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Purity Determination of Organic Compounds by a Newly Designed DTA Apparatus[1]

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An apparatus of differential thermal analysis has been designed and constructed for the purpose of determining the purity of organic compounds with as small an amount of sample as possible, within a short time and yet with an accuracy of better than ±0.001 mol%. Degussa platinum thermometers were used. They were calibrated with a precision of better than ±0.004° against a standard platinum resistance thermometer. Methods for determining the impurities in samples on the basis of irreversible thermodynamics have been developed. The results were compared with those obtained by using an adiabatic calorimeter of our laboratory and by the National Bureau of Standards. The apparatus proved to be useful in determining the purity of about 1 m*l* of samples, whose melting points lie in the temperature range −200°C—+200°C within an accuracy of ±0.004 mol% in about 1.5 hr.

Differential thermal analysis (DTA) is widely used as a dynamic method of thermal analysis in various fields. However, in order to apply it to purity determination, the apparatus and procedure should be designed taking the following facts into consideration.

The accuracy of evaluation of impurities in the sample is dependent upon the precision of the thermometer. Thermocouples are used for DTA measurements, but it is difficult to calibrate them with a precision better than ±0.01°. In the DTA apparatus reported here, platinum thermometers calibrated against a standard platinum thermometer were employed. The temperature of the sample and the temperature difference between the sample and reference substance were recorded simultaneously as functions of time.

The DTA method is a dynamic one and the observed temperature is not measured at equilibrium. It is necessary therefore to analyze the resulting curves on the basis of irreversible thermodynamics instead of reversible thermodynamics.

Before testing the DTA apparatus with the NBS Standard Sample 217b 2,2,4-trimethylpentane, a comparison of the purity obtained by the NBS and that by our adiabatic calorimeter[2] was made.

An extrapolation method as well as comparative methods for purity determination by the DTA measurements were developed.

Experimental

Apparatus. An apparatus was constructed to obtain DTA and total thermal analysis (TTA) curves simultaneously at temperatures from −200°C to 200°C. The cryostat of the apparatus was so designed that the amount of the sample can be as small as possible. The general assembly is illustrated in Fig. 1. A copper block A with two holes drilled symmetrically with respect to the center, is hung inside jacket E by means of three constantan cords. A heating wire is wound around A. In operation, the cryostat is sealed at the top plate F with Wood's metal or solder and mounted in a glass Dewar vessel containing coolant. All electric lead wires (#38 copper) come from the top of the cryostat through a stainless steel pipe at the center and are connected at the terminal D. They are then wound around A so as to secure good thermal contact. The inside of E is evacuated, and the cooling and heating rates are controlled by adjusting the amount of helium gas in it.

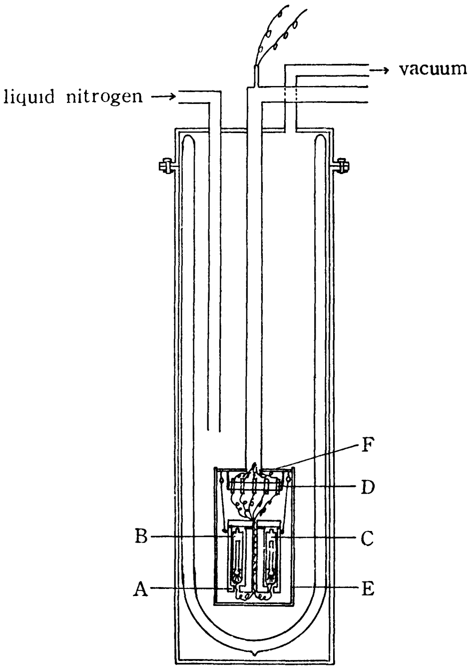

Fig. 1. Cross-section of the cryostat.
(A) copper block; (B) sample cell; (C) reference cell; (D) terminal of lead wires; (E) jacket; (F) top plate of the container

The details of sample or reference cell are shown in Fig. 2. Cell a is made of silver-plated copper (0.2 mm thick) with internal volume about 1 m*l*. Four vanes are soldered to the inside wall of the cell. The cap of the cell has a copper capillary tube c through which the inside can be evacuated. The platinum thermometer b is cast into a re-entrant well of the cell with indium alloy. Sample and reference cells, to which are attached silver-plated copper sheaths d, are set in the holes of A.

Since the cells are too small to fit standard platinum thermo-

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[2] T. Shinoda, H. Enokido, Y. Maeda, and Y. Mashiko, *unpublished.*

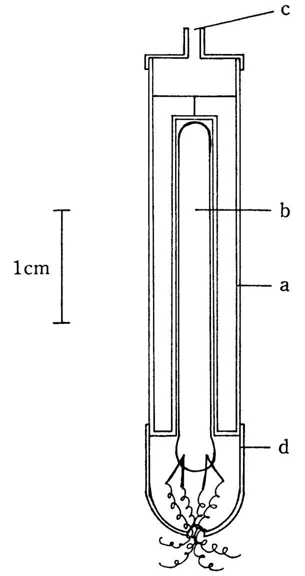

Fig. 2. Cross-section diagram of sample or reference cell.
(a) vessel of sample or reference substance
(b) Degussa platium thermometer
(c) copper capillary tube
(d) sheath

meters, small platinum-in-glass thermometers (Degussa-Hanau Model P4) are employed. The Degussa thermometer was originally supplied with two nickel lead wires. It was modified by fixing four platinum lead wires instead of two nickel wires. The thermometers were then calibrated against a Leeds & Northrup platinum thermometer certified by the National Bureau of Standards. For the intercomparison of resistance values, two kinds of thermometers were cast with indium alloy into three re-entrant wells drilled in a copper block. The copper block was placed within an adiabatic shield of the adiabatic calorimeter assembly.[2] Some 50 comparisons of each Degussa thermometer with the standard thermometer were made in the temperature range from −180°C to 70°C under practically adiabatic conditions. Attempts were made to find coefficients which would fit the following formula separately in the temperature regions above and below 0°C to the observed resistance-temperature data for each Degussa thermometer.

$$R_t/R_0 = 1+\alpha t[1 + \delta(1-t\cdot 10^{-2})10^{-2} + \beta t^2(1-t\gamma 10^{-2})10^{-6}] \qquad (1)$$

Here t is the temperature in degrees Celsius, and R_t and R_0 are the resistances of the Degussa thermometer at t°C and 0°C, respectively. Coefficients determined are given in Table 1. Deviations of the observed resistances from the calculated resistances, obtained by means of Eq. (1) are within ±0.004° as shown in Fig. 3.

The temperature of a given sample and the difference in temperature between the sample and reference substance are simultaneously recorded on a Shimadzu Precision Recording Thermometer Type CT3 whose precision is 0.01° or 0.001° according to its two ranges.

Material. 2,2,4-trimethylpentane used in this experiment was the Standard Sample 217b which was purified and certified as 99.993±0.003 mol% by the National Bureau of Standards. Commercial 2,2,4-trimethylpentane and *n*-pentadecane of Extra Pure Grade were also obtained from Tokyo Kasei Kogyo Co., Ltd. α-Al_2O_3 which was supplied by Shimadzu Co. was used as a reference substance.

TABLE 1. COEFFICIENTS DETERMINED BY FITTING THE CALIBRATION DATA TO Eq. (1) FOR DEGUSSA PLATINUM-RESISTORS

	Resistor 1	Resistor 2
	t above 0°C	
R_0 (ohms)	99.7245	99.7541
δ	1.38640	1.47009
α	0.00385854	0.00391828
β	0.0	0.0
	t below 0°C	
R_0 (ohms)	99.7225	99.7515
δ	1.59087	1.70733
α	0.00385205	0.00390511
β	0.0741392	−0.0364007
γ	1.54525	−4.05087

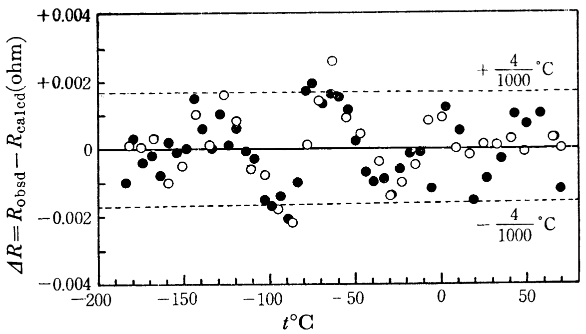

Fig. 3. Deviation of observed resistance of two Degussa thermometers from the calculated resistance by using Eq. (1).
○ thermometer 1 ● thermometer 2

Results and Discussion

Principle of Purity Determination from the Freezing or Melting Point Measurement. For impurities that are completely soluble in the liquid phase but insoluble in the solid phase, a thermodynamic relation between the amount of impurities N in mole fraction and the equilibrium temperature T, for an ideal or sufficiently dilute solution, is given by

$$-\ln(1-N)/r = (T^*_{m0}-T)\Delta H_m/\boldsymbol{R}(T^*_{m0})^2 \qquad (2)$$

where T_{m0} is the melting point of pure compound, r the fraction melted or crystallized, ΔH_m the heat of fusion at T_{m0} of the pure compound, and $\boldsymbol{R}$ the gas constant. When the temperature T given by a time-temperature curve is not measured at equilibrium, the equation for the amount of impurities should be derived from irreversible thermodynamics as follows[3]:

$$-\ln(1-N)/r = (\Delta H_m/\boldsymbol{R})(1/T-1/T_{m0}^*) + (\Delta C_p/\boldsymbol{R})[\ln(T_{m0}^*/T) + 1 - (T_{m0}^*/T)] + A(T,r)/\boldsymbol{R}T. \qquad (3)^{4)}$$

Here ΔC_p denotes the difference of the heat capacity between liquid and solid state of a pure compound,

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[3] I. Prigogin and R. Defay, "Chemical Thermodynamics," Longmans, Green and Co., Ltd, (1954) p. 373.

[4] For samples of purity above 99 mol% the approximate equation $-\ln(1\text{-}N)\simeq N$ may be used in Eqs. (2) and (3).

and $A(T, r)$ the affinity. The value of A changes as a function of given temperature or time. If A can be neglected, Eq. (3) is reduced to Eq. (2).

When $A=0$ for a specific sample, the values of temperature obtained and the fraction melted or crystallized can be used for the determination of purity by means of Eq. (2). Usually, it is however not possible to find the point at which $A=0$ in the time-temperature curve of DTA measurements. Attempts were made, therefore, to develop methods of evaluating the purity by means of Eq. (3) from the DTA and TTA curves. The methods are divided into two procedures as follows.

(a) Melting Point Depression Method Using Extrapolation: When the melting point (or freezing point⁵⁾) of a pure compound T^*_{m0} and that of a given sample T^*_m at $r=1$ are known, it is possible to give the amount of impurities in the sample from the melting point depression $T^*_{m0}-T^*_m$. In the first place, the purity of NBS Standard Sample 217b 2,2,4-trimethylpentane was reexamined using the precision adiabatic calorimeter.²⁾ The result, $99.991_2\pm0.0014$ mol%, is in excellent agreement with the given purity, 99.993 ± 0.003 mol% by the NBS within probable error. The melting point T^*_{m0} of pure compound was found to be 165.821_5°K as shown in Fig. 4. Two measurements of the heat of fusion ΔH_m were also made, and the result is in good agreement with the literature value,⁶⁾ 2198 cal/mol, as summarized in Table 2.

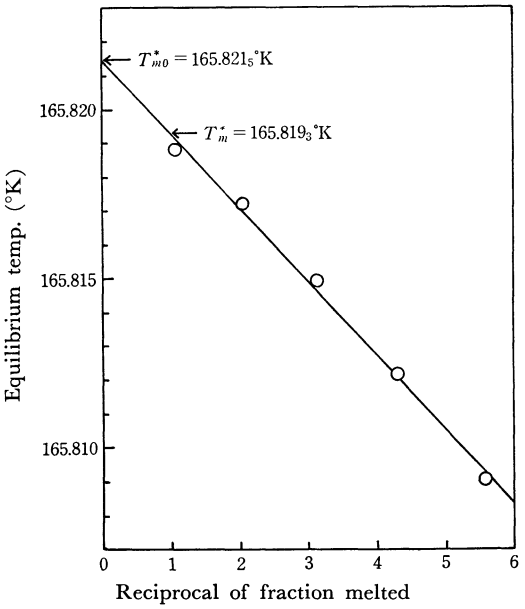

Fig. 4. Relationship between equilibrium temperatures and reciprocal of fraction melted for NBS Standard Sample 2,2,4-trimethylpentane.

TABLE 2. HEAT OF FUSION OF 2,2,4-TRIMETHYLPENTANE mol wt 114.223; 0.208706 mol

Temperature Interval (°K)	Heat Input (cal/mol)	$\int C_p dT$ (cal/mol)	ΔH_m (cal/mol)
165.027–166.219	2285.8	86.4	2199.4
165.080–166.453	2296.8	98.6	2198.2
		average	2198.8±0.6

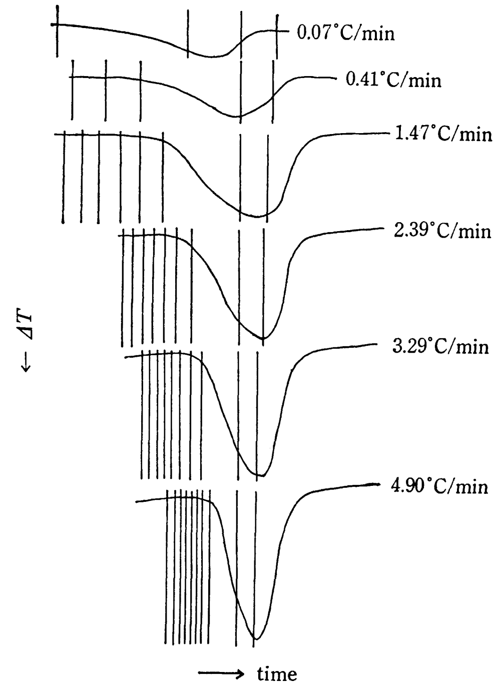

Fig. 5. DTA curves observed at various heating rates of commercial sample of 2,2,4-trimethylpentane.

DTA measurements at several heating rates were made using the NBS and commercial 2,2,4-trimethylpentane. Fig. 5 shows some examples of the DTA curves obtained.

As a matter of principle, the temperature at a peak maximum in a DTA curve obtained by this apparatus can be assumed to be equal to a quasi-melting point and depends upon the heating rate. The plots of temperatures at peak maxima ($T_{\max}$) of DTA curve *versus* heating rates (a) for two samples of 2,2,4-trimethylpentane are shown in Fig. 6. Extrapolation of the curves obtained for two samples to $a=0$ gives the values of $T_{\max}$ $(a=0)$. We may assume that at $T_{\max}$ $(a=0)$ melting is complete under equilibrium condition, *viz.*, $T_{\max}$ $(a=0)$ agrees with the true melting point T^*_m of a given sample. We can then estimate the purity of sample by means of Eq. (2), where $r=1$ (complete melting) for $T_{\max}$ $(a=0)$. The values of $T_{\max}$ $(a=0)$ for the NBS and commercial samples were found to be 165.819°K and 165.334°K, and the purities 99.990±0.004 mol% and 98.054±0.004 mol%, respectively.

(b) Comparative Method: (i) If the affinity A in Eq. (3) at $T=T_{\max}$ is denoted by $A_{\max}$, it may be assumed that the value of $A_{\max}$ for the same material is dependent only upon heating rate a as shown in Fig. 6 for a highly purified sample. Since highly accurate result has been given for the purity of the NBS standard sample by adiabatic calorimetry, the value of $A_{\max}$ for 2,2,4-trimethylpentane can be calculated as a function of the heating rate by means of Eq. (3). The plotted result shows a smooth curve as in Fig. 7. The

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5) The melting point is exactly equal to the freezing point under an equilibrium condition.

6) American Petroleum Institute Research Project 6.

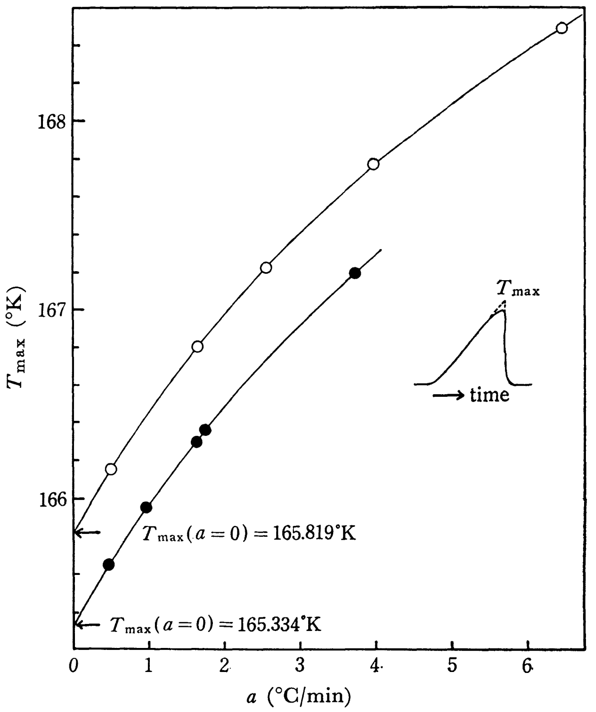

Fig. 6. Relationships between T_{max} and heating rate a for two samples of 2,2,4-trimethylpentane of different purity.
○ NBS sample ● commercial sample

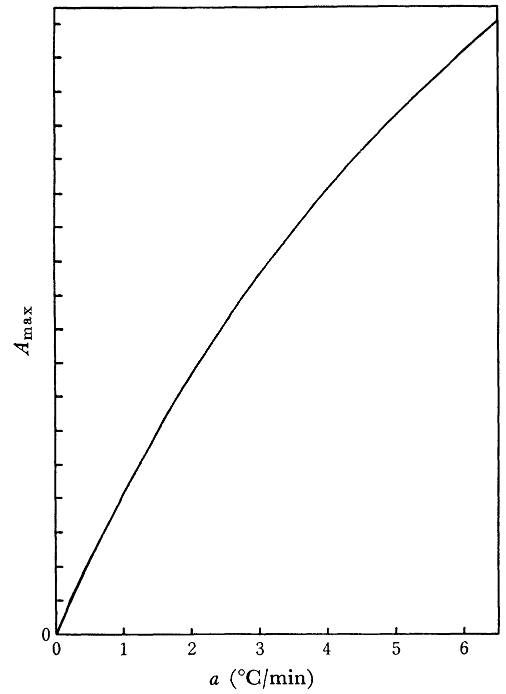

Fig. 7. Relationship between A_{max} and heating rate a for 2,2,4-trimethylpentane.

figure obtained on the NBS sample can be assumed to be applicable to the commercial sample, since the purity difference between the samples is small. Thus, from the values of T_{max} for the commercial sample observed at five different heating rates and the values of A_{max} obtained from the graph of A_{max} *versus* a of Fig. 7, the purity of the commercial sample was calculated by means of Eq. (3). The results are summarized in Table 3, and are in good agreement with that obtained by the melting point depression method (Fig. 6).

TABLE 3. RESULTS OF PURITY DETERMINATION BY COMPARATIVE METHOD (i) FROM THE DATA OBTAINED AT FIVE DIFFERENT HEATING RATES FOR COMMERCIAL SAMPLE OF 2,2,4-TRIMETHYLPENTANE

a (°C/min)	T_{max} (°K)	A_{max}/R	N (mol%)
0.47_2	165.644	2.068	98.05_4
0.96_8	165.949	4.111	98.05_4
1.61_1	166.295	6.443	98.04_8
1.73_7	166.354	6.830	98.05_0
3.72_1	167.193	12.459	98.05_6
		average	$98.05_2 \pm 0.004$

(ii) Indices 1 and 2 will be used in the following to denote two samples of different purity for DTA measurement. We will compare the purities at $T_1 = T_2 = T_{2,max}$ ($r_2 = 1$) with a fixed heating rate (a=const.). Then from Eq. (3) we obtain the relation

$$-\ln(1-N_1)/r_1 + \ln(1-N_2)/r_2 = (1/T_{2,max})(1/\boldsymbol{R})(A_1 - A_2)\,, \tag{4}$$

where r_1 is the fraction melted at $T_1 = T_{2,max}$ for sample 1. In principle, a peak area of a DTA curve is proportional to the heat of fusion of the compound.[7] We can thus estimate the value of r by making use of the ratio of the peak area against time, *i.e.*, the value of $r(t')$ at time $t = t'$ is given by

$$r(t') = \left[\int_{t_i}^{t'} (y-y_s)\mathrm{d}t + \int_{t''}^{t_f} (y-y_s)\mathrm{d}t\right] \Big/ \left[\int_{t_i}^{t_f} (y-y_s)\mathrm{d}t\right] \tag{5}$$

Here t_i and t_f are the times at which melting begins and finishes, t'' the time when $y = y(t')$ after the peak maximum, and y_s a steady state value of the differential temperature. Thus, if the amount of impurities N_1 for sample 1 is known, and the values of r_1, A_1, and A_2 ($=A_{max}$) in Eq. (4) are obtained from the $1/r_1$—$1/T$ relation, Eq. (3) and Fig. 7, respectively, then the amount of impurities N_2 for sample 2 can be calculated by means of Eq. (4). Here, sample 1 must be a substance with higher purity than the sample 2 ($N_1 < N_2$).

We employed the NBS and commercial 2,2,4-trimethylpentane as samples 1 and 2. Comparison of DTA data was made at the heating rate of 1.64_5°C/min for the NBS sample and 1.61_1°C/min for the commercial sample. The purity of the commercial sample was 98.04_8 mol% which is in good agreement with those obtained previously. Though the heating rates were adjusted to be as close as possible, it was difficult to obtain exactly the same heating rate for both samples. Method (ii) is therefore inferior to method (i) in accuracy.

Conventional Melting Point Method. In a melting curve the temperature which is given by the intersection of an extrapolated solid warming line with the extended backward liquid warming line, as shown in

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[7] M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).

Fig. 8, has been regarded as an equilibrium point ($A=0$) of the melting curve.[8] The behavior of affinity A during the melting was investigated on two samples of 2,2,4-trimethylpentane to check whether $A=0$ is actually established at this point. Fig. 9 shows plots of A *versus* $1/r$ obtained from the peak area for the NBS and commercial samples. It is seen in Fig. 9 that an equilibrium point ($A=0$) not always realized in the melting curve, and the plots of the two samples differ largely in the $1/r<2$ region but are in agreement in the $1/r<2$ region. Although it is thought that the point of half melting ($1/r=2$) is mostly at equilibrium during the melting, the closest points to equilibrium for the NBS and commercial samples give the values of 2.13 and 1.65 for $1/r$, respectively, as shown in Fig. 9. It is therefore concluded that the well-known method of thermal analysis shown in Fig. 8 can not give a highly accurate result. It is desirable to make use of the comparative methods described previously in the region of the melting curve where $1/r<2$.

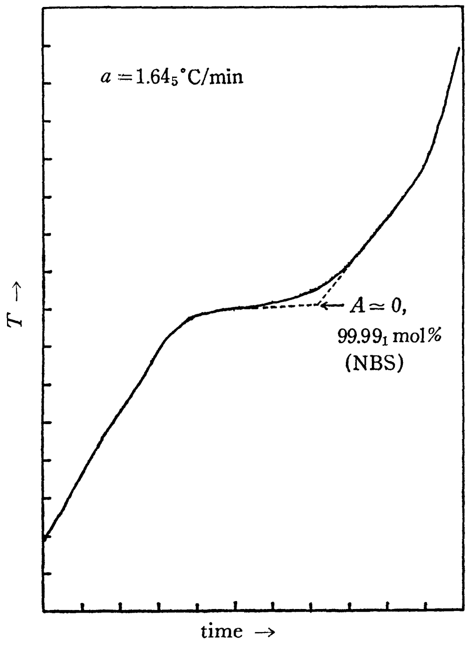

Fig. 8. Time-temperature melting curve for NBS sample of 2,2,4-trimethylpentane.

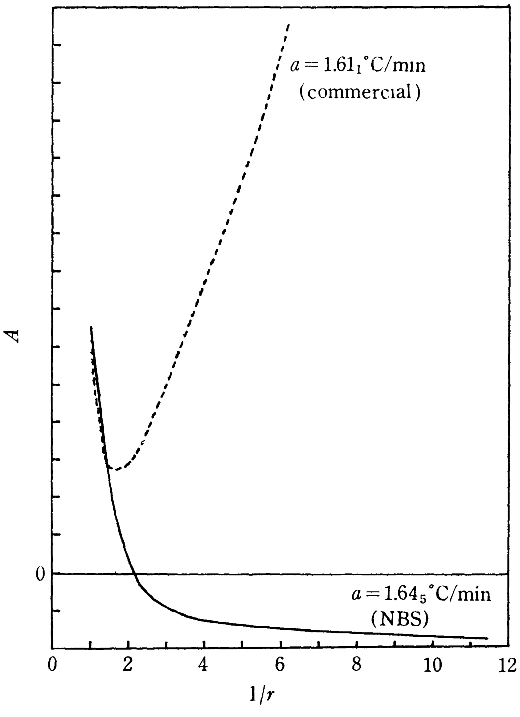

Fig. 9. Relationships between affinity A and reciprocal of fraction melted $1/r$ for NBS and commercial samples of 2,2,4-trimethylpentane.

The purity of two samples of 2,2,4-trimethylpentane determined by the methods described above are summarized in Table 4.

TABLE 4. RESULTS OF PURITY DETERMINATION BY VARIOUS METHODS FOR 2,2,4-TRIMETHYLPENTANE SAMPLES OF DIFFERENT PURITY

Method	Standard sample (NBS) (mol%)	Commercial sample (mol%)
Freezing point (NBS)	99.993 ± 0.003	—
Calorimetric	$99.991_2\pm0.0014$	—
DTA		
(a) Melting point depression using extrapolation ($T_{\max}(a=0)$)	$99.99_0\pm0.004$	98.05_4
(b) Comparative (i)	—	$98.05_2\pm0.004$
Comparative (ii)	—	98.04_8
(c) Melting point ($T(A=0)$, Fig. 8)	99.99_1	—

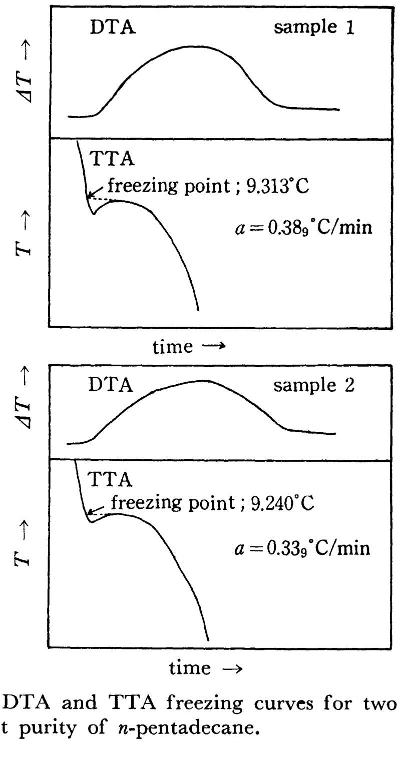

Fig. 10. DTA and TTA freezing curves for two samples of different purity of n-pentadecane.

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[8] W. J. Taylor and F. D. Rossini, *J. Res. NBS*, **32**, 197 (1944); A. R. Glasgow, Jr., A. J. Streinffand, and F. D. Rossini, *ibid.*, **35**, 355 (1945).

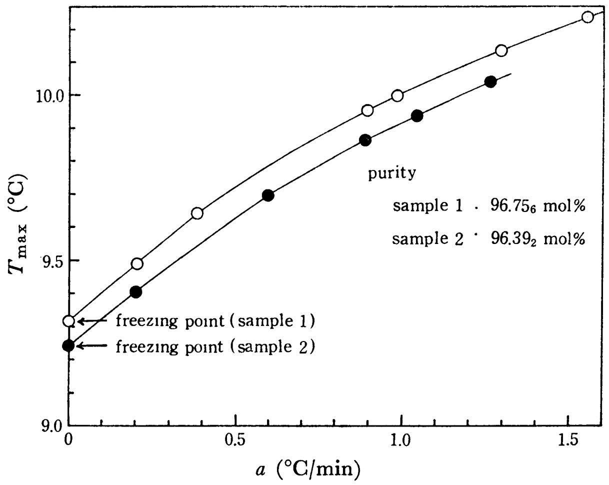

Fig. 11. Relationships between $T_{\rm max}$ and heating rate a for two samples of n-pentadecane of different purity.

Freezing DTA Measurement. The DTA data for two commercial n-pentadecane samples of different purity are given in Fig. 10. The freezing points of the samples were obtained by the well-known method[7] from the time-temperature cooling curves. The $T_{\rm max}$ ($a=0$) of the samples was obtained by the melting point depression method using extrapolation, as shown in Fig. 11. $T_{\rm max}$ ($a=0$) values are in excellent agreement with freezing points obtained from the freezing curves, and give the purity of each sample in terms of Eq. (2), as given in Fig. 11.

It can therefore be pointed out that when the sample is successfully supercooled, the freezing point obtained from the cooling curve is nearly at a temperature under equilibrium condition.

The authors wish to thank Dr. W. Wayne Meinke of the National Bureau of Standards for the supply of the Standard Sample 217b 2,2,4-trimethylpentane.