Table VIII. Relative Partial Molal Heat Content ($\overline{L}_2$) and Relative Partial Molal Heat Capacity ($\overline{J}_2$) of Hydrochloric Acid

m/Mole Kg^{-1} [a]	θ 0° C		15° C		25° C		35° C	
	$\overline{L}_2$ [b]	$\overline{J}_2$	$\overline{L}_2$	$\overline{J}_2$	$\overline{L}_2$	$\overline{J}_2$	$\overline{L}_2$	$\overline{J}_2$
	$X = 20.76$ Weight % 2-Propanol							
0.01	2171	26	2583	28	2969	29	3165	30
0.005	2022	14	2249	15	2407	16	2570	16
	$X = 87.71$ Weight % 2-Propanol							
0.1	5956	95	7424	100	8446	104	9504	107
0.02	3268	60	4196	63	4843	65	5511	67
0.01	2286	48	3040	51	3565	53	4108	55
0.002	1042	22	1392	23	1636	24	1889	25

Cal = 4.184 J

[a] Accuracy of molality within 0.05%. [b] $\overline{L}_2$, $\overline{J}_2$, cal mole^{-1}.

the appropriate coefficients presented in Tables VI and VII. The values of $\overline{L}_2$ and $\overline{J}_2$ for $X = 20.76$ and 87.71 are given in Table VIII. Determination of $\overline{L}_2$ and $\overline{J}_2$ depends on the accuracy with which the temperature coefficient of the electromotive force can be determined and is very sensitive to experimental errors. High accuracy cannot be expected for the determination of $\overline{J}_2$, because the computation of $\overline{J}_2$ involves second-order differential coefficients of the original e.m.f. data, particularly when the concentration of organic solvent (2-propanol) is high. The data obtained from calorimetric measurements are better than those derived from electromotive force measurement. The limits of error for $\overline{L}_2$ and $\overline{J}_2$ are ±30 and ±10 cal, respectively.

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Enthalpy of Formation of Bromotrinitromethane

GEORGE A. CARPENTER, MARTIN F. ZIMMER, EDWARD E. BAROODY[1], AND ROBERT A. ROBB
Naval Ordnance Station, Indian Head, Md. 20640

The energy of reaction of liquid bromotrinitromethane with diethyl phthalate as a fuel was determined in a rotating bomb calorimeter. The standard enthalpy of formation of bromotrinitromethane was calculated to be +3.22 ± 0.24 kcal per mole (estimated standard deviation of the mean) at 298.2° K. The effect of temperature on density and vapor pressure of the compound was determined at a given temperature range.

Enthalpies of formation of highly oxygenated compounds, such as bromotrinitromethane (BNF), are often determined by heat of solution techniques. This method usually requires the determination of a considerable amount of auxiliary data, thereby introducing additional experimental errors. Also, such additional data are usually applicable only for the particular compound under investigation. It is possible, but difficult, to determine enthalpies of formation by the usual calorimetric methods. The primary difficulty is the required tedious qualitative and quantitative analysis of the combustion products.

A calorimetric method developed at the Naval Ordnance Station *(10)* can be used to determine the enthalpy of formation of highly oxygenated compounds with known combustion products and standard analytical procedures. A solution of BNF (an oxidizer) and diethyl phthalate (a fuel) burns in a bomb under oxygen to form only carbon dioxide, nitrogen gas, and hydrogen bromide solution as

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[1] To whom correspondence should be addressed.

shown by the equation

$$BrC(NO_2)_3(liq) + C_{12}H_{14}O_4(liq) + 11.25\ O_2(gas) + 218.5\ H_2O(liq) \rightarrow 13\ CO_2(gas) + HBr.225\ H_2O(liq) + 1.5\ N_2(gas) \quad (1)$$

This is the equation of the idealized heat of reaction from which the enthalpy of formation of BNF at 298.2° K and 1 atm was determined in this work. Arsenous oxide solution is placed in the bottom of the bomb (*5*) to reduce any bromine gas formed to bromine ions in solution, so that bromine gas will not have to be considered as a combustion product. The energy change of bromine gas reduced to bromine ions is taken into account by arsenous oxide analysis after the experiment.

Essentially, in the calculations, the BNF-diethyl phthalate solution is treated as a compound containing carbon, hydrogen, oxygen, nitrogen, and bromine which, on combustion, forms only the products shown in Equation 1. Thus, the combustion products are known and their thermal data are well established, which eliminates the problem of determining products and product data for the determination of the enthalpy of formation of BNF. The diethyl phthalate not only desensitizes and aids in the combustion of BNF as an "auxiliary material," but it is an essential part of the reference equation. Of course, the energy of combustion of diethyl phthalate, polyethylene film, and thread used must be determined, but they are all simple carbon, hydrogen, and oxygen compounds whose energies of combustion are readily determined by the well established methods of combustion calorimetry. The thermal data for such products can conveniently be stored in a computer program.

There is still the necessity of quantitative (but not qualitative) analysis of the combustion products, as is normally done in combustion calorimetry (explained below), to verify that complete combustion has taken place and that the quantities of products agree with the theoretical amounts. The use of these analytical data in the calculation of the enthalpy of formation of BNF is limited to small correction factors, such as the heat effects of the formation of small amounts of nitric acid and the arsenous oxide–arsenic pentoxide conversion. Therefore, errors are minimized.

Since diethyl phthalate is also treated as an auxiliary compound, it is not necessary to use a stoichiometric ratio of BNF to diethyl phthalate. The actual ratio used was selected, by a series of preliminary runs, to produce a smooth, clean combustion. The optimum ratio appeared to be approximately a 50-to-50 mixture by weight.

EXPERIMENTAL

Material. BNF was synthesized at this laboratory from sodium nitroform and bromine (*6*), then purified by washing with a dilute solution of sodium bisulfite in water, followed by several washings with distilled water. The material was then dried and twice distilled (b.p. 56° C at 12 mm of Hg). The final material was checked by freezing point (f.p. = 18° C) (*6*) and refractive index ($n_D^{25} = 1.4780$, $n_D^{20} = 1.4804$) of successive fractions.

BNF is toxic and a lacrimator. It is shock-sensitive, with sensitivity increasing with impurity. It slowly decomposes at room temperature; therefore, it was kept in the solid state in a refrigerator.

Diethyl phthalate was distilled several times, and its purity checked by freezing point determinations. The energy of combustion was determined to be $\Delta E_c^\circ = -6411.64 \pm 1.66$ cal per gram.

The bags used to hold the sample were made from polyethylene film with an energy of combustion $\Delta E_c^\circ = -11078.69 \pm 0.15$ cal per gram.

The fuse used to ignite the materials was a commercial grade of cotton thread with an energy of combustion $\Delta E_c^\circ = -4050$ cal per gram (*7*).

The calorimeter was calibrated with benzoic acid, NBS sample 39h, which has a heat of combustion of 26.434 ± 0.003 absolute kilojoules per gram under certified conditions. Conversion to standard conditions (*5*) gives $\Delta E_c^\circ = -6312.96 \pm 0.72$ cal per gram, the energy of the indealized combustion reaction. ξ(calor.) was determined to be 4120.00 ± 1.05 cal per degree (mean and standard deviation for six calibration experiments).

Apparatus. The measurements were made in a platinum-lined rotating bomb calorimeter built after a design of the Bureau of Mines, Bartlesville, Okla. (*2*). In addition to the modifications to the original instrumentation previously described (*10*), the platinum resistance thermometer and Mueller bridge were replaced by a quartz thermometer with a resolution of 0.0001° C, coupled to a digital clock and a digital recorder. Calibration of the thermometer was supplied by the manufacturer.

The density measurements were made with a 5-ml Gay-Lussac pycnometer calibrated with distilled water.

Vapor pressure measurements were made with a static isoteniscope (*8*). A three-way stopcock was added to the instrument between the sample and the manometer, with the third limb connecting to a point above the opposite side of the manometer to facilitate degassing and distilling off portions of the sample. A second stopcock was added between the point of connection of the limb from the three-way stopcock and the manometer. Thus the manometer could be isolated during degassing or evaporating portions of the sample or the entire lower section could be isolated from the trap. Further, the sample bulb was connected to the instrument by means of a 14/20 ground-glass joint to simplify changing the sample. Vapor pressure–temperature points were also checked by dynamic boiling point-pressure measurements.

Procedure. The liquid BNF and diethyl phthalate were sealed in a polyethylene bag, which is resistant to organic halides. The quantities of material were chosen to give a temperature rise in the calorimeter of approximately 1.5° C. The bag was placed in a platinum crucible in the bomb. Fifteen milliliters of 0.0606*M* arsenous oxide solution were placed in the bomb. The assembled bomb was purged and pressurized to 20 atm with oxygen. (Difficulties were encountered in obtaining controlled combustion at 30-atm oxygen pressure, the pressure customarily used in bomb calorimetry.) It was then submerged in a weighed quantity of water in a bucket, which in turn was placed in a constant temperature jacket. When the temperature of the bucket reached a predetermined value, calculated to maintain the bucket temperature slightly below the jacket temperature throughout the run, the sample was ignited by means of a thread connected to a heated wire. Following ignition, the bomb was rotated to ensure a uniform final state of the products. The temperature rise was recorded prior to, during, and following the ignition.

Analytical. Complete combustions were evidenced by infrared analysis, titration of the water solution, and absorption of carbon dioxide on Ascarite. Any runs with unburned carbon were rejected. The gaseous reaction products were passed through a train of magnesium perchlorate and Ascarite to absorb water and carbon dioxide. The remaining gases were collected and checked by infrared spectra for gases produced by incomplete combustion. Also, gas samples were taken directly from the bomb without passing through any type of absorbent and were also analyzed by infrared spectra. No bromine gas was detected by the KI-starch solution test, and recovery of carbon dioxide was better than 99% in all cases. The NO_3^- was reduced to ammonia by Devarda's alloy and the ammonia was distilled into excess standardized HCl. The total acidity of the bomb washings was determined by titration with NaOH after carbon dioxide had been removed by boiling, using phenolphthalein as an indicator. The As^{-3} ions in solution after combustion were analyzed by titration with standardized $KMnO_4$.

Comparison Experiments. The calibration of the calorimeter with standard benzoic acid does not allow for the use of arsenous acid solutions in the bomb. To reduce the data to standard states, the solubility and heat of solution of carbon dioxide in solutions of arsenous oxide, arsenic pentoxide, and hydrobromic acid are necessary, but cannot be obtained by the standard calibration procedures. Therefore, the energy equivalent of the calorimeter was determined by a series of comparison experiments for which benzoic acid was used (*2*). The amounts were adjusted to evolve nearly the same energy and quantity of carbon dioxide as in the combustion experiments.

RESULTS AND DISCUSSION

All data reduction for the combustion experiments was performed by a digital computer (*1*). The auxiliary data used for the calculations are given in Table I. The data and calculations of the heats of reaction and formation are summarized in Table II. To calculate enthalpy of formation of BNF, the following enthalpies of formation were used: $CO_2(g) = -94{,}051.8$ cal per mole; $H_2O(l) = -68{,}317.5$ cal per mole; and $HBr.225\ H_2O(l) = -28{,}878$ cal per mole.

The density of BNF was determined between 18° and 55° C. The plot of density *vs.* temperature gave a straight line with the equation

$$d = -0.00194\,t + 2.0732 \qquad (2)$$

Table I. Density, Heat Capacity, and $(\delta E/\delta P)T$ for Bromotrinitromethane and Auxiliary Materials

	Density, G/Ml	C_p Cal/ Deg G	$(\delta E/\delta P)T$, Cal/Atm G
Bromotrinitromethane	2.025[a]	0.21[b]	−0.0028[b]
Diethyl phthalate	1.123[c]	0.40[c]	−0.0063[c]
Polyethylene bag	0.9[a]	0.31[b]	−0.0008[b]
Thread	1.5[d]	0.40[e]	−0.007[b]

[a] Determined by authors. [b] Estimated. [c] (*3*). [d] (*7*). [e] (*5*).

where d = density in grams per ml and t = temperature in ° C.

The vapor pressure was determined from 45° to 62° C. The plot of the log of the vapor pressure *vs.* $1/T$ gave a straight line with the equation

$$\text{Log}_{10}P = -\frac{2496.32}{T} + 8.6652 \qquad (3)$$

where P = pressure in millimeters of Hg corrected to 0° C, T = temperature in ° K. The heat of vaporization, L_e, at 25° C, estimated from Equation 3, is 11.41 kcal per mole.

Br—C Bond Energy. To estimate the C—Br bond energy in bromotrinitromethane, the following hypothetical reaction is considered:

$$(NO_2)_3CBr(g) + \tfrac{1}{2}\,H_2(g) \rightarrow (NO_2)_3CH(g) + \tfrac{1}{2}\,Br_2(g) \qquad (4)$$

Thus:

$$\Delta H_r = \Delta H_f(NO_2)_3CH(g) - \Delta H_f(NO_2)_3CBr(g) = E(\text{C—Br}) + \tfrac{1}{2}\,E(\text{H—H}) - \tfrac{1}{2}\,E(Br_2) - E(\text{C—H})$$

The following bond energies, in kilo calories per mole, were used:

$\tfrac{1}{2}\,E(\text{H—H})$ (*10*) = 52.09
$\tfrac{1}{2}\,E(\text{Br—Br})$ (*10*) = 23.2
$E(\text{C—H})$ (*10*) = 99.297

With the estimated heats of vaporization L_e = 13.1 kcal per mole for trinitromethane (NF) and L_e = 11.41 kcal per mole for BNF, the enthalpies of formation for the gaseous NF and BNF are −3.15 and +14.63 kcal per mole, respectively. Thus the bond energy for the bromo-carbon bond in BNF is $E(\text{C—Br})$ = 52.63 kcal. The C—Br bond energy in bromomethane has been reported as 70 kcal (*4*). For comparison purposes, some properties of the halogen compounds of the trinitromethane series as determined in this laboratory are listed in Table III.

Table II. Summary of Calorimetric Data for Bromotrinitromethane

	Run No.					
	97694	97695	97698	97699	03826	93827
m'(cpd), g	0.804316	0.899568	0.874051	0.835985	0.858207	0.839982
m''(diethyl phthalate), g	0.814103	0.831304	0.862260	0.752224	0.855092	0.846048
m'''(polyethylene), g	0.126975	0.115588	0.122549	0.116292	0.121330	0.129279
m''''(fuse), g	0.008211	0.008516	0.008201	0.008116	0.008901	0.008642
$n^i(H_2O)$, moles	0.82772	0.82015	0.80615	0.81595	0.80823	0.80867
$\Delta t_c\, t_f - t_i - \Delta t_{corr}$), deg	1.7124	1.7194	1.7854	1.5918	1.7684	1.7738
Δt_{corr}, deg	0.0216	0.0215	0.0209	0.0242	0.0209	0.0204
ξ(calor.)$(-t_c)$, cal	−7055.05	−7084.03	−7356.01	−6558.14	−7285.68	−7307.99
ξ(cont.)$(-t_c)$, cal	−29.18	−29.12	−29.83	−26.77	−29.60	−29.70
ΔE_{ign}, cal	0.91	0.91	0.95	0.95	0.95	0.95
ΔE, corr st. states, cal	10.27	10.51	10.75	9.62	10.65	10.68
ΔE_{dec} (HNO_3), cal	20.22	16.40	14.66	14.88	14.85	10.40
ΔE_{dec} As_2O_5, cal	60.03	67.90	82.35	70.93	74.72	75.16
$n''\ \Delta E_c^\circ$ (diethyl phthalate), cal	−5219.74	−5330.02	−5528.50	−4822.99	−5482.54	−5424.56
$n'''\ \Delta E_c^\circ$ (polyethylene), cal	−1406.72	−1280.56	−1357.68	−1288.36	−1344.18	−1432.24
$n''''\ \Delta E_c^\circ$ (fuse), cal	−33.25	−34.49	−33.21	−32.87	−36.05	−35.00
ΔH_c, kcal	−1518.16	−1518.12	−1517.05	−1517.64	−1517.07	−1518.39
ΔE_c, kcal	−1520.09	−1520.04	−1518.98	−1519.56	−1519.00	−1520.32
ΔH_f°, kcal/mole	+3.64	+3.60	+2.53	+3.12	+2.55	+3.88
Average						
ΔH_c, kcal	−1517.74 ± 0.24[a]					
ΔE_c, kcal	−1519.66 ± 0.24					
ΔH_f°, kcal/mole	+3.22 ± 0.24					

Table III. Properties of Trinitromethane Compounds

	$(NO_2)_3CH$	$(NO_2)_3CF$	$(NO_2)_3CCl$	$(NO_2)_3CBr$
Density, g/ml	1.59 (24° C)	1.595 (20° C)[a]	1.66 (20° C)	2.034 (20° C)
Melting point, ° C	+27–28	−29	+5.7	+18
Heat of vaporization, kcal per mole	13.1 (25°)	8.171 (25°)	10.86 (25° C)	11.41 (25° C)
Enthalpy of formation, kcal per mole	−16.25 ± 0.75	−51.99 ± 0.48	−5.57 ± 0.18	+3.22 ± 0.24
Estimated halogen-carbon bond energy, kcal	. . .	10.35	73.2	52.63

[a] Through oversight densities of trinitrofluoromethane are reported incorrectly in *(11)*. The first digits (.7 and .6) in the density series should read 5 and 4—i.e., 1.595 instead of 1.795; 1.489 instead of 1.689.

NOMENCLATURE

m = mass of (′)compound, (″)auxiliary material, (‴)polyethylene film, and (⁗)fuse, grams

n = number of moles of (′)compound, (″)auxiliary material, (‴)polyethylene film, and (⁗)fuse

n^i = initial number of moles of water in bomb

t_i = initial temperature of calorimeter, ° C

t_f = final temperature of calorimeter, ° C

t_h = reference temperature to which combustion reaction is referred (25° C)

Δt_{corr} = rise in temperature of calorimeter due to thermal leakage of outer jacket

Δt_c = $t_f - t_i + \Delta t_{corr}$

ξ(calor.) = energy equivalent of calorimeter, cal per deg

ξ(cont.) = energy equivalent of contents, cal per deg [ξ^i (cont.)$(t_i - 25)$ + ξ^f (cont.)$(25 - t_f + \Delta t_{corr})$ where ξ^i (cont.) and ξ^f (cont.) are energy equivalents of contents before and after combustion, respectively]

ΔE_{ign} = energy released due to ignition, cal

ΔE_{corr} st. states = energy reduction to standard states, cal *(5, 7)*

ΔE_{dec} (HNO_3) = energy released from formation of nitric acid, cal

ΔE_{dec} (As_2O_5) = energy released from formation of As_2O_5, cal

ΔE_c° = standard energy of idealized combustion reaction, calories per mole

ΔH_c = heat of reaction between 1 mole of diethyl phthalate + 1 mole of bromotrinitromethane, oxygen, and water as given in Equation 1 at constant pressure, kcal

ΔE_c = energy of reaction between 1 mole of diethyl phthalate + 1 mole of bromotrinitromethane, oxygen, and water as given in Equation 1 at constant volume kcal

ΔH_f° = enthalpy of formation of bromotrinitromethane, kcal per mole

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Natural Convection Heat Transfer from a Horizontal Cylinder to a Reacting Gas

$N_2O_4 \rightleftarrows 2NO_2$ System

FRANK T. BROWN[1], BOO-GOH ONG, and DAVID M. MASON
Department of Chemical Engineering, Stanford University, Stanford, Calif. 94305

The transfer of heat between a solid surface and a fluid may be significantly affected by the occurrence of a homogeneous chemical reaction in the fluid and/or a heterogeneous reaction on the surface of the solid. The general problem of transport in reacting systems is discussed by Brokaw *(3)*, Brokaw and Butler *(4)*, and Rosner *(8)*. In a reacting medium, temperature gradients induce concentration gradients, causing diffusion of the reacting species. In this diffusional process, the enthalpy of each species is transported, making a major contribution to the thermal conductivity, and thus to heat transfer when the enthalpy of reaction is large.

Values of the equilibrium thermal conductivity of the N_2O_4 system, which is a nonmonotonic function of temperature, are presented by Svehla and Brokaw *(9)*. The rate of dissociation of N_2O_4 is so large that for all subsonic-flow regimes at pressures above 0.1 atm the system is effectively at equilibrium and thus the equilibrium proper-

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[1] *Present address,* Monsanto Co., Springfield, Mass. 01101.