alkyl bromides¹³¹. There remain, however, several disturbing gaps, coupled with a general need for confirmation of many of data currently accepted. A

KEY HEAT OF FORMATION DATA

reliable value for methyl bromide is lacking, and the heat of formation of phenyl bromide is uncertain: Bjellerup's value for n-propyl bromide is inconsistent in relation to the "best values" available for ethyl bromide and butyl bromide. A new measurement of the heat of formation of benzyl bromide (from the heat of reduction by $\text{LiH}/\text{LiAlH}_4$) by Carson¹³² is in poor agreement with the value obtained by Benson and Buss from equilibrium studies¹³³. Lacher^{133a} has recently reported that new measurements on the heats of hydrogenation of alkyl bromides are being made at Boulder, and that reliable values for methyl and ethyl bromide should soon become available.

A seemingly reliable value for methyl iodide is available from Carson, Carter and Pedley's measurements¹³⁴ of the heat of reduction with $\text{LiH}/\text{LiAlH}_4$. The same method has been applied to ethyl iodide and benzyl iodide¹³²: however, the alkyl iodides remain for the most part badly defined in respect of their heats of formation. As regards alkyl fluorides, virtually no information is available except for the heats of hydrogenation of propyl and isopropyl fluorides, reported by Lacher and co-workers¹³⁵.

CONCLUSION

This report is confined to compounds of key importance to *experimental thermochemistry*, and ignores all other aspects such as technological or theoretical importance. As such it is very limited, yet it is evident that there is ample scope for more complete and more precise re-investigation of many of the "bread and butter" data required by modern thermochemistry. No less important is a realistic appraisal of the uncertainty intervals attached to each item of key importance currently in use. In this connexion I am convinced of the need for a new critical compilation of thermochemical data, comparable to Circular 500 and available for general sale, and am informed that the task of revising Circular 500 is already under way, under the direction of Dr W. H. Evans.

I wish to express my thanks to W. D. Good, W. N. Hubbard, S. R. Gunn, W. H. Johnson, D. D. Wagman, W. H. Evans, G. Waddington, S. Sunner, D. Stull and J. D. Cox for helpful advice (and in some cases, access to unpublished results) in the preparation of this paper.

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