this third case was $a = 8.798$ A. It was concluded from these data that a miscibility gap exists in the system.

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Enthalpy of Formation of Germanium Tetrafluoride

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The energy of formation of germanium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter. From these measurements the standard enthalpy of formation $\Delta H_f^\circ(\mathrm{GeF_4}, g) = -284.42 \pm 0.38$ kcal. mole^{-1} was obtained.

THERMODYNAMIC STABILITIES of Group IV tetrafluorides can be measured by many techniques, but direct fluorinations should be the most reliable and lead to the fewest ambiguities. In an extended series of measurements, the authors studied the reaction of elemental germanium with fluorine, and repeated some earlier unpublished measurements which were cited by O'Hare *et al.* (*14*) as being approximately 10 kcal. mole^{-1} less negative than their value. This discrepancy has now been resolved, and the value obtained supports the other recently published results (*4*, *14*).

EXPERIMENTAL

Materials. Germanium, in ingot form, was purchased from Alfa Inorganics, Inc.; it had a specified purity of 99.995%. Spectrographic analysis failed to reveal any impurity. However, a sample which had been ground for combustion had an oxygen impurity of 225 ± 18 p.p.m. (fast neutron activation analysis). Fluorine, 99.8% pure, was supplied by the Allied Chemical Corp. Impurities of hydrogen fluoride were removed by passing the fluorine through a trap packed with sodium fluoride. Tungsten foil and wire, both 99.99% pure, were obtained from A. D. Mackay and Co. A listing of the nature and level of impurities in the tungsten was provided by the supplier. Calculations showed that the impurity level had no effect on the energy of fluorination of tungsten. The Teflon powder used in these experiments was manufactured by Du Pont (TE 3086, Lot 20022), and its energy of fluorination had been determined by Wood *et al.* (*16*).

Calorimeter and Combustion Technique. The calorimeter used was identical to the Argonne National Laboratory Design CT-3986. Combustions were carried out in a Parr 1004 nickel bomb adapted so the two-chamber principle (*9*) could be employed in effecting combustion. An inner nickel chamber, filled with helium, contained the sample, which was isolated from the fluorine in the main chamber by a diaphragm of tungsten 0.001 inch thick. The ignition system utilized a condenser discharge unit, similar to that described by Lacina *et al.* (*10*), delivering a pulse of 1.8 cal. of electrical energy. This ignition pulse reached the tungsten diaphragm via a short length of tungsten wire, ignited the diaphragm, and consequently initiated the reaction. Temperatures were recorded using a Dymec Model 2801-A quartz thermometer. The corrected temperature rise associated with the bomb reaction was calculated using standard methods (*1*) and a suitable computer program.

The energy equivalent of the calorimeter, ε(calor.) was measured by combustion of standard benzoic acid (NBS sample 39i with certified energy of combustion 26434 ± 3 abs. joules gram^{-1}). A series of six calibration experiments gave ε(calor.) = 3706.02 cal. deg.$^{-1}$ with a standard deviation of the mean of 0.5 cal. deg.$^{-1}$ (1 cal. ≡ 4.184 abs. joules).

In a series of preliminary experiments, powdered germanium from Alfa Inorganics was burned, but answers consistently lower than previously published data were obtained. However, x-ray powder patterns of this material showed not only germanium lines, but also strong germanium oxide lines. The energy of fluorination per gram of this material would thus be expected to be less than that of pure germanium. The ground germanium ingot used in the final combustion experiments gave x-ray powder patterns which showed no indication of germanium oxide impurity.

After several exploratory experiments, essentially complete combustion was achieved when an intimate mixture of ground germanium ingot and Teflon was ignited in a prefluorinated nickel cup using 5.4 atm. of fluorine. Infrared spectra of the gaseous products, after removal of excess fluorine, showed the presence of $\mathrm{GeF_4}$, $\mathrm{CF_4}$, and $\mathrm{WF_6}$ (*11*). No other gaseous products were identified. The small amount of solid residue remaining after combustion was weighed accurately. Analysis of the residue, from a typical experiment, by Schwarzkopf

Table I. Results of Germanium Combustion Experiments

	Experiment No.			
	1	2	3	4
1. Mass of germanium, grams	1.01898	1.03088	1.03618	1.02034
2. Mass of Teflon, grams	0.18091	0.18597	0.18231	0.17964
3. Mass of tungsten burnt, grams	0.22209	0.21353	0.22187	0.21980
4. Δtc, deg.	1.3191	1.3333	1.3448	1.3248
5. ε (calor.) $(-\Delta tc)$, cal.	−4888.61	−4941.24	−4983.86	−4909.74
6. ΔE (contents), cal.	−1.17	−1.19	−1.20	−1.18
7. ΔE (gas), cal.	−0.25	−0.25	−0.25	−0.25
8. ΔE (ignition), cal.	1.80	1.80	1.80	1.80
9. ΔE (Teflon), cal.	446.50	458.99	449.95	443.36
10. ΔE (tungsten), cal.	495.68	476.58	495.19	490.57
11. ΔE (carbon residue), cal.	−30.00	−22.77	−12.41	−18.15
12. $\Delta Ec°/M$ (sample), cal. gram^{-1}	−3901.99	−3907.42	−3909.34	−3913.98

Mean $\Delta Ec°/M$ (sample) = -3908.18 ± 2.48 cal. gram^{-1}
Impurity correction = -1.85 ± 0.15 cal. gram^{-1}
$\Delta Ec°/M$ (Ge, c) = -3910.03 ± 2.48 cal. gram^{-1}

Microanalytical Laboratories, Woodside, N. Y., showed it to be carbon. Any tungsten foil or wire remaining was also weighed.

RESULTS

Table I lists the results of four combustion experiments. The symbols used are mostly self-explanatory, or have been used previously *(6)*. The weights of germanium *(5)*, tungsten *(15)*, and Teflon *(2)* were reduced to vacuo, using the densities 5.35, 19.265, and 2.24 grams cc.$^{-1}$, respectively. For the calculation of ΔE (contents) in item 6, the following values were used: 0.106, 0.077, 0.032, and 0.28 cal. deg.$^{-1}$ gram^{-1} for nickel *(8)*, germanium *(8)*, tungsten *(8)*, and Teflon *(2)* for the heat capacities at constant pressure, and 19.57, 12.61, 26.46, 5.49, and 4.97 cal. deg.$^{-1}$ mole^{-1} for the heat capacities at constant volume for $GeF_4(g)$ *(8)*, $CF_4(g)$ *(12)*, $WF_6(g)$ *(7)*, $F_2(g)$ *(12)*, and He(g) *(8)*, respectively. For the calculation of items 9 through 11, the following $\Delta Ec°/M$ values were used: Teflon −2468.06 *(16)*; tungsten −2231.9 *(13)*, carbon −18520.4 *(3)* cal. gram^{-1}. The impurity correction was calculated assuming all the oxygen was present as germanium dioxide, whose energy of combustion in fluorine was −145.7 kcal. mole^{-1} *(4)*. The function $\Delta Ec°/M$ (Ge, c) represents the energy change per gram of germanium for the reaction:

$$Ge(c) + 2F_2(g) \rightarrow GeF_4(g)$$

The enthalpy of formation of germanium tetrafluoride can thus be calculated: ΔH_f^0 $(GeF_4,g) = -284.42 \pm 0.38$ kcal. mole^{-1}. The error quoted is the uncertainty interval calculated as per standard procedures given by Rossini *(1)*.

This result is in acceptable agreement with the recently published results of O'Hare *et al.* *(14)*, −284.57 ± 0.21 kcal. mole^{-1}, and of Gross *et al.* *(4)*, −284.37 ± 0.15 kcal. mole^{-1}.

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