Figure 1. Plot of log D vs. $1/T$ for near-saturated potassium sulfate solutions

Figure 2. Plot of $D\eta$ vs. temperature for potassium sulfate

molecules through nonelectrolytes. However, a similar empirical equation has also been found to exist in certain concentrated electrolyte systems over a limited range of temperature and concentration (7). This gives rise to a useful working correlation which is particularly valuable considering the lack of diffusivity data and the complexity of theoretical equations for electrolytes (4). Figure 2 shows a plot of $D\eta$ against t, the temperature in degrees centigrade and gives rise to a correlation of the form:

$$D\eta \times 10^8 = 8.1 + 0.071\, t$$

In this plot, the viscosity values are in poises and are available in the literature (5). The correlation is suitable for calculating differential diffusivity values for this system at concentrations approaching saturation and over the temperature range, 15–50° C.
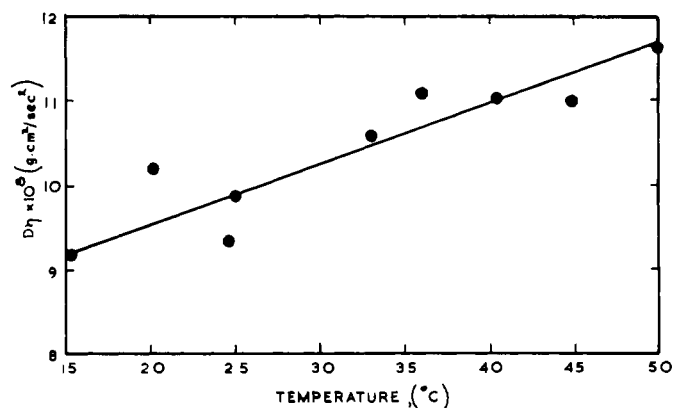
LITERATURE CITED

(1) Creeth, J.M., *J. Am. Chem. Soc.* **77**, 6428 (1955).
(2) Emanual, E., Olander, D.R., J. CHEM. ENG. DATA **8**, 31 (1963).
(3) Gillam, D.G., *Aust. J. of Sci. Res.* **4A**, 84 (1951).
(4) Harned, H.S., Nuttall, R.L., *J. Am. Chem. Soc.* **71**, 4155 (1952).
(5) International Critical Tables, 1st ed., Vol. V, p. 17, McGraw-Hill, New York, 1926.
(6) Longsworth, L.J., *J. Am. Chem. Soc.* **74**, 4155 (1952).
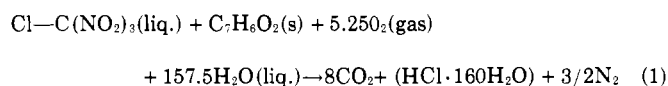(7) Mullin, J.W., Cook, T.P., *J. Appl. Chem.* **13**, 423 (1963).

Heat of Formation of Trinitrochloromethane by Combustion Calorimetry

M. F. ZIMMER, E. E. BAROODY, MARVIN SCHWARTZ, and M. P. McALLISTER
Research and Development Department, U. S. Naval Propellant Plant, Indian Head, Md.

The energy of combustion of liquid trinitrochloromethane with benzoic acid as fuel was determined in a rotating bomb calorimeter. The standard heat of formation at 25° C. was calculated using a computer program which has been developed for compounds containing C, H, O, N, and Cl. The heat of formation of trinitrochloromethane is −5.57 ± 0.18 kcal./mole (±0.18 is estimated standard deviation of the mean). Some other properties—such as vapor pressure, latent heat of vaporization, density, refractive index, freezing point, surface tension, and heat capacity—for better characterization of trinitrochloromethane were also measured and are reported.

THE REACTION was carried out in an oxygen atmosphere using benzoic acid as the fuel. The equation of the idealized heat of reaction from which the heat of formation is determined is:

$$Cl—C(NO_2)_3(liq.) + C_7H_6O_2(s) + 5.250_2(gas)$$

$$+ 157.5H_2O(liq.) \rightarrow 8CO_2 + (HCl \cdot 160H_2O) + 3/2N_2 \quad (1)$$

Difficulties were encountered in determining the proper ratio of trinitrochloromethane to benzoic acid for a complete reaction; 45% trinitrochloromethane produced a clean combustion. Noticeable amounts of carbon and, in some instances, unburned trinitrochloromethane appeared in the bomb after the combustion if the trinitrochloromethane content was under 45%. Chlorine gas liberated in the reaction was converted to the chloride ion by adding arsenious acid solution to the bomb (8).

EXPERIMENTAL

Material. Trinitrochloromethane was synthesized and purified by distillation and vapor-liquid chromatography. No impurity was detected by either the gas chromatograph or

the IR spectrophotometer. The following properties were measured for the trinitrochloromethane.

Density: 1.66 grams/ml. at 20° C.
Freezing point: + 5.75° C.
Refractive index at 25° C.: 1.4471
Vapor pressure at several temperatures, T:
    T = 26.80° C., 5.35 mm.Hg
    T = 45.51° C., 19.80 mm.Hg
    T = 53.50° C., 30.30 mm.Hg
    T = 59.65° C., 41.50 mm.Hg
Heat of vaporization: 10.86 kcal./mole 25° C.
Surface tension: γ 20° C. = 34.2 dynes per cm.
Heat capacity: 0.21 cal./gram degree

The density was measured with a 2-ml. pycnometer (calibrated at 25° C.). Variation of the pycnometer volume with temperature was corrected (5).

The freezing point was obtained from freezing curves and determined by a technique developed by the National Bureau of Standards (6). The uncertainty of the method was ±0.05° C. The uncertainty of the refractive index (measured with a Baush and Lomb refractometer) was ±0.0003. The vapor pressure was measured in a tensiometer using standard procedure, the pressure being read with a cathetometer. The second digits were estimated.

The surface tension was measured by the maximum bubble pressure method using a Cassel Surface Tensiometer (2, 7). The uncertainty of the measurements was ±0.1 dyne/cm. The heat capacity was determined with an uncertainty of ±0.02 cal./gram degree. The uncertainties are estimated standard deviations of the mean.

The benzoic acid used for calibration of the calorimeter and as a fuel in the combustion experiment was a standard sample 39h of the National Bureau of Standards, having a certified heat combustion of −6318.3 cal./gram mass in vacuum. The fuse was an unmercerized cotton thread ($\Delta Ei/M = -4050$ cal./gram). The bag to contain the sample was made from a polyester film, 100 gage, Mylar type, and the value of $\Delta Ei/M$ was −5459.41 cal./gram.

Apparatus. The combustion experiments were carried out in a rotating bomb calorimeter built after a design of the Bureau of Mines, Bartlesville, Okla. (4). The modifications to the original instrumentation were that the ignition circuit was modified to provide a constant current ignition pulse, a precision timer was installed to program the ignition current, and the jacket heater circuit was modified to obtain a constant jacket temperature of ±0.002° C.

The bomb(fabricated from stainless steel) has a 0.030-inch thick platinum lining. The internal fittings, including the gas inlet tube, electrodes, crucible, and gimbal were made of platinum. The sealing gasket was of fine gold (1/16 inch thick).

The average deviation from the mean in these measurements was 0.035%, and the maximum deviation was 0.059%. The temperature increments were measured with a platinum resistance thermometer and a Mueller bridge for precision resistance measurements accurate to 0.001° C.

Procedure. The ratio of trinitrochloromethane(CNF) to benzoic acid was 45 to 55. The liquid CNF was sealed in a polyester film which is resistant to organic halides, and the benzoic acid was pressed into pellets. The quantities of material were chosen to give a temperature rise in the calorimeter of approximately 1.5° C. Both the benzoic acid and the CNF in the polyester bag were placed in the platinum crucible of the bomb. Ten milliliters of 0.000849M arsenious acid solution were placed in the bomb. The assembled bomb was closed, purged, and pressurized to 30 atm. with oxygen, placed in a constant temperature jacket, and allowed to come to thermal equilibrium. When the temperature of the bucket reached a predetermined value, the sample was ignited, and the temperature rise was observed. During this period, the bomb was rotated to ensure a uniform final state of the products.

Analytical. Evidence for the complete combustion of the trinitrochloromethane was obtained by infrared analysis of the gaseous reaction products. The spectrum showed only carbon dioxide. This method, of course, is limited to molecules with dipole moments. Since chlorine is not detected by the IR spectrophotometer, the gaseous reaction products were vented into a vacuum system and passed through a starch-KI solution. Thus, incomplete combustions, according to Equation 1, were easily noted by the presence of either nitrogen oxides or chlorine in the gas phase, and the runs were rejected. The carbon dioxide resulting from the combustion was also determined by absorption on Ascarite within 2% of the calculated value. Chloride concentration in the final bomb solution was determined by the Volhard method. The NO_3^- and any NO_2^- were 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 CO_2 had been removed by boiling and using phenolphthalein as indicator. The As^{-3} ions (in the solution after combustion) were analyzed by titration with standardized $KMnO_4$. The analysis showed that 8 to 27% of the chlorine in CNF burned to Cl_2, which was then converted to HCl by H_3AsO_3.

Comparison Experiments. The calibration of the calorimeter with standard benzoic acid does not allow the use of arsenious acid solutions in the bomb. To reduce data to standard states, the solubility and heat of solution of carbon dioxide in solutions of arsenious oxide, arsenic oxide, and hydrochloric 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 n-hexadecane and benzoic acid were used (4). The amounts were so adjusted as to evolve nearly the same energy and quantity of carbon dioxide as in the combustion experiments.

Results. Table I lists the measurements. The heats of formation are summarized in Table II. The heat of reaction at 25° C. is −866.883 kcal./mole and has an uncertainty of ±0.172 kcal./mole (estimated standard deviation of the mean). To calculate the heat of formation of CNF, the following heats of formation for CO_2 = −94051.8 cal./mole and H_2O = −68317.5 cal./mole were used.

The calculations were made on a RCA 501 digital computer for which a special program has been developed (1). The estimated standard deviation of the mean is ±0.18 kcal./mole. Using Equation 2, the heat of formation of CNF was estimated to be ±0 kcal./mole.

$$\Delta H_f = -\sum_i n_i q_i + \sum_j (\Delta H_A) j \qquad (2)$$

Table I. Values of Density, Heat Capacity, and $(\delta E/\delta P)_T$ of Trinitrochloromethane and Auxiliary Material

	Density, Grams/Ml.	c_p, Cal./ Degree-Gram	$(\delta E/\delta P)_T$, Cal./Atm.-Gram
$Cl\text{-}C(NO_2)_3$	1.66	0.210	...
Benzoic acid	1.2659	0.289(4)	0.0028(4)
Hexadecane	0.7751	0.495	...
Mylar bag	1.38(9)	0.315(9)	0.0008(9)
Thread	1.5 (9)	0.40 (9)	0.007 (3)

Table II. Heats of Formation of Trinitrochloromethane

Run No.	ΔH_f
39,751	−5.50
39,760	−4.99
39,763	−5.61
39,766	−6.09
39,769	−5.68
Av.	−5.57

where n_i and q_i are the numbers and bond energies of the i-th bond in the molecule and $(\Delta H_A)j$ the heat of formation of the j-th gaseous atoms produced by complete decomposition of the compound. The bond energies for $C-NO_2$ were calculated from the heat of formation of $C(NO_2)_4(3)$ assuming that the bond energies in both molecules, CNF and $C(NO_2)_4$ are approximately the same. The difference of the two heats of formation, the measured one $- 5.57$ kcal./mole and the estimated one ± 0 kcal./mole, is probably due to the fact that the $C-Cl$ bond is influenced by the three nitro groups and vice versa. Using the same bond energies for $C-NO_2$ in CNF as in $C(NO_2)_4$, the bond energy for $Cl-C$ in CNF was calculated from the measured heat of formation to be 72.8 kcal./mole as compared with 78.3 kcal./mole for the reported value (10).

Probably the largest source of error is the determination of the arsenic oxide formed by converting Cl_2 in Cl. Another source of error is the estimation of the nitric acid formed from the CNF compound besides the nitric acid formed by oxidation of nitrogen. Some data are still unavailable on the combustion of chlorine compounds in the presence of arsenious acid. If these errors lie in the range of 5 cal. per mole, the heat of formation changes approximately within 1 kcal./mole.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Baroody, E.E., Wynne, J., Zimmer, M.F., U.S. Naval Propellant Plant NavWeps Report 8686, Tech. Rept. 154, 1964.
(2) Cassel, H.M., U.S. Patent 2, 448,768 (Sept. 7, 1948).
(3) Gardener, D.N., Grigger, J.G., J. Chem. Eng. Data 8, 73 (1963).
(4) Good, W.D., Scott, D.W., Waddington, G., J. Phys. Chem. 68, 1080 (1956).
(5) Jasper, J.J., "Laboratory Methods of Physical Chemistry," pp. 36-9, Riverside Press, Cambridge, Mass., 1947.
(6) Glasgow, P.R., Jr., Streiff, A.J., Rossini, F.D., J. Res. Nat. Bur. Std. 35, 355 (1945).
(7) Harvis, N.L., Zisman, W.A., NRL Rept. 5306, 1959.·
(8) Rossini, F.D., "Experimental Thermochemistry," pp. 90, 107, Interscience, New York, 1956.
(9) Skinner, H.A., Ibid., Vol. II, p. 25-8, Interscience, New York, 1962.
(10) Wilkins, R.L., "Theoretical Evaluation of Chemical Propellants," p. 125, Prentice-Hall, Englewood Cliffs, N.J., 1963.

Compressibilities of Liquid Methyl Borate

RICHARD G. GRISKEY and LAWRENCE N. CANJAR[1]
Virginia Polytechnic Institute, Blacksburg, Va.

No liquid density data for methyl borate has been reported other than some orthobaric values. The present work measured compressibilities of liquid methyl borate from 180 to 209.79° C. and pressures from 17.00 to 40.00 atmospheres.

VAPOR PRESSURES of methyl borate have been measured by Webster and Dennis (7), Hansen and Hughes (4), and Griskey, Gorgas, and Canjar (3). The third set of investigators also measured compressibilities of the superheated vapor. No liquid density data were reported other than some orthobaric densities given by Hansen and Hughes (4).

The present work used an apparatus that was a modification of the design of Keyes (5) and Beattie (1). A detailed description of the apparatus has been published by Cherney, Marchman, and York (2) except for certain changes reported by Li and Canjar (6).

The methyl borate was prepared from 99.9% pure material in the apparatus depicted in Figure 1. A third of the material was distilled in the presence of sodium from flask B to flask 2 where it was condensed. Next, the middle third of the original sample was distilled and

condensed in flask 3. This portion was solidified by a dry ice-acetone mixture, evacuated, melted, resolidified, again evacuated, and melted once more. The sample was then transferred to ampules (4, 5), condensed by the dry ice-acetone mixture, evacuated, solidified, and sealed.
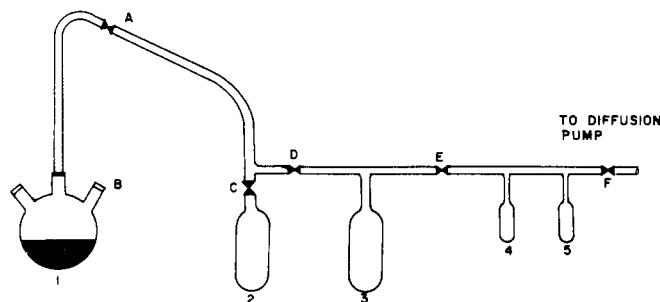

Figure 1. Methyl borate charging apparatus

[1] Present address: Carnegie Institute of Technology, Pittsburgh 13, Pa.