Purity Determination of Organic Compounds by Time-temperature Freezing or Melting Curves with a Simplified Apparatus[1]

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A simplified apparatus has been constructed for determining the purity of organic compounds by time-temperature freezing or melting curves. The sample cell is small and the amount of the sample needed in only 0.2 m*l* or 2 m*l*. The thermometers used are a Shimadzu platinum resistance thermometer calibrated by the measurement of fixed points and a chromel *p*-constantan thermocouple calibrated against a standard platinum thermometer with a precision better than $\pm 0.03°$. Purities of several hydrocarbons were determined by measuring their freezing and melting curves.

The apparatus and procedure for determining the purity of compounds from time-temperature freezing and melting curves were developed by Taylor and Rossini, and Glasgow *et al.*,[3] and are widely used. However, the temperature observed by the time-temperature technique is not real equilibrium temperature and differs from that observed with the use of a precision adiabatic calorimeter, especially in a simplified apparatus. Though purity determination by using the adiabatic calorimeter is more accurate, the apparatus and technique are complicated and the time required for measurement usually exceeds several hours.

This paper describes an apparatus and technique to simplify the method and save time in purity determination by means of time-temperature freezing and melting curves. The method was applied to the purity determination of several hydrocarbons. The results show that the well-known method of analyzing data should be improved to give highly accurate results.

Experimental

Apparatus. A small apparatus was constructed to obtain time-temperature freezing and melting curves. The general assembly is illustrated in Fig. 1. The sample cell and container are made of hard and pyrex glass, respectively. The details of the sample cells are shown in Fig. 2. The cells were closed in a vacuum system so that the sample could be analyzed in the absence of air and water vapor. A platinum thermometer or a thermocouple was inserted into the re-entrant well and the cells were then set in a hole of a copper cylindrical block, with wall of 0.2 mm thickness and heater wound around it. The cells were hung inside the container by means of three constantan wires. The container was evacuated, and the cooling and heating rates were controlled by adjusting the amount of helium gas inside the container. The whole assembly was mounted in a constant temperature cooling or heating bath. The temperature at the beginning of measurement was so selected that it differed from the freezing or melting point of a sample by approximately 10—50°C.

The sample temperature was measured with the platinum thermometer or the thermocouple. As the sample cell was small, a standard platinum thermometer could not be fitted. Instead, a small platinum-in-stainless steel resistance thermometer, 3.5 mm in diameter and 3 cm long, (Shimadzu Co.) was employed. It has four platinum leads, and was certified by the measurement of fixed points. The resistance value was about 100 ohms at room temperature. The thermocouple, a chromel *p*-constantan type, was calibrated by comparison with a Leeds & Northrup platinum thermometer certified by the National Bureau of Standards as well as against the melting point of benzoic acid and the freezing point of tin.

Each comparison was made under practically adiabatic conditions: the emf of the thermocouple and the resistance of the standard thermometer were measured at the same time. Some 40 comparisons were made in the temperature range of 15 to 500°K. Two formulas which each fit the data in the temperature regions above and below 0°C, are based on the expansion of emf in terms of absolute temperature T as follows:

$$\text{emf}\,(\mu\text{V}) = \sum_{n=0}^{m} A_n (T)^n \qquad (1)$$

where the upper limit of m is 4 and 9 for above and below 0°C, respectively. Coefficients determined are listed in Table 1. The deviations of the observed values from the calculated

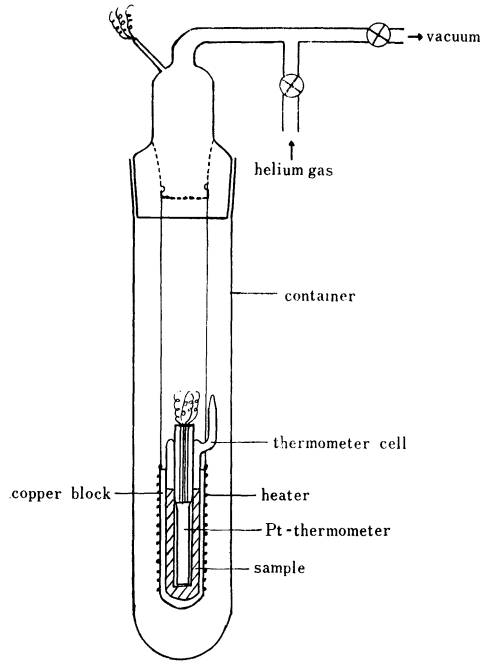

Fig. 1. Simplified apparatus for purity determination.

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

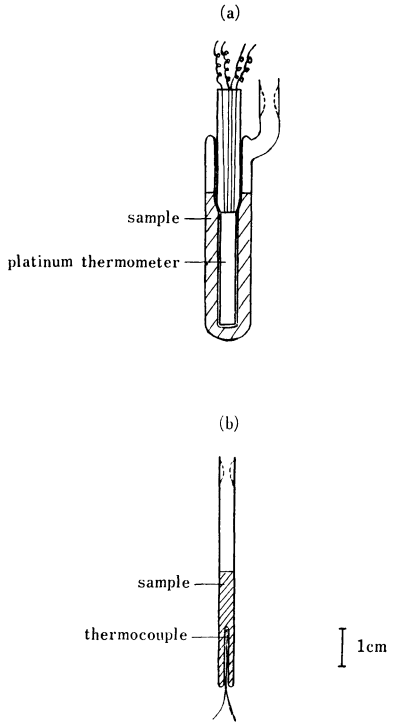

Fig. 2. Cross-sectional diagram of sample cells: (a) platinum thermometer cell (b) thermocouple cell.

TABLE 1. COEFFICIENTS DETERMINED BY FITTING EQ. (1) TO THE CALIBRATION DATA OF CHROMEL *p*-CONSTANTAN THERMOCOUPLE

	0°C$<T<$240°C	15°K$<T<$273°K
T	Celsius degree	Kelvin degree
A_0	−1.46271	9979.5
A_1	59.3394	−0.729544
A_2	0.0514691	−0.234398
A_3	-4.30948×10^{-5}	0.00180392
A_4	-7.06495×10^{-8}	-3.64454×10^{-5}
A_5	0.0	4.97434×10^{-7}
A_6	0.0	-3.85761×10^{-9}
A_7	0.0	1.68203×10^{-11}
A_8	0.0	-3.85227×10^{-14}
A_9	0.0	3.60646×10^{-17}

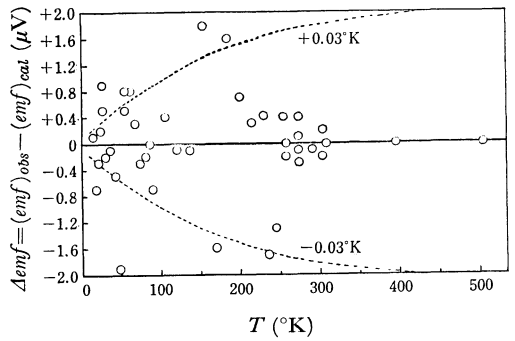

Fig. 3. Deviation of observed emf of a chromel *p*-constantan thermocouple from the calculated one by using Eq. (1).

ones by using Eq. (1) were within ±0.03° as shown in Fig. 3.

The resistance of the thermometer is recorded on a Shimadzu Precision Temperature Recorder CT3. An ice-water bath was used as a reference for the thermocouple, and the difference in emf between the cell thermocouple and a Yokogawa DC Potentiometer P-7B was amplified with an Ohkura DC Microvolt Meter AM-101, and then recorded on a Yamatake-Honneywell Recorder Electronic 19 as a function of time. All measurements were carried out automatically, except for the manual control of freezing or melting rates. The time required for the measurement of a sample was about fifteen minutes.

Material. The thermometer and thermocouple cells were filled at the same time with extra pure grade reagents *n*-octane, *n*-undecane, *n*-tridecane and *n*-docosane obtained from Tokyo Kasei Kogyo Co., Ltd. After removing the trace of air from the sample by pumping out at liquid nitrogen temperature, the cells were sealed in a vacuum system.

The amount of sample used was about 2 m*l* for the thermometer cell and 0.2 m*l* for the thermocouple cell.

Results and Discussion

Principle of Purity Determination from the Freezing or Melting Point. For impurities that are completely soluble in the liquid phase but insoluble in the solid phase, the thermodynamic relation between the amount of impurities and the equilibrium temperature in the case of an ideal or sufficiently dilute solution, is

$$-\ln(1-N)/r = (T^*_{f0}-T)\Delta H_m/R(T^*_{f0})^2 \qquad (2)$$

where N is mole fraction of the impurities, T^*_{f0} the melting point of pure compound, T the given temperature at equilibrium, r the fraction melted or crystallized, ΔH_m the heat of fusion at T^*_{f0} of pure compound and R the gas constant. However, the temperature T given by the time-temperature curve is not always at equilibrium, and the corresponding equation should be derived from irreversible thermodynamics as follows:[4]

$$-\ln(1-N)/r = (\Delta H_m/R)(1/T-1/T^*_{f0}) + (\Delta C_p/R)[\ln(T^*_{f0}/T)+1-(T^*_{f0}/T)] + A(T,r)/RT. \qquad (3)$$

Here ΔC_p denotes the difference of heat capacity of pure compound in liquid and solid states, and $A(T,r)$ the affinity. However, A usually has some finite value, and to estimate the value of A as a function of temperature or time is difficult, especially with a simplified apparatus and technique. If $A=0$, the temperature and fraction melted or crystallized are applicable for determining the purity of the sample by means of Eq. (2).

As a matter of principle it may be assumed that in the time-temperature curves of freezing or melting, the temperature of sample when $r=1/2$ is most nearly at equilibrium, and so Eq. (2) is applicable for determining the purity.

Purity Determination of Hydrocarbons. The time-temperature curves of freezing or melting for several hydrocarbons were obtained by using both the platinum thermometer and the thermocouple cells. As was described in the previous section, determination of

4) I. Prigogin and R. Defay, "Chemical Thermodynamics," Longmans Green and Ltd. (1954), p. 373; Y. Mashiko, T. Shinoda, and H. Enokido, to be published.

purity was made by measuring the temperature most nearly at equilibrium. The results were compared with those obtained by using the method of Rossini *et al.*[3]

As an example, time-temperature melting and freezing curves for *n*-undecane and *n*-docosane obtained by using the thermocouple cell are shown in Fig. 4.

i) Purity of n-*Undecane Obtained by the Melting Curve.* Temperature x, shown in Fig. 4(a), which is a point of inflexion of a quasi-equilibrium portion of the melting curve, seems to be the melting point of the sample. Also the temperature when $r=1/2$ seems to be given by the intersection y of the extension of the melting curve, where a major portion of the sample is melted, with the backward extension from the point x of the heating curve of liquid. The amounts of impurities in the sample of *n*-undecane estimated from the temperatures of point x and y corresponding to $r=1$ and 1/2, respectively, and the value of the melting point reported by Finke *et al.*[5] are in good agreement with each other within —0.03 mol%, and give the average value 99.2_3 mol%.

On the other hand, the melting points of the same sample and of zero impurity of *n*-undecane were calculated from the melting curve by Rossini's method. A GHI-line in Fig. 4(a) represents a quasi-equilibrium portion of melting curve which was explained by Rossini *et al.* The obtained values are 247.21_2°K and 248.30_0°K, respectively, and give a purity of 98.3_6 mol%. If the literature value 247.592°K is used as the melting point for zero impurity, the significantly different value of 95.3_7 mol% is obtained. Thus it can be seen that it is not appropriate to analyze the time-temperature melting curve obtained with a simplified apparatus in terms of Rossini's method, since it is difficult to observe the melting curve under equilibrium condition in a simplified apparatus as compared with Rossini's larger apparatus.

ii) Purity of n-*Docosane Obtained by the Freezing Curve.* If supercooling is successfully observed with a small peak, a major portion of the freezing curve may be assumed to be nearly at equilibrium. Therefore, analysis of the freezing curve was made for *n*-docosane by Rossini's method, as shown in Fig. 4(b). The result, 99.1_9 mol%, is in better agreement with ours (99.2_9 and 99.2_2 mol%) obtained by means of the melting curve than that determined by applying Rossini's method.

The results of the purity determination of hydrocarbons are given in Table 2 together with those obtained with a Yanagimoto Gas Chromatograph GCG-5DH.

It can be seen from Table 2 that of the four procedures for determining the purity from freezing and melting curves of the same sample, treatment of the melting curve, where the obtained temperature is not considered to be at equilibrium, gives results which are in good agreement with those obtained from the freezing curve when the sample was successfully supercooled. Application of Rossini's method to the melting curve was unsuccessful. This is probably due to the fact that it is easier to establish an equilibrium in the freezing process than in the melting one. However, if supercooling is carried out to the extent that a quasi-equilibrium portion of the freezing curve is not given, it is difficult to determine the purity with high accuracy. This will be seen in the purity determination of *n*-octane by the freezing curves using a thermocouple cell (97.4_0 mol%) and *n*-undecane using a platinum thermometer cell (97.4_7 mol%) with a high freezing rate. It was observed from many measurements that our treatment of the melting curve also could not give highly accurate results when the heating rate was greater than 0.5°C/min. Point y in Fig. 4(a) did not always give the temperature where $r=1/2$. It can be said that the melting curve may be obtained at an arbitrary heating rate as long as it is smaller than 0.5°C/min. However, results obtained without considering the equilibrium are less accurate than those obtained from a well-performed freezing curve.

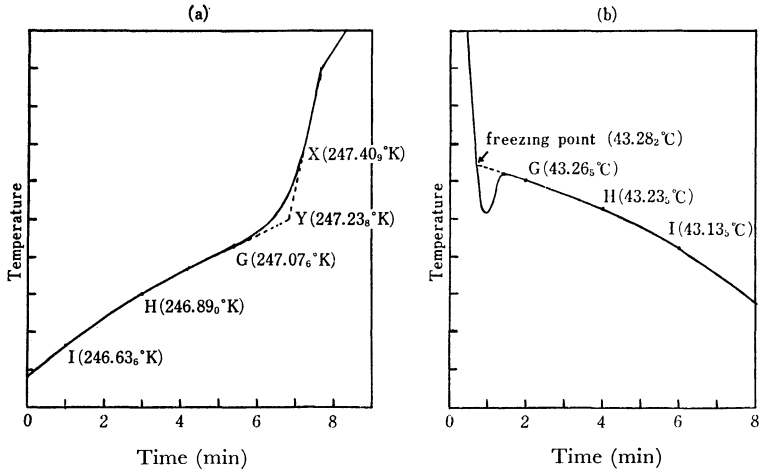

Fig. 4. Time-temperature melting and freezing curves for determining the purity: (a) melting curve of *n*-undecane (b) freezing curve of *n*-docosane.

5) H. L. Finke, M. E. Gross, Guy Waddington, and H. M. Huffman, *J. Amer. Chem. Soc.*, **76**, 333 (1954).

TABLE 2. PURITY DETERMINATION OF HYDROCARBONS

		n-Octane (n-C_8H_{18})			*n*-Undecane (n-$C_{11}H_{24}$)		
		Purity (Rossini's method mol %)	Purity (improved method mol %)	Rate (°C/min)	Purity (Rossini's method mol %)	Purity (improved method mol %)	Rate (°C/min)
Melting curve	Pt-therm. cell	(99.1_7)	99.4_2	0.45	(96.7_5)	99.2_5	0.20
	T. C. cell	(98.8_8)	99.4_3	0.19	(98.3_6)	99.2_3	0.17
Freezing curve	Pt-therm. cell	99.4_3	—	0.38	(97.4_7)	—	0.97
	T. C. cell	(97.4_0)	—	0.51	99.6_4	—	0.58
Gas chromatography			99.4			99.5	

		n-Tridecane (n-$C_{13}H_{28}$)			*n*-Docosane (n-$C_{22}H_{46}$)		
		Purity (Rossini's method mol %)	Purity (improved method mol %)	Rate (°C/min)	Purity (Rossini's method mol %)	Purity (improved method mol %)	Rate (°C/min)
Melting curve	Pt-therm. cell	(97.1_5)	96.5_7	0.46	—	99.2_9	0.29
	T. C. cell	(96.2_4)	96.1_9, 97.9_1	0.23	(97.9_7)	99.2_2	0.40
Freezing curve	Pt-therm. cell	—	96.6_8	2.46	99.7_0	—	0.57
	T. C. cell	—	—	—	99.1_9	—	0.54
Gas chromatography			99.6			99.5	

The difference in the purity of *n*-tridecane obtained by thermodynamic methods and gas chromatography is probably due to some impurities which could not be observed by gas chromatography (Table 2).

Finally, from the results of the present experiments the following remarks are given for determining the purity of a compound from time-temperature freezing or melting curve with a simplified apparatus.

i) The sample cell should be closed in a vacuum system in order to carry out analysis in the absence of air and water vapor.

ii) The thermometer should be calibrated against a precision temperature scale, since the determination of melting point for zero impurity is less accurate than that obtained with the use of time-temperature curves. Thus, if we can find a value obtained with the use of a precision adiabatic calorimeter, it would be better to use it.

iii) The temperature of the equilibrium portion of the freezing or melting curve is not always at equilibrium. According to the accuracy required for purity determination, the observed curve should be analyzed on the basis of the theory of irreversible thermodynamics instead of by the well known method.

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