

PURITY DETERMINATION BY DIFFERENTIAL SCANNING CALORIMETRY

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(Received April 3rd, 1972; revised June 23rd, 1972)

ABSTRACT

A review of the literature on the DSC method for purity determination is presented, with a discussion of the most important aspects, *i.e.* theory, sample handling, calibration of the instrument, evaluation of melting curves, and the conditions and accuracy of the measurement of eutectic impurities.

A number of mathematical descriptions of the solid–liquid equilibrium for eutectic binary systems is applied to the calculation of theoretical phase diagrams and specific heat functions, which are then compared with experimental phase diagrams and melting curves. The applicability of the DSC method to systems of solid solutions is discussed.

Both the experimental procedure and the evaluation by computer methods required to obtain accurate impurity determinations by DSC are presented. A number of practical examples is included.

INTRODUCTION

The measurement of the melting point of a substance as a method of identification dates back to the early days of chemistry. Many different observations on organic and inorganic substances were made during the thermal treatment necessary for a melting point determination.

The observations were summarized and interpreted in terms of phenomena like polymorphism, sublimation, thermal decomposition, solid solutions, eutectic systems, congruently-melting compounds, glass transitions and others. Kofler¹ turned the melting point determination by microscopic observation into an extremely useful method in the field of analytical chemistry. Kofler's treatise on purity determinations is excellent, but of course, today, it is not easy to agree with the statement in *Thermomikromethoden*: "The method of purity determination with the microscopical observation of the melting point, however, will finally replace all the others". Somehow, the development of the analytical methods for purity determination since 1950 has appeared to prove the opposite, namely that all the other analytical methods would replace the melting point determinations. Kofler's melting point method is nowadays performed with many different types of apparatus. The method is used

because it is the simplest analytical method for getting information about the purity and about the crystal form of the sample under investigation. The melting point method is based on the determination of the absolute temperature of the substance assuming an infinitely small amount of solid substance in the solid-liquid equilibrium. A reference standard of a high purity is required to make the temperature measurement only a relative one. This high purity standard is also used for the relation between the purity and the melting point difference given in Eqn. (1)

$$\Delta T = T_1 - T_s = x_0 \cdot k_r \quad (1)$$

where ΔT is the melting point difference in °K, T_1 is the melting point of the high purity standard in °K, T_s is the melting point of the sample in °K, x_0 is the mole fraction of the impurity, and k_r is the cryoscopic constant in °K.

The cryoscopic constant is defined as

$$k_r = \frac{RT_1^2}{\Delta H_{f,1}} \quad (2)$$

where R is the gas constant and $\Delta H_{f,1}$ is the molar heat of fusion of the high purity standard, and is experimentally determined by means of Eqn. (1) or with a measurement of the heat of fusion $\Delta H_{f,1}$ and the melting point of the reference standard.

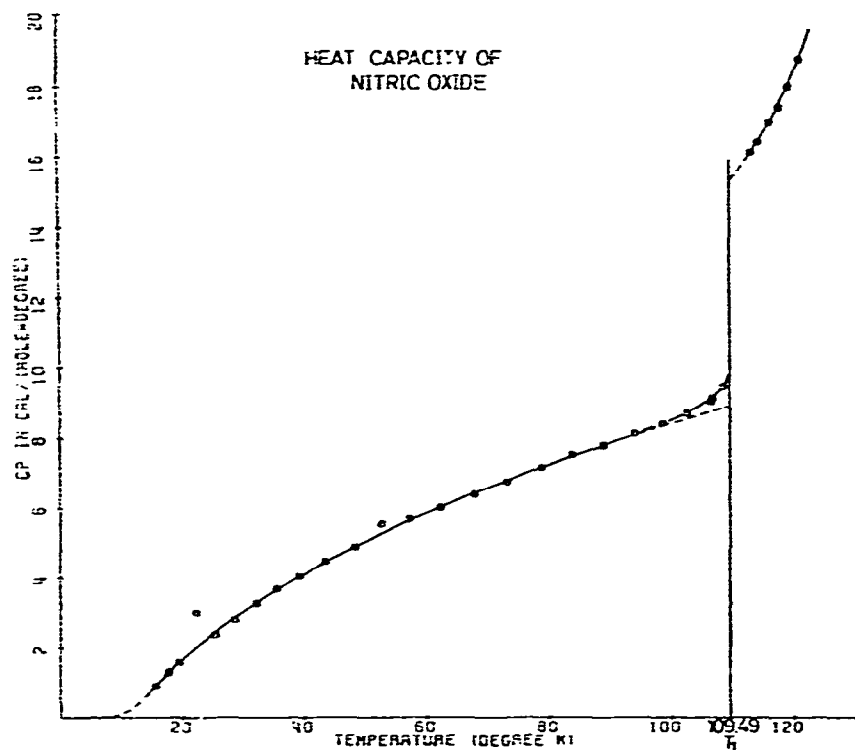


Fig. 1. Heat capacity of nitric oxide measured by Johnston and Giauque³. (Melting point $T_1 = 109.49^\circ\text{K}$.)

Today, a second method seems to replace at least partially the microscopic observation of the melting point. This second method is known as differential scanning calorimetry (DSC). The DSC method measures the endothermic amount of energy which is afforded by the premelting process of substances. The method of premelting as a purity determination dates back to the 1920's in a form used by Eucken and Karwat² and Johnston and Giauque³ for the measurement of the heat capacity of nitric oxide in the melting point region. In 1929, Johnston and Giauque³ reported from the Chemical Laboratory of the University of California in Berkeley on the heat capacity of nitric oxide from 14°K to the boiling point.

The paper of Johnston and Giauque is interesting enough for a brief discussion. In Fig. 1, the heat capacity of nitric oxide is shown as a function of temperature, according to the measurements of Johnston and Giauque. The extremely sharp melting region of the nitric oxide sample at about 110°K should be noted. The nitric oxide used by Johnston and Giauque was produced by the reaction of potassium nitrite and potassium iodide in distilled water. The generated nitric oxide was purified over several distillation steps.

As an example, the same purified sample, containing $n_0 = 3.769$ moles of nitric oxide, was used for the premelting measurements and also the measurements of the heat capacity, the heat of fusion, and the melting point. Johnston and Giauque measured the following values for this sample of nitric oxide: molar heat of fusion, $\Delta H_{f,1} = 549.5 \pm 1.0 \text{ cal.mole}^{-1}$; melting point, $T_1 \cong T_s = 109.49 \pm 0.05 \text{ }^\circ\text{K}$.

The purity of the nitric oxide was calculated by applying Eqn. (3), which holds for low concentration of impurities

$$x_{0,2} = \frac{\Delta H_{f,1}}{RT_1^2} (T_1 - T)r \quad (3)$$

where $x_{0,2}$ is the eutectic impurity of the sample as mole fraction, $\Delta H_{f,1}$ is the molar heat of fusion of the pure nitric oxide, T_1 is the melting point of the pure nitric oxide, T is the temperature of the solid-liquid equilibrium, r is the molten fraction of the system at temperature T , and R is the gas constant.

The heat of premelting Δq_p , necessary for a temperature rise of the solid-liquid equilibrium from T' to T'' , is related to the corresponding molten fractions of the sample r' and r'' . We can write the equation

$$\Delta q_p = \Delta H_{f,1} n_0 (r'' - r') \quad (4)$$

The method of Johnston and Giauque enables the measurement of the total amount of heat Δq for a temperature rise of the substance from T' to T'' . This total amount of heat is the sum of the heat of premelting Δq_p and an amount Δq_c given by the specific heat of the substance and the known temperature interval $\Delta T = T'' - T'$

$$\Delta q = \Delta q_p + \Delta q_c \quad (5)$$

The calculation of the heat of premelting (Δq_p) is possible from Eqn. (5), with the

measurement of the heat capacity of nitric oxide (Δq) and with an extrapolation of the specific heat from a region with practically no premelting into the selected region of premelting. The eutectic impurity of the nitric oxide is calculated for a corresponding set of temperatures and molten fractions (T', r' ; T'', r'') and with the aid of Eqns. (3) and (4).

$$x_{0,2} = \frac{\Delta q_p}{n_0 RT_1^2} \cdot \frac{(T_1 - T'')(T_1 - T')}{T'' - T'} \quad (6)$$

With Eqn. (6) and the values of the measurements on nitric oxide, it is possible to calculate exactly the same values of eutectic impurities as found by Johnston and Giaque. The values and results are presented in Table I.

TABLE I
PREMELTING MEASUREMENTS ON NITRIC OXIDE

Temperatures ($^{\circ}K$)		Heat of premelting between T' and T'' , q_p (cal)	Eutectic impurities $x_{0,2}$ (mole fraction)
T'	T''		
104.71	108.59	0.171	7.9×10^{-6}
107.63	109.15	0.365	6.4×10^{-6}

Johnston and Giaque came to the conclusion that the nitric oxide used in their measurements contained less than 10^{-3} mole percent of eutectic impurities, or, the so-called purity is of the order of 99.999%. The authors excluded the possibility of noneutectic impurities because of the method of preparation of the nitric oxide used for these investigations. Johnston and Giaque explained that no analyses of the purified gas were made since accurate melting point and heat capacity data provide a more sensitive test of impurity than that given by chemical analysis. Johnston and Giaque made an equivalent statement to Kofler's about the measurement of impurities by the melting point method. It seems to be clear that such excellent investigators as Giaque and Kofler did not emphasize the melting point and premelting method in such a way without being deeply impressed by the possibilities of these two methods.

If we want to compare the excellent work from the low temperature laboratory at the University of California in Berkeley (the laboratory was named Giaque Hall in 1967) with the premelting measurements, mainly DSC and DTA, performed in the 1970's, we have to consider several points. The difference between the calorimetric method of Johnston and Giaque and the DSC or DTA method is not in thermodynamics but rather in the instrumentation and in the properties of the methods of measurement.

In Table II we compare some of the aspects of the two methods, selecting the DSC-IB of the Perkin-Elmer Corporation for the second group.

TABLE II
COMPARISON OF THE PREMELTING METHOD OF JOHNSTON AND GIAUQUE
AND THE PURITY DETERMINATION WITH THE DSC-IB

<i>Condition or property measured</i>	<i>Calorimetric method of Johnston and Giauque³</i>	<i>DSC-IB (Perkin-Elmer Corp.)</i>
Weight of the sample	100 g	3 mg
Accuracy of the absolute temperatures	$\pm 10^{-2} \text{ } ^\circ K$	$\pm 3 \times 10^{-1} \text{ } ^\circ K$
Accuracy of the relative temperatures	$\pm 2 \times 10^{-3} \text{ } ^\circ K$	$\pm 10^{-2} \text{ } ^\circ K$
Accuracy of the measured heat of fusion	$\pm 2 \times 10^{-1} \%$	$\pm 5\%$
Accuracy in the purity value for high-purity substances	$\pm 10^{-4} \%$	$\pm 5 \times 10^{-2} \%$
Time for a premelting measurement	2-4 days	20 min

The great disadvantage of the calorimetric method developed by Johnston and Giauque, especially in industrial use, is the extremely long running time required for one measurement which is of course due to the enormous sample weights and the necessity for an equilibrium between the liquid and solid phases of the sample at all temperature points⁴. It is also clear, however, that somehow one has to pay for such a high accuracy in purity measurements. Between the measurements on purity with thermoanalytical methods of the 1920's and the 1970's, a great number of papers were published on purity measurements by the freezing point method. We mention only one paper, which we regard as representative of all the papers on thermoanalytical purity measurements produced during this period: Determination of Purity by Measurement of Freezing Points, by Glasgow, Krouskop, Beadle, Axilrod and Rossini⁵.

Following these preliminary and historical remarks, we will concentrate on purity work performed with the DSC-IB, an instrument of the Perkin-Elmer Corporation. The development of new DSC- and DTA-systems will certainly change the issue of the purity determination, *e.g.* enhance the accuracy of the measurement of eutectic impurities and solid solutions without increasing the running time for one measurement.

DISCUSSION ON THE DSC LITERATURE ON PURITY

In this discussion we shall not attempt a complete report of the DSC literature. We will arrange our discussion according to theoretical and experimental points of the DSC-purity method.

(a) *Theory of the purity measurements*

As far as we know, all DSC results on purity in the literature are calculated

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