(4) Finke, H.L., Gross, M.E., Messerly, J.F., Waddington, G., *J. Am. Chem. Soc.* **76**, 854 (1954).
(5) Guthrie, G.B., Jr., Scott, D.W., Hubbard, W.N., Katz, C., McCullough, J.P., Gross, M.E., Williamson, K.D., Waddington, G., *Ibid.*, **74**, 4662 (1952).
(6) Hubbard, W.N., Finke, H.L., Scott, D.W., McCullough, J.P., Katz, C., Gross, M.E., Messerly, J.F., Pennington, R.E., Waddington, G., *Ibid.*, **74**, 6052 (1952).
(7) Janz, G.J., "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, New York, 1967.
(8) Justice, B.H., Ph.D. dissertation, University of Michigan, Ann Arbor, Mich., 1961; USAEC Rept. **TID 12722** (1961).
(9) McCullough, J.P., Douslin, D.R., Hubbard, W.N., Todd, S.S., Messerly, J.F., Hossenlopp, I.A., Frow, F.R., Dawson, J.P., Waddington, G., *J. Am. Chem. Soc.* **81**, 5884 (1959).
(10) McCullough, J.P., Sunner, S., Finke, H.L., Hubbard, W.N., Gross, M.E., Pennington, R.E., Messerly, J.F., Good, W.D., Waddington, G., *Ibid.*, **75**, 5075 (1953).
(11) Meyer, R., chemistry dissertation (D. E. S.), University of Aix-Marseille, France, 1963.
(12) Pennington, R.E., Finke, H.L., Hubbard, W.N., Messerly, J.F., Frow, F.R., Hossenlopp, I.A., Waddington, G., *J. Am. Chem. Soc.* **78**, 7055 (1956).
(13) Phan Tan Luu, P., Chemistry Department, University of Aix-Marseille, France, personal communication, October 1967.
(14) Roussel, P., Metzger, J., *Bull. Soc. Chim. France* **1962**, 2075.
(15) Scheinker, N., Kouchkin, V.V., Postovskiĭ, I., *Zh. Fiz. Khim.* **31**, 214 (1957).
(16) Scott, D.W., Berg, W.T., Hossenlopp, I.A., Hubbard, W.N., Messerly, J.F., Todd, S.S., Douslin, D.R., McCullough, J.P., Waddington, G., *J. Phys. Chem.* **71**, 2263 (1967).
(17) Soulié, A., University of Aix-Marseille, France, personal communication, October 1967.
(18) Szasz, G.J., Morrison, J.A., Pace, E.L., Aston, J.G., *J. Chem. Phys.* **15**, 8 (1947).
(19) Vincent, E.J., Phan Tan Luu, P., Metzger, J., *Bull. Soc. Chim. France* **1966**, 3530.
(20) Waddington, G., Knowlton, J.W., Scott, D.W., Oliver, G.D., Todd, S.S., Hubbard, W.N., Smith, J.C., Huffman, H.M., *J. Am. Chem. Soc.* **71**, 797 (1949).
(21) Westrum, E.F., Jr., *J. Chem. Educ.* **39**, 443 (1962).

RECEIVED for review February 8, 1968. Accepted May 31, 1968.

Some Thermodynamic Properties of High Purity Dimethyl Terephthalate

JOHN H. ELLIOTT and MARJORIE D. CHRIS
Research Center, Hercules, Inc., Wilmington, Del. 19899

To use the freezing point as a criterion of purity of 99.9+ mole % dimethyl terephthalate (DMT), its freezing point with zero impurity (t_{f_0}) was determined by the method of Schwab and Wichers. t_{f_0} in equilibrium with 1 atm. of N_2 is 140.655° ± 0.002° C.; in equilibrium with 1 atm. of air, 140.648° ± 0.002° C. on the international practical temperature scale. Its heat of fusion is 7560 cal. per mole, giving a cryoscopic constant of 0.0228 mole fraction per degree C. These results enable the purity of DMT to be estimated to 0.005 mole % by platinum resistance thermometry. The heat capacity of DMT from 30° to 200° C. was determined using an adiabatic calorimeter. The triple point of DMT is estimated to be 140.636° ± 0.004° C., and the variation of its freezing point with pressure is 0.042° C. per atmosphere. Thermometric cells, based on freezing DMT, maintain a temperature which is constant to 0.002° C. for at least 2 hours and are stable after prolonged heating at 155° C. and after 11 years' aging.

DIMETHYL TEREPHTHALATE (DMT), a large volume industrial chemical, is an important intermediate in the manufacture of polyesters. For this use, high purity (99.9+ mole %) is essential. The freezing point, t_f, of DMT is a commonly used criterion of purity. For this criterion to be meaningful, however, it is necessary to know the freezing point with zero impurity t_{f_0}, and the cryoscopic constant.

The lack of literature data on t_{f_0} or the cryoscopic constant prompted the present report of an extensive investigation of some thermodynamic properties of DMT which was carried out in our laboratories some years ago. The major portion of this paper deals with the establishment of t_{f_0} and the auxiliary data necessary to use the freezing point of DMT as a quantitative measure of purity. Certain other thermodynamic properties of DMT which were measured during the course of this work are included.

These studies demonstrated that DMT is a useful secondary thermometric standard. The preparation, reproducibility, and stability of thermometric cells employing DMT are discussed.

EXPERIMENTAL

Temperatures, on the international practical temperature scale (*11*), were measured by means of platinum resistance thermometers in conjunction with a Mueller bridge, a d.c. amplifier, and a recording potentiometer. Details of the equipment and calibrations are given below.

The Mueller bridge was the Leeds & Northrup Model G-2, reading in absolute ohms. It was calibrated by the National Bureau of Standards and this calibration was checked frequently with a standard 10.0099-ohm resistor (Leeds & Northrup), certified by both Leeds & Northrup and the National Bureau of Standards. Within the range of interest, bridge corrections never exceeded 0.0002 ohm or 0.002° C.

The detection circuit, in lieu of the usual galvanometer, was a Liston-Becker Model 14 d.c. amplifier and a Brown electronic strip chart recorder. The output of the amplifier was connected to the recorder through a 50-ohm attenuator. The recorder (50-mv., full scale) was modified so that the null point was at mid-scale. This measuring arrangement was stable and not affected by mechanical vibration. By suitable adjustment of the attenuator and amplifier gain controls, the desired sensitivity was obtained. All measurements were made with a bridge temperature of 35.0° C. and a bridge current of 2.0 ma., the current used by the National Bureau of Standards in calibrating the thermometers.

The platinum resistance thermometers were constructed by the late C. H. Meyers, Arlington, Va. These were calibrated by the National Bureau of Standards and its constants for the Callendar-Van Dusen equation (*13*) were used in the temperature calculations.

The resistance of a platinum resistance thermometer at the ice point, R_0, must be determined frequently, as it changes slightly as strains are relieved in the platinum coil. Suitable ice baths for the determination of R_0 were prepared by slowly cooling distilled water, with stirring, until a slush of ice was formed, which was then placed in a Dewar flask and R_0 measured (*10*). The preparation of the slush involved a good bit of art and was time-consuming. Consequently a water triple point cell (J. and J. Instrument Co., Silver Spring, Md.) was used. The triple point of water has been fixed as 0.0100° C. (*9*). A comparison of the resistance at the triple point of water and R_0, for three thermometers over a period of 4 months, showed differences between these points of 0.0010 to 0.0011 ohm, corresponding to 0.010° C. R_0 was subsequently determined by subtracting 0.0011 ohm from the resistance measured in the triple point cell.

As an additional check on the precision and accuracy of the thermometry, the temperature of a National Bureau of Standards benzoic acid thermometric standard (cell 52, 122.357° ± 0.003° C.) was determined every time R_0 was measured. In all cases the measured temperature of this standard fell within the certified range.

The freezing point of DMT with zero impurity, t_{f_0}, was established using the method of Schwab and Wichers (*6*, *7*). This method involves the comparison of corresponding portions of two time-temperature freezing curves, the first being that of a highly pure sample which, however, still contains an unknown mole fraction impurity, x. The second is that of the same material with a known added impurity of mole fraction a, or a total mole fraction impurity of $(x + a)$. The freezing curves must be run under highly reproducible conditions for this method to be valid. The cell used in these determinations (Figure 1) was securely mounted in a well stirred oil bath. The temperature of the bath, located in a constant temperature room at 25° C., was maintained constant to ± 0.05° C. to ensure a constant thermal head during the freezing of the DMT. The jacket of the cell was evacuated to 4 to 5 microns by means of an oil diffusion pump and a mechanical fore pump. Agitating gas was passed at a constant rate through the frit at the bottom of the freezing tube to provide uniform agitation. DMT (70 grams) was charged into the tube and melted by passing a current through the heating tape. Before freezing, the Nichrome stirrer was lifted into the vapor space above the sample where some DMT condensed on it, thus, providing seed crystals. During the freezing, the stirrer was occasionally raised and lowered to make sure that no solid DMT accumulated on the thermometer. Agitation by the gas stream remained uniform for 3½ to 4 hours after the onset of freezing.

Repeated melt-freezes were done on the sample until peak readings checked to within 0.00005 ohm, indicating the removal of all volatile impurities. The final time-temperature curve was allowed to record for 3 to 4 hours. The sample was then remelted and the impurity, accurately weighed on a microscope cover glass, introduced. A time-temperature curve on the sample plus impurity was then recorded in exactly the same manner as before.

Heat capacity and heat of fusion measurements were made in an adiabatic calorimeter. Its design and operation are described in detail (*4*, *12*). A charge of 57.78 grams was used and heated in approximately 15° C. steps. Accuracy of the electrical measurements is estimated to be 0.2%, temperature differences 0.5%, and heat capacity 2%. The heat capacity of the empty calorimeter was approximately twice that of the sample.

Thermometric cells (Figure 2) followed the design of the National Bureau of Standards benzoic acid cells. The cells were filled with vacuum-sublimed DMT using the

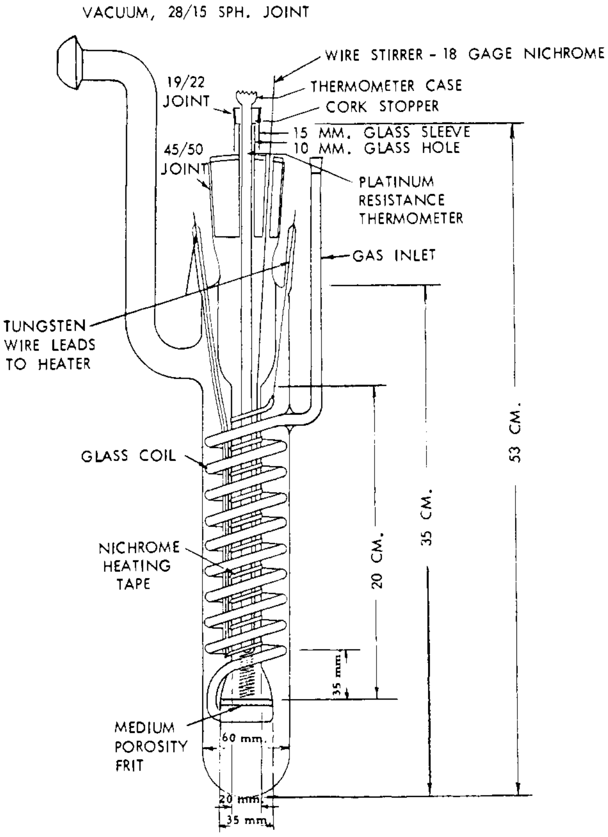

Figure 1. Modified Schwab and Wichers cell for t_{f_0} determination of DMT

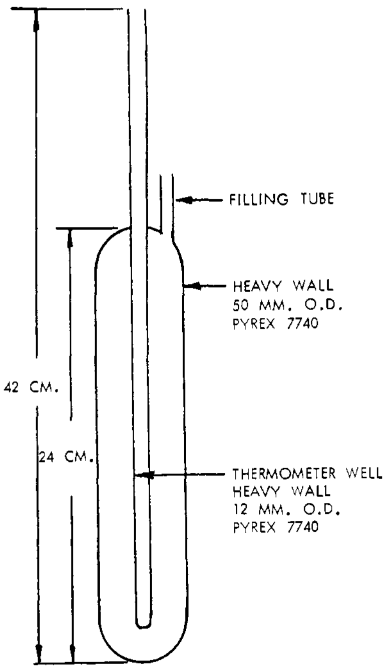

Figure 2. DMT thermometric cell

arrangement shown in Figure 3. After 300 to 400 grams of DMT had been sublimed into the 500-ml. flask, the pressure in the system was raised to approximately 100 mm. of Hg and the DMT melted into the thermometric cell. The DMT in the cell was then melted and frozen several times at 10 mm. of Hg pressure (the vapor pressure of DMT at its freezing point). A partial pressure of N_2 was added before sealing to minimize "hammering" during the freezing operation. The variation of the freezing point with pressure, dT_f/dp, was measured in a thermometric cell while still attached to the pressure system. The DMT in the cell was melted and frozen several times at its vapor pressure to remove volatile impurities. After an equilibrium freezing temperature was reached, the pressure over the DMT was increased with N_2. Care was taken not to agitate the cell, so that the N_2 dissolved in the DMT only at the gas-liquid interface. Within a few minutes of the pressure increase, a new temperature equilibrium was established. This procedure was repeated at several different pressures. Finally, the cell was re-evacuated to 10 mm. of Hg, at which the temperature was found to decrease to the initial freezing temperature.

MATERIALS

The DMT used in this work were laboratory and production lot samples of DMT produced by Hercules Inc. and several samples from E. I. du Pont de Nemours & Co., Inc. All samples showed a purity of 99.93+ mole % by freezing point.

Methyl *p*-toluate and anthracene were used as added impurities in the determination of t_{f_0}. The methyl *p*-toluate, a Hercules production sample, was distilled through a column having 100 theoretical plates, packed with stainless steel helices, at a pressure of 100 mm. of Hg and a reflux ratio of 100 to 1. No component other than methyl *p*-toluate was detected by ultraviolet analysis.

Anthracene (Eastman Kodak Co.) was used without further purification. Agitating gases were lamp grade nitrogen from the Cleveland Wire Works and Linde compressed air.

RESULTS AND DISCUSSION

Preliminary Experiments. It is necessary to know t_{f_0} and to measure t_f to ±0.002° C. to estimate purity to 0.005 mole %. A number of measurements were made using the apparatus involving mechanical agitation, described by Glasgow, Streiff, and Rossini (*2*) employing their method of extrapolation to obtain t_f and t_{f_0}. This method gave satisfactory results for t_f, but the desired precision (±0.002° C. maximum) in t_{f_0} could not be obtained. This is due to the nature of the extrapolation procedure, which requires temperature measurements to be made to one or two more significant figures than the number desired in t_{f_0}.

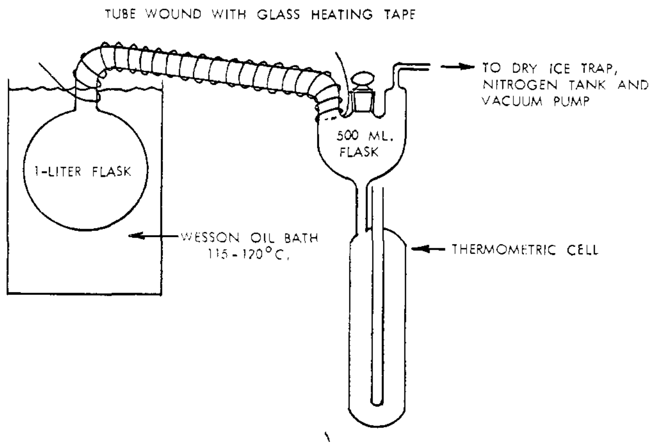

Figure 3. Vacuum sublimation apparatus for filling DMT thermometric cells

Attempts were made to determine t_{f_0} using White's method (*14*). Here, the complete time-temperature curve is obtained and t_{f_0} is determined from the temperature at which the sample is one-half frozen. Difficulties were encountered in estimating the fraction of the DMT frozen, and this approach was abandoned. In this work, and for the determination of t_f on a large number of samples, a freezing point cell agitated by pulsating N_2 pressure was used, which was a concentric modification of the U-tube cell described by Herington and Handley (*3*).

Using this pulsating freezing point apparatus, which is a substantially closed system, t_f tended to increase slightly when the sample was repeatedly melted and frozen. This behavior strongly suggested that a trace of volatile impurity was present. In many cases, DMT is purified by recrystallization from methanol and hence traces of methanol may be trapped in the sample. A likely impurity in DMT is methyl *p*-toluate which, unlike methanol, would interfere in its subsequent use in polyester manufacture. The data shown in Table I demonstrate that sparging the molten sample with N_2 for 120 seconds removed the traces of volatile impurity but did not remove methyl *p*-toluate. All samples were given a N_2 sparge prior to the determination of t_f. In the t_{f_0} measurements, the gas agitation sparged the sample.

Methyl *p*-toluate was selected as the added impurity for the determination of t_{f_0} by the Schwab and Wichers method. To establish its suitability, the freezing point–composition diagram was determined for this system. Temperatures were measured using mercury-in-glass thermometers. No evidence of solid solution or compound formation was found and, in fact, over the range 10 to 100 % DMT, the system appears to be an ideal solution. This is shown in Figure 4, where the logarithm of the mole fraction of DMT is linear in $1/T$ over this range. The slope of this line corresponds to a heat of fusion,

Table I. Effect on N_2 Sparging on Freezing Point of DMT

Sparge Time, Sec.	Freezing Point, ° C. Original sample	 After addition of methyl *p*-toluate to previously sparged sample
0	140.605	140.531
60	140.630	. . .
120	140.633	140.532

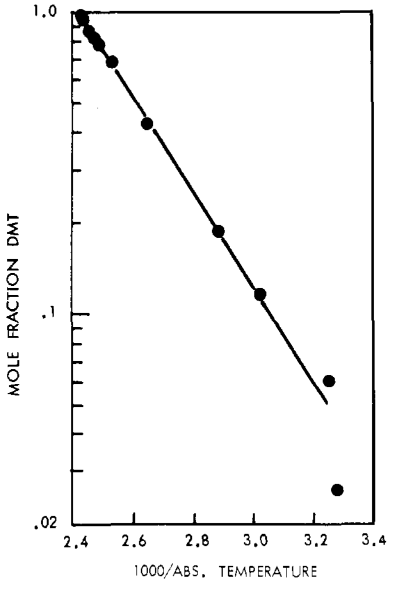

Figure 4. DMT–methyl *p*-toluate system

Log mole fraction DMT vs. $1/T_f$ (ordinate, mole fraction DMT) (abscissa, 1000/absolute temperature)

ΔH_f, of 7250 cal. per mole, which is in moderately good agreement with the calorimetrically determined value of 7560 cal. per mole.

The calorimetric value of ΔH_f gives a cryoscopic constant of 0.0228 mole fraction per degree C. The purity range of interest is 99.9+ mole % or higher and, as pointed out by Schwab and Wichers (*6, 7*), it is unnecessary to use the exact freezing point equation. The simple equation,

$$x = \frac{\Delta H_f \cdot \Delta T}{RT_f^2} \qquad (1)$$

where x is the mole fraction impurity, is adequate.

If x is the unknown mole fraction impurity in the sample and a is the mole fraction of the added impurity, then,

$$\frac{x}{a} = \frac{(T' - T'')_x}{(T' - T'')_{(x+a)} - (T' - T'')_x} \qquad (2)$$

where T'_x and T''_x represent two freezing temperatures of the original samples and $T'_{(x+a)}$ and $T'_{(x-a)}$ represent freezing temperatures observed after the addition of the known concentration of impurity, a, at exactly corresponding stages of freezing. Over these very small temperature ranges, thermometer resistances, R, may be used instead of temperatures in Equation 2. With x established, t_{f_0} is calculated from the t_f of the sample using the previously established cryoscopic constant. Table II gives the results from the freezing point curves shown in Figure 5. The results of a number of t_{f_0} determinations are given in Table III. The same values are obtained when either anthracene or methyl *p*-toluate is the added impurity. With N_2 as the agitating gas, the average t_{f_0} is 140.655° C., whereas when air is used, the average is 140.648° C. This lower value is undoubtedly due to the greater solubility of oxygen in the molten DMT. These t_{f_0} values are believed to be accurate to within ±0.002° C. on the international practical temperature scale.

Experimental values of the heat capacity of DMT are given in Table IV and found to follow the equations:

$$c_p(\text{cal./gram }^\circ\text{C.}) = 0.3056 + 0.615 \times 10^{-3}t + 0.78 \times 10^{-6}t^2 \text{ (Solid: } 30^\circ\text{C.} < t < 140.6^\circ\text{C.)} \qquad (3)$$

Table II. Estimation of Impurity Concentration in DMT by Comparison of Freezing Ranges

Time Interval,[a] Min.	$(R' - R'')_{(x+a)}$	$(R' - R'')_x$	x/a	t_{f_0}, ° C.
80-90	11×10^{-5}	3×10^{-5}	0.38	140.656
90-100	14×10^{-5}	4×10^{-5}	0.40	140.656
100-110	13×10^{-5}	4×10^{-5}	0.44	140.657
100-120	15×10^{-5}	5×10^{-5}	0.50	140.658
120-130	15×10^{-5}	3×10^{-5}	0.25	140.653
130-140	16×10^{-5}	4×10^{-5}	0.33	140.655
140-150	17×10^{-5}	5×10^{-5}	0.42	140.657
150-160	20×10^{-5}	4×10^{-5}	0.25	140.653
160-170	21×10^{-5}	6×10^{-5}	0.40	140.656
170-180	22×10^{-5}	7×10^{-5}	0.47	140.658
180-190	28×10^{-5}	7×10^{-5}	0.33	140.655
			Av.	140.656

t_f = 140.647° C. a = 0.0526 mole % methyl *p*-toluate.

[a] Time zero taken as end of supercooling.

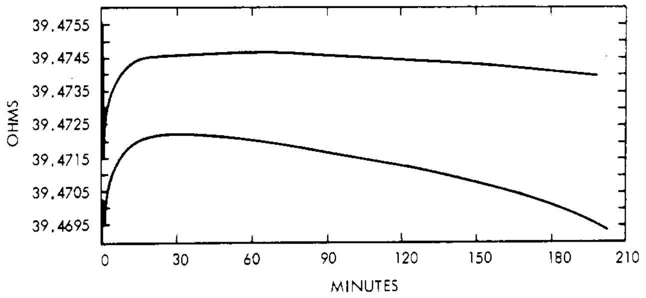

Figure 5. Time-temperature freezing curves for t_{f_0} determination by Schwab and Wichers method

Lower curve for 0.0526 mole % added methyl *p*-toluate, (ordinate, ohms)(abscissa, minutes)

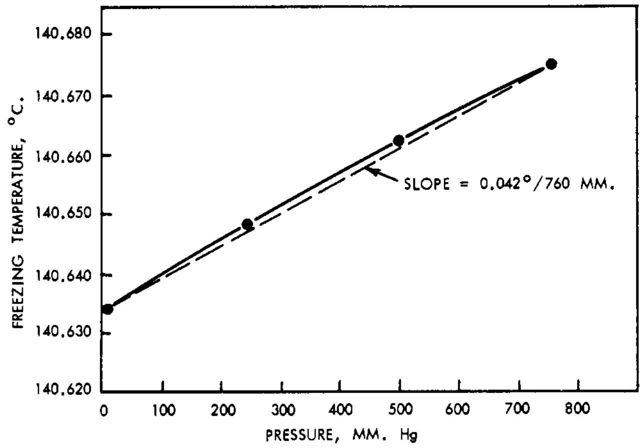

Figure 6. Variation of freezing temperature of DMT with pressure

(Ordinate, freezing temperature, ° C.) (abscissa, pressure, mm. Hg)

Table III. t_{f_0} Determinations

Sample	Agitating Gas	Bath Temp., ° C.	Benzoic Acid Cell Check[a]	Sample t_f, ° C.	Added Impurity, Mole %	t_{f_0}, ° C.
Hercules AWT-2749	N_2	135.0	122.360	140.644	Methyl *p*-toluate 0.0474	140.656
					Methyl *p*-toluate 0.0358	140.654
Hercules AWT-65	N_2	137.5	122.358	140.647	Methyl *p*-toluate 0.0526	140.656
					Av.	140.655
Hercules AWT-2749	Air	135.0	122.359	140.640	Methyl *p*-toluate 0.0484	140.648
Hercules AWT-65	Air	135.0	122.359	140.642	Anthracene 0.0392	140.647
		137.5	122.358	140.643	Methyl *p*-toluate 0.0253	140.650
Du Pont	Air	135.0	122.359	140.638	Methyl *p*-toluate 0.0492	140.648
					Av.	140.648

[a] National Bureau of Standards value 122.357° ± 0.003° C.

Table IV. Heat Capacity of DMT

Run No.	Mean Temp., ° C.	Heat Capacity, Cal./Gram ° C.
1	44.20	0.333
2	58.14	0.344
3	73.04	0.356
4	87.77	0.365
5	102.24	0.376
6	116.50	0.388
7	130.53	0.400
	(Fusion)	
9	150.25	0.459
10	164.75	0.466
11	179.06	0.473
12	193.20	0.482
13 (recheck)	54.19	0.340

and

$$c_p(\text{cal./gram °C.}) = 0.4371 - 0.135 \times 10^{-3}t + 1.88 \times 10^{-6}t^2 \quad (\text{Liquid: } 140.6° \text{C.} < t < 200° \text{C.}) \qquad (4)$$

These values for both the solid and liquid DMT are 0.01 to 0.02 cal. per gram ° C. higher than those reported by Smith and Dole (*8*). No reason for this discrepancy is apparent.

The variation of the freezing temperature with pressure dT_f/dp is shown in Figure 6, and is 0.042° C. per atmosphere. As a result of several sets of measurements, the triple point of DMT is estimated to be 140.636° ± 0.004° C.; its vapor pressure at the triple point is approximately 10 mm. of Hg.

Using this value for dT_f/dp and the calorimetric heat of fusion, the Clausius-Clapeyron equation

$$\frac{dT_f}{dp} = \frac{T_f(V_L - V_S)}{\Delta H_f} \qquad (5)$$

yields $V_L - V_S = 0.1659$ cc. per gram for the difference between the specific volumes of the liquid and solid at the freezing point. Dilatometric measurements using a hook-type dilatometer with mercury as the confining liquid gave 0.1575 cc. per gram. Inasmuch as dilatometric values for V_S near the melting point were found to decrease slowly with time, the calculated value of $V_L - V_S$ from dT_f/dp is believed to be the more reliable. V_L at T_f was found to be 1.0480 cc. per gram with a temperature coefficient, dV_L/dT, of 8×10^{-4} cc. per gram ° C.

THERMOMETRIC CELLS

Freezing point studies of DMT indicated that it has many of the necessary characteristics for use as a thermometric standard. High purity DMT is commercially available and further purification is relatively simple. It is stable and has a sufficiently large ΔH_f, together with a high velocity of crystallization.

A series of thermometric cells (Figure 2) was prepared and filled with vacuum-sublimed DMT using the apparatus shown in Figure 3. The sealed cells were melted and frozen following the procedure recommended by the National Bureau of Standards for their benzoic acid cells (*5*) except for the higher melting temperature of 155° C. As shown in Table V, these cells gave a temperature which was constant to 0.002° C. for at least 2 hours. Cell 4 was measured at the Bureau of Standards. A value of 140.6360° C. was found (*1*), which confirms our value of 140.633–140.637° C. based on a large number of determinations.

The stability of the DMT also is shown in Table V, which gives temperature data on cells 4 and 5 after the indicated number of weeks of storage at 155° C. Unfortunately, cell 5 is the only cell of the original series that has survived to the present. Table V shows values of its freezing point when this work was actively under way in 1955. A determination, made after 11 years of occasional use, gave 140.636° C., in excellent agreement with the earlier values.

Table V. Stability of DMT Thermometric Cells—(Temperature *vs.* Time)

Time of Storage at 155° C.	Time after Freezing							
	Cell 4				Cell 5			
	30 min.	60 min.	120 min.	150 min.	30 min.	60 min.	120 min.	150 min.
	Temperature, ° C.							
0	140.639	140.639	140.638	140.637	140.635	140.636	140.636	...
1 day	140.637	140.637	140.637	140.637	...	...	...	...
1 week	140.640	140.640	...	...	140.637	140.637	140.637	140.634
2 weeks	140.635	140.635	140.634	140.632	140.632	140.633	140.631	...
3 weeks	140.633	140.633	...	140.631	140.635	140.635	...	...

After 11 years of occasional use, cells gave a temperature of 140.636° C.

These data show that DMT is suitable for use as a secondary temperature standard.

ACKNOWLEDGMENT

Many persons contributed to the work reported here, especially F. S. Stow, Jr., R. W. Davison, F. H. Wetzel, W. E. Osberg, and H. C. Adams. Grateful acknowledgment to all who participated in the program is made.

LITERATURE CITED

(1) Enagonio, D., National Bureau of Standards, Gaithersburg, Md., private communication, 1958.

(2) Glasgow, A.R., Jr., Streiff, A.J., Rossini, F.D., *J. Res. Natl. Bur. Std.* **35**, 355 (1945).

(3) Herrington, E.F.G., Handley, R., *J. Chem. Soc. (London)* **1950**, 199.

(4) Horowitz, K.H., Stow, F.S., Jr., *Anal. Chem.* **21**, 1571 (1949).

(5) National Bureau of Standards, Gaithersburg, Md., "Benzoic Acid Thermometric Standards. Notes and Precautions," 1953.

(6) Schwab, F.W., Wichers, E., *J. Res. Natl. Bur. Std.* **34**, 333 (1945).

(7) Schwab, F.W., Wichers, E., "Temperature, Its Measurement and Control in Science and Industry," p. 256, Reinhold, New York, 1941.

(8) Smith, C.W., Dole, M., *J. Polymer Sci.* **20**, 37 (1956).

(9) Stimson, H.F., *J. Res. Natl. Bur. Std.* **42**, 209 (1949).

(10) Stimson, H.F., National Bureau of Standards, Washington, D. C., private communication, 1954.

(11) Stimson, H.F., "Temperature, Its Measurement and Control in Science and Industry," Vol. 3, Part 1, p. 59, Reinhold, New York, 1962.

(12) Stow, F.S., Jr., Elliott, J.H., *Anal. Chem.* **20**, 250 (1948).

(13) Van Dusen, M.S., *J. Am. Chem. Soc.* **47**, 326 (1925).

(14) White, W.P., *J. Phys. Chem.* **24**, 393 (1920).

RECEIVED for review February 12, 1968. Accepted July 3, 1968.