The Heat of Combustion of Teflon in Fluorine

A Check on the Heat of Formation of Carbon Tetrafluoride

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The heat of combustion in fluorine of a Teflon sample whose heat of formation was previously known has been determined as −246.84 ± 0.07 kcal. mole^{-1}. This information combined with other available thermodynamic data gives $\Delta H_f^\circ[CF_4(g)]$ = −223 ± 1 kcal. mole^{-1}.

IN RECENT years numerous workers have determined the heat of formation of $CF_4(g)$ both by direct and indirect methods. The early value of $\Delta H_f^\circ[CF_4(g)]$ reported by von Wartenberg (*19*) of −162 ± 2 kcal. mole^{-1} by the direct combination of the elements was in error owing to the formation of higher fluorides. During the period of 1954–65, the reported values for $\Delta H_f^\circ[CF_4(g)]$ approached −219.0 ± 0.83 kcal. mole^{-1} (*1, 2, 10, 11, 14, 16, 18*). From several of these data (*10, 14, 16, 18*) and more recent values for the heats of formation of aqueous and gaseous hydrogen fluoride (*6, 8*), the JANAF tables (*17*) report $\Delta H_f^\circ[CF_4(g)]$ to be −222 ± 2 kcal. mole^{-1}.

Cox, Gundry, and Head (*2*) have listed the results of the previous determinations of $\Delta H_f^\circ[CF_4(g)]$ and have recalculated this value based upon their redetermination of the heat of formation of aqueous hydrogen fluoride (*3*) and the more recent value of $\Delta H_f^\circ[HF(g)]$ (*6*). The average value of $\Delta H_f^\circ[CF_4(g)]$ reported by Cox is −224.4 ± 0.80 kcal. mole^{-1}, about 2 kcal. more negative than the JANAF value.

Perhaps the most obvious method of determining $\Delta H_f^\circ[CF_4(g)]$ is by the direct fluorination of graphite in a reaction bomb. Recently Domalski and Armstrong (*5*) have reported a heat of fluorination for graphite which yields $\Delta H_f^\circ[CF_4(g)]$ = −222.87 ± 0.04 kcal. mole^{-1}, in good agreement with the JANAF average. Characterization of the graphite presents a problem however, and different graphites have been shown to have different heats of combustion in oxygen (*12*). The authors also observed that the thermal history of a graphite sample can cause significant variations in its heat of combustion in oxygen.

Recently, the heat of combustion of a Teflon sample in fluorine was determined (*4*) in conjunction with a study on the heat of formation of aluminum trifluoride. A value for $\Delta H_f^\circ[CF_4(g)]$ was calculated from this data using the heat of formation of Teflon reported by Scott, Good, and Waddington (*16*). The value calculated was $\Delta H_f^\circ[CF_4(g)]$ = −221.77 kcal. mole^{-1}. These authors pointed out that, since Teflon was a rather undefined substance, this value for $\Delta H_f^\circ[CF_4(g)]$ could not be taken as absolute. Clearly, if a sample of the same Teflon used by Scott, Good, and Waddington (*16*) were burned in fluorine this would yield a more reliable value for the heat of formation of $CF_4(g)$.

EXPERIMENTAL

The calorimeter bomb used in the combustion experiments was a Parr 1003 Monel bomb with internal fittings constructed of nickel and a volume of 360 ml. Temperature measurements were made using a Hewlett-Packard Dymec quartz thermometer. A further description of this apparatus is to be published elsewhere (*20*).

Five combustion experiments were performed on Teflon pellets prepared from a Teflon sample (Dupont TE 3086, Lot 20022). The Teflon was burned as received. Each pellet was made by hand on a modified Parr Instrument Co. press and had dimensions of approximately 3 cm. in diameter × 1 cm. A prefluorinated nickel crucible was used in all combustion experiments. Ignition of the Teflon samples was accomplished using a short fuse of Teflon weighing approximately 1.0 mg. and having a heat of combustion of −2467.7 ± 0.7 cal. gram^{-1} (four determinations). Combustions of the Teflon samples went smoothly with only a small amount (usually 0.50 mg. or less) of white residue adhering to the walls of the crucible after combustion. This unburned material was assumed to be Teflon on the basis of its appearance and insolubility in common solvents. Based upon the small quantity of residue and the realization that any other solid fluorocarbon would have a heat of combustion per gram only moderately different from that of Teflon, the assumption that the residue was Teflon seemed reasonable. An appropriate correction was made to the sample weight based on the residue weight. Mass spectral and infrared analyses of the combustion product gases in a typical experiment revealed only CF_4 as the combustion product.

The fluorine used was supplied by Allied Chemical Co. (98% purity, typical) and it was passed through a NaF-trap prior to use to remove HF. For all combustion experiments a fluorine pressure of 60 p.s.i.a. was used. Standard techniques for evacuating the bomb prior to use and filling the bomb with fluorine were used (*7*).

A series of six calibration runs was made in the calorimeter system used in this work with NBS sample 39h benzoic acid. The results of these experiments were $\sum^\circ$(calor.) = 3608 ± 1.0 cal. degree^{-1} over a 1° temperature interval (six determinations). Standard deviations for both $\sum$(calor.) and the results in Table I were calculated using the methods given by Rossini (*15*).

RESULTS

Standard state corrections on the combustion data for the Teflon sampler were performed in a manner similar to that described by Hubbard (*7*). The heat capacity of Teflon was 0.285 cal. gram^{-1} degree^{-1} from the experimental data given by Marx and Dole (*13*). The results of the six combustion experiments are shown in Table I. In the calculations, the thermochemical calorie was used along with the 1961 atomic weights. The corrected temperature changes were calculated using a computer program and standard procedures to make corrections for heat gained from the jacket and the heat of stirring (*9*).

Table I. Teflon Combustion Experiments[a]

	I	II	III	IV	V
m, Teflon, g.[b] (in vacuo)	1.46737	1.46647	1.46706	1.46639	1.46676
m, Residue, g.	0.00035	0.00035	0.00054	0.00025	0.00044
Δt_c°, deg.	1.00826	1.00790	1.00700	1.00748	1.00715
$\sum^\circ$(calor.) $(-\Delta t_c)$, cal.	−3637.80	−3636.50	−3633.26	−3634.99	−3633.80
ΔE contents, cal.	−1.86	−1.85	−1.85	−1.85	−1.85
ΔE ign, cal.	1.80	1.80	1.80	1.80	1.80
ΔE gas, cal.	0	0	0	0	0
ΔE Teflon fuse, cal.	−16.07	−18.75	−12.83	−14.56	−13.47
$\Delta E_c^\circ / M$, cal. g.$^{-1}$	−2468.2	−2467.0	−2467.8	−2469.0	−2468.3

Average $\Delta E_c / M = -2468.06$ cal./g. Standard deviation of the mean = ±0.74 cal./g.

[a] The definitions of these standard symbols are given in (*9*). [b] Mass corrected for residue.

The observed heat of combustion for the sample of Teflon was $\Delta H_{298}^\circ = -246.84 \pm 0.07$ kcal. mole^{-1} for reaction 1.

$$C_2F_4 \text{ (solid, polymer)} + 2F_2(g) = 2CF_4(g) \qquad (1)$$

The previously reported value (*5*) was $\Delta H_{298}^\circ = -247.43 \pm 0.01$ kcal. mole^{-1}. Scott, Good, and Waddington (*16*) measured the heat of reaction 2 to be $\Delta H_{298}^\circ = -160.3 \pm 0.9$ kcal. mole^{-1}

$$C_2F_4\text{(solid, polymer)} + O_2(g) + 2H_2O(l) = 2CO_2(g) + 4HF \cdot 10H_2O(l) \qquad (2)$$

With a value of $\Delta H_f^\circ[HF \cdot 10H_2O(l)] = -77.367$ kcal. mole^{-1} (*3*), Good's results yield a value for the heat of formation of Teflon of -200.64 ± 1.10 kcal. mole^{-1}. Combined with the value for the heat of reaction 1 the heat of formation of CF_4(gas) becomes $\Delta H_f^\circ = -223.74 \pm 0.64$ kcal. mole^{-1}. Armstrong and Domalski's combustion results yield $\Delta H_f^\circ = -224.03 \pm 0.55$ kcal. mole^{-1} with these same reference data.

One may also consider the data for reactions 1 and 3:

$$C_2F_4 \text{ (solid, polymer)} + O_2(g) = CO_2(g) + CF_4(g) \qquad (3)$$

for which $\Delta H_{298}^\circ = -118.8 \pm 0.5$ kcal. mole^{-1}. Combination of these data yield $\Delta H_f^\circ[CF_4(g)] = -222.3 \pm 0.6$ kcal. mole^{-1}.

Since major uncertainty about the heat of formation of Teflon has been removed in this work, one is left with the conclusion that there are still errors and/or inconsistencies in the thermodynamic data for aqueous or gaseous HF. The direct fluorination of graphite (*5*) and the direct fluorination of a well-characterized Teflon (*4*) yield -222.87 ± 0.04 and -222.3 ± 0.6 kcal. mole^{-1} for $\Delta H_{298}^\circ[CF_4(g)]$. When one introduces the HF-data as presented by Cox and Harrop (*3*), a large shift of the heat of formation is observed to -224.03 ± 0.55 or -223.74 ± 0.64 kcal. mole^{-1}, respectively.

In summary, the heats of oxidation and of fluorination of Teflon may be used with various calorimetric data to establish $\Delta H_{298}^\circ[CF_4(g)] = -223 \pm 1$ kcal. mole^{-1} where most of the uncertainty arises because of inconsistencies in the thermodynamic data for aqueous and gaseous HF.

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