296. *A Simple Melting-point Calorimeter for Moderately Precise Determinations of Purity.*

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A melting-point calorimeter has been constructed for a rapid (3—4 hr.) determination of the purity of a 3 ml. sample by measurement of the solid–liquid equilibrium temperature as a function of the fraction which is liquid. The heat of fusion is determined to about ±10% and the molar percentage of impurity to about ±20%. Melting points, heats of fusion, and purities are given for diverse samples of m. p. −140° to −14°.

The reliability of a measured physical property depends on the purity of the sample. A generally applicable method for determining the purity of an organic sample is to compare its freezing point with the value for zero impurity. Time–temperature analysis of controlled freezing or melting is widely used for this, the most accurate methods being those developed by the American Petroleum Institute Research Project 6.[1] An alternative is the calorimetric procedure in which the solid–liquid equilibrium temperature is measured as a function of the fraction of the sample liquid. The two procedures have been experimentally compared by Glasgow *et al.*[2] In the calorimetric method, the depression of freezing point and the heat of fusion, and thereby the cryoscopic constant, are determined in a single experiment and this procedure can yield more precise results than the former. Low-temperature specific heat calorimeters are used to investigate purity during entropy determinations,[3] but are too complex for this to be their main use. Consequently several calorimeters designed for purity determinations only have been described. Pilcher's [4] is very precise but requires a 50 ml. sample and Aston, Fink, Tooke, and Cines's [5] is rather complex. Tunnicliff and Stone [6] described a moderately precise semi-automatic apparatus. One of the simplest designs, that by Clarke, Johnston, and de Sorbo,[7] requires only 3 ml. but has the disadvantage that the calorimetric conditions are not strictly adiabatic. The calorimeter now described has been developed from that design and determines purities of small samples of a wide variety of compounds comparatively rapidly (3– 4 hr.) with moderate precision.

The theory of the calorimetric method has been given by Rossini.[8] For samples in

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[1] Mair, Glasgow, and Rossini, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 591; Glasgow, Streiff, and Rossini, *ibid.*, 1945, **35**, 355.

[2] Glasgow, Ross, Horton, Enagonis, Dixon, Saylor, Furukawa, Reilly, and Henning, *Analyt. Chim. Acta*, 1957, **17**, 54.

[3] Ruhrwein and Huffman, *J. Amer. Chem. Soc.*, 1943, **65**, 1620.

[4] Pilcher, *Analyt. Chim. Acta*, 1957, **17**, 144.

[5] Aston, Fink, Tooke, and Cines, *Analyt. Chem.*, 1947, **19**, 218.

[6] Tunnicliff and Stone, *ibid.*, 1955, **27**, 73.

[7] Clarke, Johnston, and de Sorbo, *ibid.*, 1953, **25**, 1156.

[8] Rossini, " Chemical Thermodynamics," Wiley, New York, 1950.

which the impurity is liquid-soluble solid-insoluble, the solid–liquid equilibrium temperature T is related to the mole-fraction of impurity in the liquid phase, N_2, by $N_2 = A(T_1^* - T)$, where A, the cryoscopic constant of the major component, $= \Delta H_\mathrm{m}/\boldsymbol{R}T_1^{*2}$ where ΔH_m is the molar heat of fusion and T_1^* the freezing point for zero impurity. If N_2^s is the mole-fraction of impurity in the total sample and N_2 that in the liquid phase for a fraction r of the sample melted, then $N_2 = N_2^\mathrm{s}/r$. Combination of these equations gives, $T = T_1^* - (N_2^\mathrm{s}/A)(1/r)$. The mole-fraction of impurity in the sample is obtained from the slope of the plot of T against $(1/r)$ and the intercept at $(1/r) = 0$ gives T_1^*.

The theory depends upon the application of the ideal-solution laws which is reasonable for very pure samples as only dilute solutions of impurity are involved. It is assumed that the impurity is liquid-soluble solid-insoluble. Solid solutions can occur when the impurity has molecular dimensions similar to those of the major component or when the latter has a small heat of fusion, and cause the curve of T against $(1/r)$ to be concave upwards. Mastrangelo and Dornte's treatment can then be used to estimate the impurity.[9]

The limitations of the calorimetric procedure have been discussed by McCullough and Waddington.[10] As the method is essentially a determination of the mole-fraction of impurity, for nearly pure samples a large error in " impurity determination " will result in a small uncertainty in the degree of purity.†

Construction and Operation of the Calorimeter.—The calorimeter E [Fig. 1(*a*)], of internal volume *ca.* 3 ml., consists of the copper portion of a Housekeeper seal ($\frac{1}{2}$ in. o.d. × $1\frac{3}{4}$ in. closed at the bottom) sealed at A to 16 mm. diam. Pyrex glass. Six thin horizontal copper vanes, silver-soldered to a central wire B, promote temperature equilibrium and prevent solid particles settling during melting. 30 Ohms of 40 S.W.G. copper wire D wound non-inductively on the copper tube acts as resistance thermometer and heater. Temperature changes will not strain the wire as it has the same coefficient of thermal expansion as the calorimeter. The coil, insulated with glyptal varnish and by a layer of " Scotch " electrical insulating tape, is covered with copper foil C to minimise radiation loss. Two leads only are attached.

The calorimeter is surrounded by a copper shield G ($1\frac{1}{4}$ in. i.d. × $\frac{1}{16}$ in. thickness), as a constant-temperature jacket, heated by a winding of 400 ohms (J) of 35 S.W.G. Eureka wire, insulated and covered (K) as above. The shield temperature is measured around its centre with a copper resistance thermometer H of similar characteristics to that of the calorimeter.

The central glass filling tube is covered with a thin copper sheath wound with 400 ohms of 35 S.W.G. Eureka wire M as heater and a third copper resistance thermometer L is placed at its lower end. The tube temperature must be maintained slightly above that of the calorimeter to prevent distillation of the specimen. The calorimeter leads are placed in intimate contact with the shield before being passed up beneath the tube heater. The tube heater is also protected as above and covered with a closely fitting conical tube O (0·2 mm. thickness, copper). The constant-temperature shield is held in position by three stout copper wires N soldered to the conical tube.

The whole assembly P, Q, R, M [Fig. 1] is inside a vacuum-tight glass jacket S (6 cm. i.d. × 40 cm. long) which can be immersed in a cooling bath of liquid nitrogen or solid carbon dioxide–acetone. U is a B55 ground-glass joint, V is a picein seal. Vacuum is applied at Y, and communicates with the calorimeter through holes F.

Temperature Measurement.—The calorimeter, shield, and tube temperatures are obtained from the thermometer resistances [*ca.* 30 ohms at 25°]. No compensation is made for the leads [*ca.* 0·3 ohm] but these will not change significantly during an experiment because they are kept together and are not disturbed. Mercury switches are used to ensure reproducible contact resistances. The error in absolute resistance measurement is assessed at ±0·1 ohm, corresponding to a temperature error of ±1°. Purity determinations, however, require temperature differences, and thus sensitive temperature measurements rather than high absolute accuracy.

† For a sample of purity 99·9 moles %, a 20% error in " impurity determination " would fix the purity within 99·88 to 99·92 moles %.

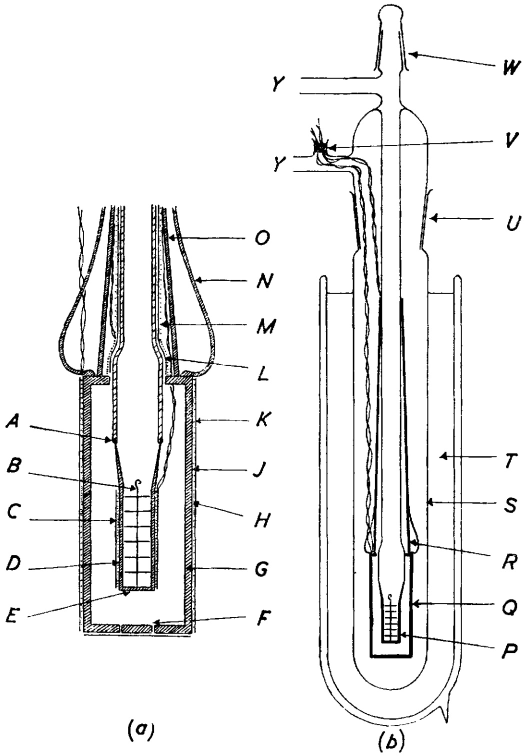
[9] Mastrangelo and Dornte, *J. Amer. Chem. Soc.*, 1955, **77**, 6200.

[10] McCullough and Waddington, *Analyt. Chim. Acta*, 1957, **17**, 80.

The thermometer resistances are balanced in a Wheatstone bridge whose measuring arm is two parallel resistances R_1 and R_2; the measured resistance is $R_1R_2/(R_1 + R_2)$. R_1 is a good-quality resistance box, adjustable in 0·1 ohm steps, set 0·1 ohm above the resistance to be measured. R_2, the variable arm of an inexpensive resistance bridge (0—10,000 ohms in 1 ohm steps), is adjusted for balance and kept as large as possible, generally around 2000 ohms when a 1 ohm change in R_2 corresponds to an overall change of $<0{\cdot}0001$ ohm; thus contact resistance variations in R_2 are negligible. The current through the thermometer coil is *ca.* 2 mA and the heating effect is insignificant. A Cambridge short period galvanometer [25 ohms; 300 mm./μA at 1 m.] is used to detect the balance point and the overall sensitivity of temperature measurement is about 0·0003°.

Electrical Energy Measurement.—The current (i A) through the calorimeter coil is measured with a calibrated milliammeter (0—200 mA) and timed to 0·2 sec. with a stop-clock.

FIG. 1. *Apparatus.*



The coil resistance (R ohms) is taken as the mean of its values at the beginning and end of the heating period (t sec.) because the coil is in good thermal contact with the calorimeter and can be assumed to be always at calorimeter temperature. The electrical energy supplied is then i^2Rt joules and is accurate to about ±1%. The current, from lead storage cells, is adjusted with a variable resistance and a dummy heater which allows the current to become steady before switching to the calorimeter.

Temperature Control of Shield and Tube.—The shield is maintained constant at approximately the m. p. of the sample and the tube about 1° above this, both ±0·05°, which is satisfactory as the thermal leakage between the calorimeter and its environment is small. The current through the heaters, from a stabilised transformer (10—50 v), is controlled by resistances.

Procedure.—A known weight of compound is either distilled *in vacuo* into the calorimeter or injected and then degassed, and measurements are done under its vapour pressure (*i.e.*, triple points are examined). An approximate m. p. can be found from a time–temperature freezing curve or more accurately from the slow-melting curve (with the jacket evacuated and the shield at about 10° above the calorimeter). From the latter an approximate heat of fusion and degree of purity can be estimated as in ref. 1 (1945).

The solid sample is held about 10° below the m. p. whilst the shield and tube temperatures are adjusted to the required values and these are observed and controlled during the experiment. Calorimeter temperatures are read at 3 min. intervals to establish temperature drifts. Energy inputs are made, at first to determine the effective heat capacity of the calorimeter plus contents and then to melt the sample in stages, the inputs being arranged so that fractions of about $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, and almost unity of the sample are liquid at the end of each stage. The sample is finally melted, the heat capacity again determined, and temperature drift rates remeasured.

The heat-capacity measurements are accurate to about ±3% and a mean value for the solid and the liquid state is used in the calculation. From the calorimeter temperature drift rates before and after melting the rate of heat input to the calorimeter from the surroundings can be calculated for intermediate temperatures. This exchange heat input must be added to the electrical energy input to give the total energy absorbed which is distributed between the melting process and the raising of the temperature of the system. The energy absorbed in melting in each stage can then be calculated and from the total heat of fusion the fractions melted obtained. After an electrical-energy input about 10—15 min. must be allowed for the system to regain equilibrium and these temperature equilibrium points are chosen to be the end points of the stages.

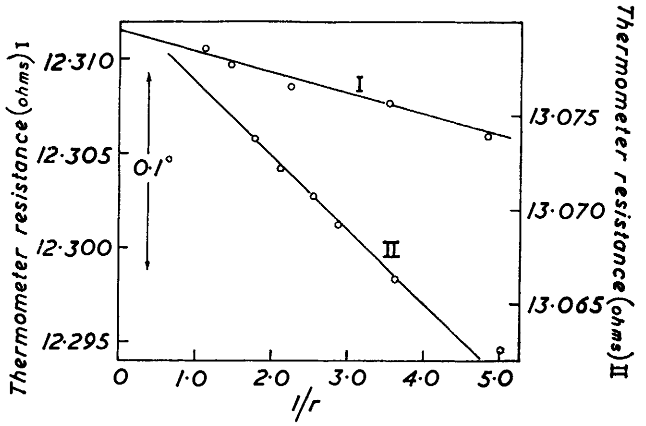


FIG. 2. *Plots for diethyl ether* (*I*; 99·96 ± 0·004 *moles* %) *and tetrahydrofuran* (*II*; 99·87 ± 0·02 *moles* %).

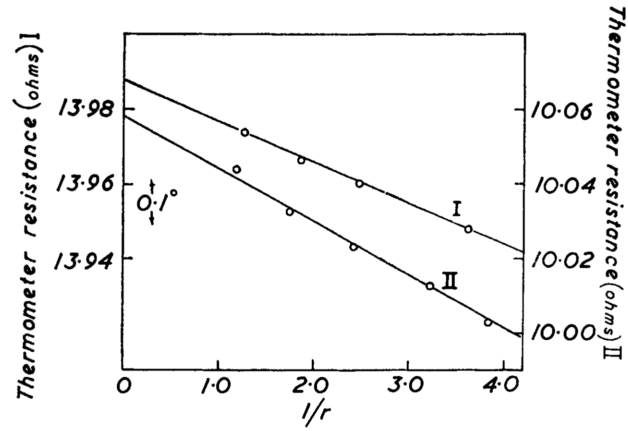


FIG. 3. *Plots for divinyl ether* (*I*; 99·68 ± 0·06 *moles* %) *and hex*-1-*ene* (*II*; 99·17 ± 0·06 *moles* %).

Results.—Several classes of compound have been examined. Hex-1-ene, from the National Chemical Laboratory (Standard Sample No. 19-4407) had been found at the National Bureau of Standards, Washington, to be 99·22 ± 0·10 moles % pure, in good agreement with our value, 99·17 ± 0·06 moles %. Diethyl ether (" AnalaR ") was dried over sodium. Remaining samples were either prepared in this department or obtained commercially and were generally fractionally distilled through a 50 cm. column of Dixon rings. The results are summarised in the Table, which shows that the heat of fusion measured is accurate to *ca.* ±10%, this being satisfactory for calculation of the cryoscopic constant. When a more accurate value for this constant is available it is preferred. Fig. 2 shows some curves of T against $(1/r)$ obtained for samples of high purity and Figs. 3 and 4 for samples of moderate and low purity respectively.

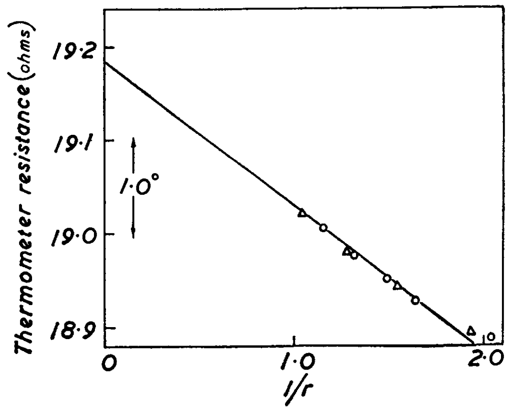


FIG. 4. *Plot for two experiments with trimethylphenyltin* (96·1 ± 0·8 *moles* %).

Because the calorimeter is not adiabatic it is not practicable to start experiments far below the m. p., so for impure samples some may be liquid at the starting temperature. From the mole-fraction on impurity at first obtained the initial fraction melted is calculated and the " observed " heat of fusion and fractions melted corrected. Successive approximations can be made, as for trimethylphenyltin.

Usually the slope can be obtained to ±10%, and thus the molar percentage of impurity to ±10% if the cryoscopic constant is known accurately, otherwise to ±20%. The total time taken is 3—4 hr; this cannot be extended because the calorimeter is not adiabatic. This limits its use, because some substances take a long time for the solid and liquid phases to reach thermodynamic equilibrium, particularly when the latter is very viscous. No such difficulties were encountered with the above compounds.

Compound	M. p.	ΔH_m (cal. mole^{-1}) Obs.	ΔH_m (cal. mole^{-1}) Lit.	A (deg.$^{-1}$)	Purity (moles %)
Hex-1-ene	−140°	2200 ± 200	2234[a]	0·06318	99·17 ± 0·06
Trimethylene oxide	−97	1550 ± 150		0·025	99·81 ± 0·04
Furan	−86	890 ± 100	908·8 ± 0·2[b]	0·01301	99·78 ± 0·02
Tetrahydrofuran	−109	2175 ± 200		0·040	99·87 ± 0·02
Tetrahydropyran	−49	425 ± 50		0·0039	99·81 ± 0·04
Diethyl ether	−116	1650 ± 150	1745[c]	0·036	99·96 ± 0·004
Divinyl ether	−100	1900 ± 200		0·032	99·68 ± 0·06
Benzonitrile	−14	2170 ± 200		0·016	99·24 ± 0·15
Bicyclo[2,2,1]heptadiene	−68	1670 ± 150		0·020	99·34 ± 0·10
Trimethylphenyltin	−51	2410 ± 200		0·025	96·1 ± 0·8

[a] McCullough, Finke, Gross, Messerly, and Waddington, *J. Phys. Chem.*, 1957, **61**, 289. [b] Guthrie, Scott, Hubbard, Katz, McCullough, Gross, Williamson, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 4662. [c] Parks and Huffman, *ibid.*, 1926, **48**, 2788.

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