The Heat of Formation of Thallium Azide[1]

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The heat of formation of thallium azide has been determined by explosion in a helium atmosphere and measurement of the heat evolved. There have been no thermodynamic data published on metallic azides in recent years. In 1917, Wohler and Martin[2] prepared a number of azides and fulminates and determined their "heat of detonation." Experimental details of the determinations are not given and their value of 232 cal./gram for TlN_3 is 7 cal./gram higher than that observed by this Laboratory. The average of five determinations made by this Laboratory is 224.8 ± 0.8 cal./g.

Products of the decomposition of TlN_3 which took place in a calorimetric bomb containing 30 atmospheres of helium are metallic thallium and nitrogen. The ΔH_f of formation is in this case practically the negative of the ΔH_e of explosion. The correction, being the ΔH of expansion at constant temperature of one and a half moles of nitrogen from 30 to 1 atmosphere, was computed from the expression

$$H_{(T_1P_2)} - H_{(T_1P_1)} = (B - T\mathrm{d}B/\mathrm{d}T)(P_2 - P_1)$$

where B is the second virial coefficient for nitrogen.

		kcal.
$TlN_3 \rightarrow 3/2N_{2(30\text{ atm., }24°)} + Tl(c)$	ΔH_e	$= -55.390 \pm 0.2$
$3/2N_{2(30\text{ atm., }25°)} \rightarrow 3/2N_{2(1\text{ atm., }25°)}$	ΔH	$= 0.054$
$Tl(c) + 3/2N_{2(1\text{ atm., }25°)} = TlN_3$	ΔH_f	$= +55.34 \pm 0.2$

Details of the calorimetric equipment and procedure are given so that the character of this work may be ascertained.

Calorimetric Equipment and Procedure.—Thallium azide detonates on ignition and shatters the sample holder, therefore an expendible porcelain crucible was used in a standard Parr, 360-ml., double valve oxygen bomb.

The loaded bomb was twice filled with 25 atmospheres of grade A oil-free helium and then vented to remove any air present. It was then filled with helium to an absolute pressure of 30 atmospheres. Helium by mass spectrographic analysis showed an oxygen content of the order of 0.003 mole per cent. If it is assumed that all the oxygen present during the burning process reacts to form Tl_2O the heat evolved is 1.91 cal. This would result in the values given being too high by 0.95 cal./g.

The bomb was placed in the calorimeter, consisting of an inner and an outer metal vessel separated from each other by a 1-cm. air space. The opposing vessel surfaces are chrome-plated to reduce radiation losses. The inner jacket contains a weighed quantity of water (2000 ± 0.2 g.), a stirrer, and the charged bomb. A close-fitting lid covers the inner jacket, and a large double lid covers both the inner and outer calorimeter vessels. This outer lid is of hollow construction so that water from the bath may be drawn up into it. The calorimeter is thus completely enclosed by a 1-cm. air space which in turn is surrounded by a constant-temperature (±0.002°) bath. The ignition wires are attached, the stirrer is connected, and the calorimeter is allowed to sit until the change of temperature in the calorimeter with respect to time becomes uniform.

Temperature measurements are made with a platinum resistance thermometer using a Mueller type G-2 resistance bridge.

Heat transfer between the calorimeter and the constant temperature bath is determined by measuring the rate of temperature change before and after igniting the sample. Time intervals are recorded on a Gaertner four-channel chronograph.

The thermal-leakage coefficient and the heat of stirring are obtained by the solution of two equations of the form

$$\mathrm{d}T/\mathrm{d}t = QK + W$$

where $\mathrm{d}T/\mathrm{d}t$ is the change of temperature with respect to time in the calorimeter; Q, the thermal head, is the difference between the bath temperature and the calorimeter temperature; K is the thermal-leakage coefficient; and W is the rise in temperature produced through stirring. The total heat loss is obtained by graphic integration of the temperature–time plot.

Other corrections are made for electrical heating of the iron ignition wire and for the heat capacity of the reactants and products back to 25°.

The calorimeter was calibrated against samples of benzoic acid no. 39f supplied by the National Bureau of Standards. The experimental data are summarized in Table I.

Preparation of Material.—Thallium azide was prepared by dissolving thallium sulfate in sufficient hot water for solution, sodium azide was then added and the material permitted to cool. The precipitated thallium azide was filtered, and recrystallized from water, washed with alcohol and dried in a vacuum oven at 50°. The dried material was then pressed into 2-g. pellets in preparation for the calorimetric determination. The sample analysis gave 99.64% and 99.83% purity in two batches.

Table I

Experimental Data

Energy equivalent of calorimeter = 2280.27 cal.

Measured temp. rise, °C.	0.1977	0.1968	0.1826	0.1977	0.1957
Heat loss, °C.	+ .0011	+ .0014	+ .0018	+ .0017	− .0003
Stirring correction, °C.	− .0036	− .0018	− .0024	− .0053	− .0038
Total heat evolved, cal.	445.11	447.85	415.01	442.60	436.90
Electrical heating, cal.	3.60	1.73	1.58	1.80	1.87
C_p reactants $(25 - T_1)$, cal.	+2.53	−0.22	+0.79	+0.77	+0.66
C_p products $(T_2 - 25)$, cal.	−2.08	+0.73	−0.37	−0.29	−0.19
Weight of sample, g.	1.9673	1.9683	1.8482	1.9695	1.9419
Heat of explosion, cal./g.	224.65	226.90	223.92	224.27	224.26

Heat of explosion (av.) = 224.80 ± 0.84

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(2) Wohler and Martin, *Ber.*, **50**, 595 (1917).

The Formation and Dissolution of Metal Sulfides[1]

By Herbert A. Pohl

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The precipitation of metal sulfides by the action of H_2S in solutions of the salts of the metals may be caused by the interaction of the metal ion with $S^=$ ion, with the HS^- ion or with molecular H_2S. It would appear from the work described that the

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