INVESTIGATIONS ON SKAU'S DYNAMIC CRYOMETRY DETERMINATION OF THE PURITY OF ORGANIC SUBSTANCES

ZYGMUNT BUGAJEWSKI AND ANDRZEJ BYLICKI

Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw (Poland)

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ABSTRACT

The results of studies on the course of cryometric curves obtained by the Skau technique and suggestions of a new procedure to be based on the use of the inflection point of the melting curve for the determination of the "equilibrium" range of the cryometric curve are described.

INTRODUCTION

Of the various cryometric techniques developed for determining the purity of substances, the dynamic technique that has recently been very widely applied is the one due to Skau, which was proposed as early as the mid-1930s[1]. This technique involves measuring the temperature of the substance being melted under the conditions of linearly varying ambient temperature so as to record either the sample's own temperature or its difference with respect to the ambient temperature as a function of time.

The Skau technique is advantageous in many respects and especially in that it requires a small amount of sample and short measurement time and may be readily automated. However, although numerous investigators have spared no effort to refine the technique, interpretation of the experimental results continues to be fraught with numerous difficulties.

The cryometric measurement essentially involves equilibration and registration of the solid–liquid equilibrium temperature during melting or freezing as a function of the reciprocal fraction of the liquid phase at equilibrium. To determine the fraction melted (F), Skau assumes the surface area bounded by the lines representing the surrounding temperature T_j and the sample temperature (Fig. 1, curve ILFM) to be directly related to the amount of heat required to melt the sample and to raise it from the initial temperature T_1 to the final temperature T_M. There are many reasons for deviations from this assumption, which render correct evaluation of the F-value difficult.

The dynamic nature of the process opposes the complete establishment of the thermal and thermodynamic equilibrium and may well give rise to erroneous determina-
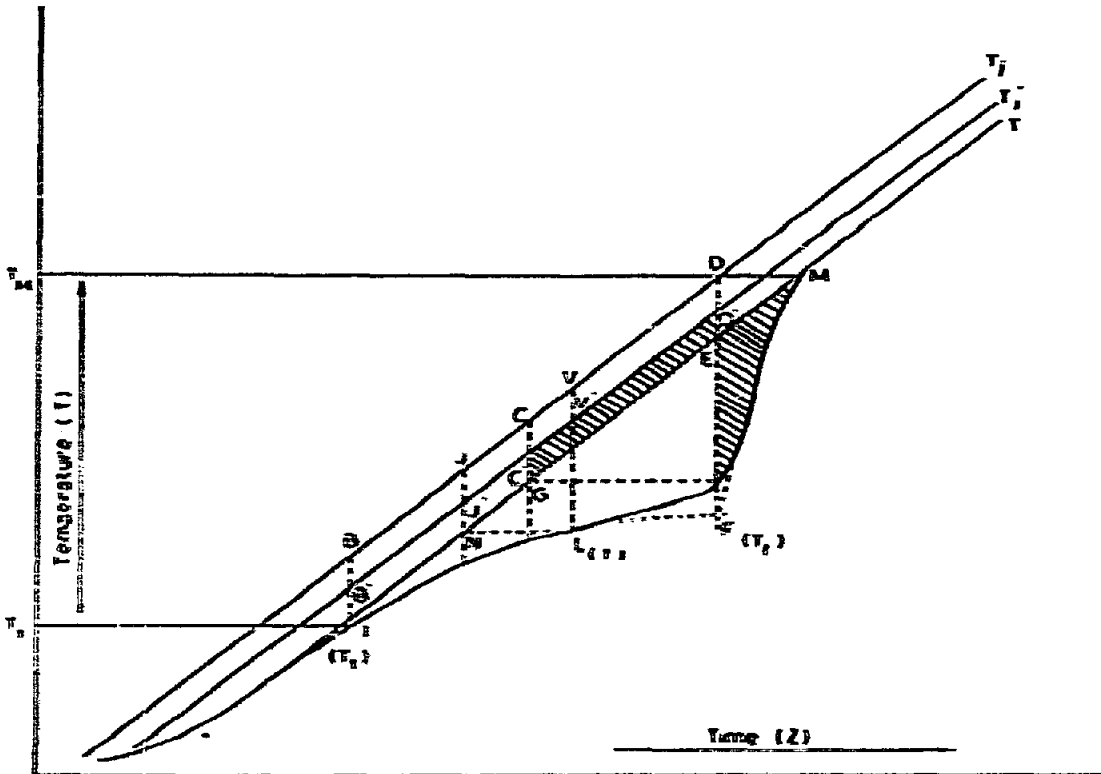
Fig. 1. Interpretation of the kinetic melting curve obtained for linear temperature change of heating block.

$$F = \frac{\text{area IB'V'LI}}{\text{area IB'D'FLI}} : \text{ fraction melted with correction for the heat dissipated in the thermocouple leads etc. (correction 1).}$$

$$F = \frac{\text{area INI'V'LI}}{\text{area IGC'D'FLI}} : \text{ fraction melted with correction 1 and 2 (for the heat consumed to warm the system comprising the examined sample, the sample holder etc.).}$$

tion of the equilibrium temperature (T). As a result, Skau's experimental cryometric curves usually follow courses inconsistent with the theory based on relationships suitable for the given solid–liquid transition, whereby they become still less susceptible to unequivocal interpretation.

Much effort has been devoted[2–4] to enhancing the accuracy of evaluation of F via suitable corrections introduced into the calculation based on the experimental melting curve. The two major corrections are: (1) for the heat dissipated in the thermocouple leads and in the sample suspending wires, and (2) for the heat consumed to warm the system comprising the sample examined, the sample holder, thermocouple, etc. as the temperature of the melting process is increased, i.e. the heat not involved in the actual phase transition.

The graphical methods used to establish the two corrections are presented in Fig. 1. These methods are described in detail in ref. 4 and lead the replacement of the line of the changing temperature of the heating block, T_j, by another correction line T_j.
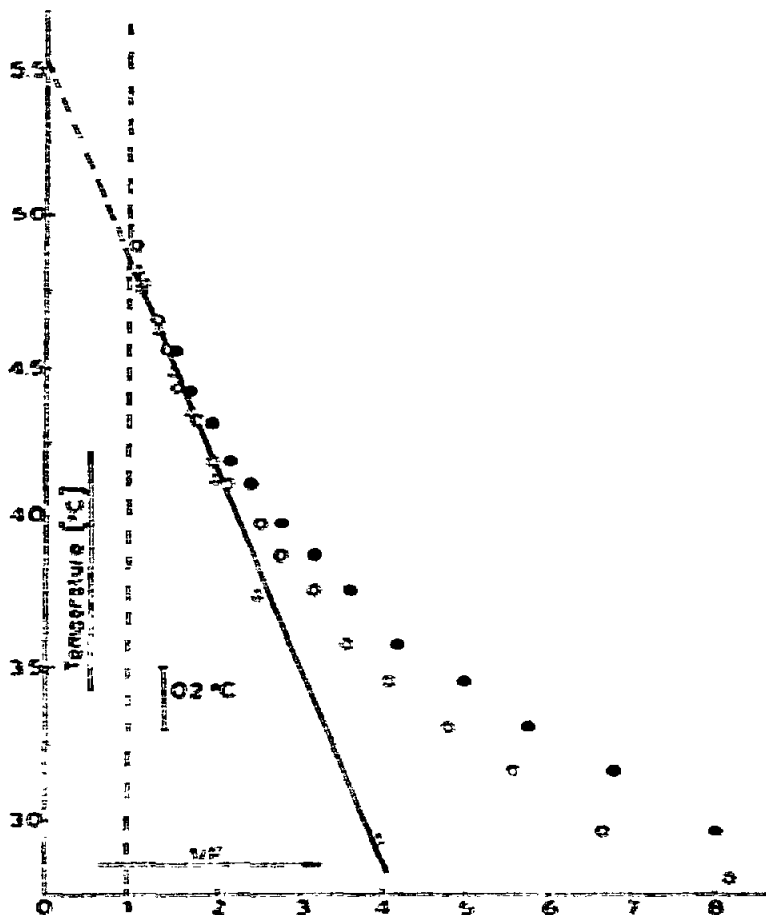
Fig. 2. Comparison of the theoretical cryometric curves (eqn. (1)) with those ascertained by the dilatometric and Skau's techniques for samples containing 1.000 mole %$_n$ of n-heptane in benzene. △, dilatometric technique; ○, Skau's technique with correction 1 applied; ●, Skau's technique with corrections 1 and 2 applied. Solid straight lines represent the theoretical course (eqn. (1)).

When considered in terms of heat-transfer theory the procedure adopted represents a considerable over-simplification. However, this problem goes beyond the scope of the present work.

In practice it is essential to know that, even if thoroughly applied, these corrections fail to eliminate the systematic errors inherent in the determination of the F-value. Attempts to introduce extra corrections based on the trial-and-error method have also led to unsatisfactory results.

To overcome these difficulties efforts have been made to establish general guidance principles for choosing a section in the cryometric curve ($T = f(1/F)$) which obeys eqn. (1) to a satisfactory approximation.

To determine the impurity content, Lyashkevich[5] used either the slope of the cryometric curve over the range $1/F = 1-2$, or extrapolated the curve from $1/F = 1$ to $1/F = 0$. Cisse et al.[6] have recommended the range $1/F = 2$ to 6 for this purpose.

Evidently, no generally consistent conclusions can be deduced from such investigations.

The present work describes results of studies on the course of cryometric curves obtained by the Skau technique and suggests a general procedure which enables the accuracy of purity determination to be enhanced.

In order to distinguish manifestly the effects associated with the interpretation of the Skau melting process from the effects due to thermodynamic properties of the system examined, benzene + n-heptane was chosen as a model system of well-known properties, which had once been used as the object of an international comparative study programme on the cryometric techniques of purity determination performed under the IUPAC auspices[7].

At n-heptane content lower than 5 mole %, benzene + n-heptane may be regarded as an ideal system which follows the simplest form of the cryometric equation

$$T = T_{f_m} + \frac{x_2^0}{A}\frac{1}{F} \qquad (1)$$

where, T_{f_m} is the freezing temperature of the solvent; x_2^0 is the mole fraction of the solute, and A is the cryometric constant of the solvent.

The course of the cryometric curves obtained by the Skau technique was compared with the result obtained by the static dilatometric technique[8] (Fig. 2); the latter allows the measurements under equilibrium conditions and to eliminate wholly or to a considerably reduced extent, the systematic errors involved in determining F and T.

EXPERIMENTAL

Preparation of substances

A standard benzene sample, purity 99.989 ÷ 0.003 mole %, prepared at this Institute, was used. The degree of purity of the benzene sample was established by the Świętosławski dilatometric[8] and the Rossini dynamic techniques[9]. Preparation and the determinations of purity and of constants characterizing the physico-chemical properties of the standard benzene sample are described elsewhere[10].

Synthetic mixtures with compositions known to within 0.001 mole % were

TABLE I

MIXTURE SAMPLE COMPOSITIONS

Mixture	No. 1	2	3	4	5	6	7
n-Heptane added (mole %)	0.108	0.150	0.390	0.660	0.890	1.000	1.640
Total impurity (mole %)	0.119	0.291	0.531	0.801	1.031	1.141	1.781

prepared by adding portions of 99.6 mole % (by GLC) pure n-heptane to the standard benzene sample. The mixtures prepared are listed in Table 1.

Apparatus

The apparatus used was constructed at this Institute and is described elsewhere[11].

The temperature programme in the heating block was maintained linear within the limits of 0.003°C. The sample temperature was taken with a copper–constantan thermocouple. The sensitivity of the temperature measuring system, established on the basis of the galvanometer and the thermocouple constants, was found to be 0.003°C. Time was measured with an accuracy of 0.02 min. Samples were placed in test tubes 30 mm long and 5 mm across. The thermocouple was immersed directly in the substance examined. In choosing the shape and size of the test tube, recourse was taken to the results of extensive investigations carried out by Lyashkevich[5, 12, 13]. The amount of sample examined was about 0.1 g.

Procedure

Since small samples subjected to freezing or melting are difficult to agitate, use was made of Lyashkevich's[5] idea to crystallize rapidly the sample at temperatures about 75°C lower than the freezing point to ensure a uniform distribution of impurities. Dry ice + ethanol was used as a cooling mixture.

The sample thus crystallized was placed inside the heating block immersed in the cryostat. In view of Cisse and Clechet's finding[4] that the equilibrium section of the melting curve becomes reduced as the heating rate is increased, the linear increase of the block temperature was applied as low as possible, viz., 0.1°C min^{-1}.

The liquid phase fraction, F, was evaluated from the melting curve at a given equilibrium temperature, T, by using suitable corrections[4] and the cryometric curves $(T = f(1/F))$ were constructed.

TABLE 2

INPURITY DATA EVALUATED FOR STANDARD BENZENE SAMPLES WITH THE AID OF THE INFLECTION POINT IN THE MELTING CURVE

No.	x_2 (mole %)		Absolute error (mole %)	Relative error (mole %)	Standard deviation ($100 \times S_x$)
	Actual	Observed			
1	0.119	0.132	+ 0.013	10.92	0.59
2	0.291	0.332	+ 0.041	14.09	3.10
3	0.531	0.552	+ 0.051	9.60	2.21
4	0.501	0.581	+ 0.080	10.00	1.82
5	1.091	0.960	− 0.131	12.00	1.40
6	1.141	0.973	− 0.167	14.72	2.37
7	1.781	1.315	− 0.466	26.15	3.47

Repeatability of the final results of measurements was established by calculating the standard deviation of the mean from three measurements (Table 2).

RESULTS AND DISCUSSION

For comparison, the cryometric curves established by the dialtometric and Skau's technique are plotted in Fig. 2. Theoretical curves are also plotted according to eqn. (1) with $A = 0.01523$ deg^{-1} taken for the first cryometric constant of benzene.

Figure 3 shows the Skau cryometric curves obtained for the seven samples (Table 1), ascertained with due correction for heat dissipation.

In Fig. 4, the $(1/F)$-parameter ranges are shown within which the slopes of the cryometric curves coincide with the correct values of x_2^0/A at the given impurity contents.

As evident from Fig. 2, the Skau cryometric curves, unlike the dilatometric,
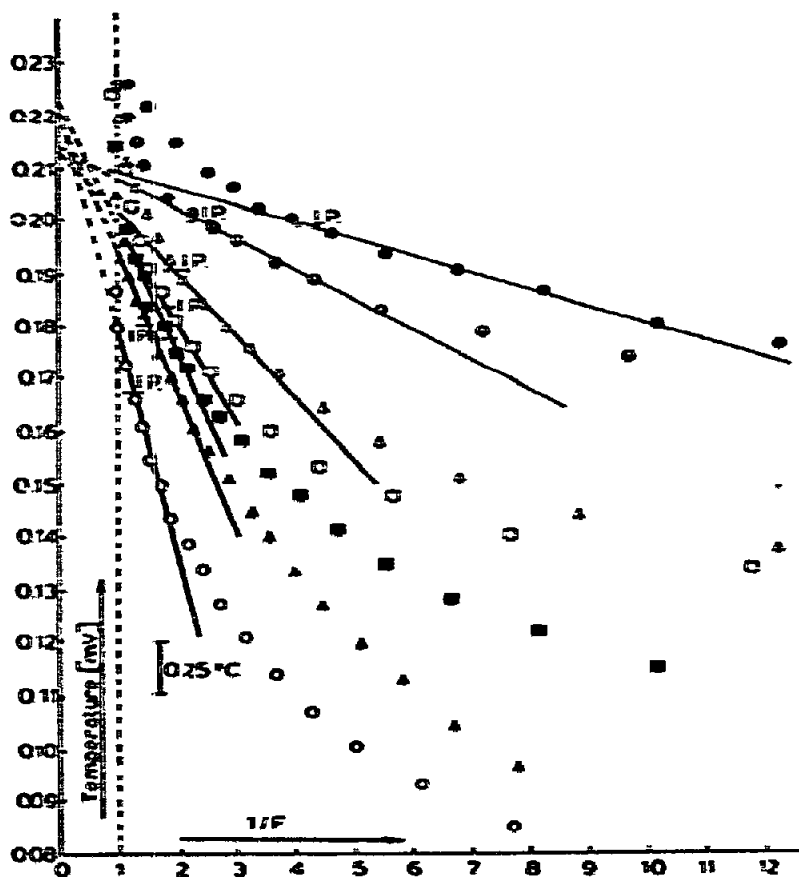

Fig. 3. The cryometric curves ascertained by Skau's technique for benzene samples containing various impurity proportions, with correction 1 applied. ●, sample 1: ⊕, sample 2. ⚏. sample 3: ☐, sample 4; ■, sample 5; ▲, sample 6; ○, sample 7. The straight lines drawn through suitable experimental points in each curve determine the slope conforming to the theoretical course for individual benzene samples. I.P., inflection point of the melting curve.
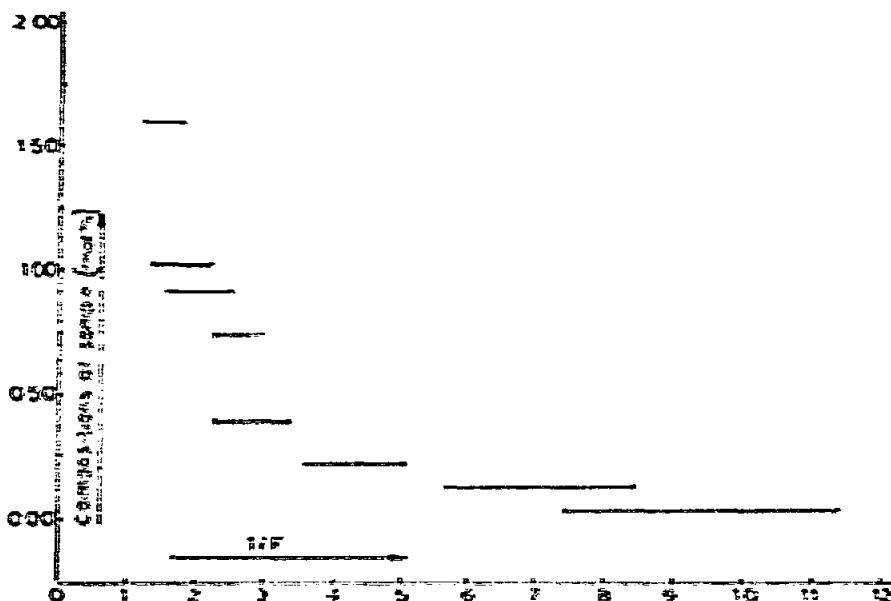
Fig. 4. Intervals of $1/F$-values within which the slopes of the Skau cryometric curves agree with the actual impurity contents in the benzene samples of varying impurity proportions.

exhibit considerable deviations from the rectilinear course characteristic of the benzene + n-heptane system at limiting dilutions and do not allow the establishment of the degree of purity directly from the experimentally measured T and $(1/F)$-values. The strict analogy of the curve shapes within the whole series of measurements (Fig. 3) indicates that the deviations are caused by systematic, rather than random, errors associated with measuring the liquid-phase fraction, F, or equilibrium temperature, T. The corrections recommended in the literature were found to reduce the deviations to an unsatisfactory degree, leaving no possibility of adequately interpreting the results.

As shown in Fig. 3, by reference to the cryometric curves obtained for the series of the seven samples of varying n-heptane contents, the sections of the cryometric curves with slopes approximately consistent with the actual values of x_2^0/A do not fall in a common interval of the $(1/F)$-parameter. This range varies with the mole % impurity in the sample investigated. Thus, the common section of the cryometric curve claimed to correspond to a constant $(1/F)$-parameter interval, $1-2^5$ or $2-6^6$, is hardly justified. Evidently, this range varies from $(1/F) = 1.2-1.8$ to $(1/F) = 7-11$ at impurity contents of 1.5 and 0.1 mole %, respectively; that is, as the impurity content is raised, the range moves considerably toward lower $(1/F)$-values. To explain this fact, the courses of the melting curves recorded at a linear temperature programme were subjected to critical analysis; it is actually these curves that form the basis for the determination of the cryometric curves $T = f(1/F)$.

A theoretical cryometric curve transformed by eqn. (1) into the plot of a melting curve $T = f(z)$ for the liquid phase mole fractions, F adopted from the Skau technique measurements is presented in Fig. 5.
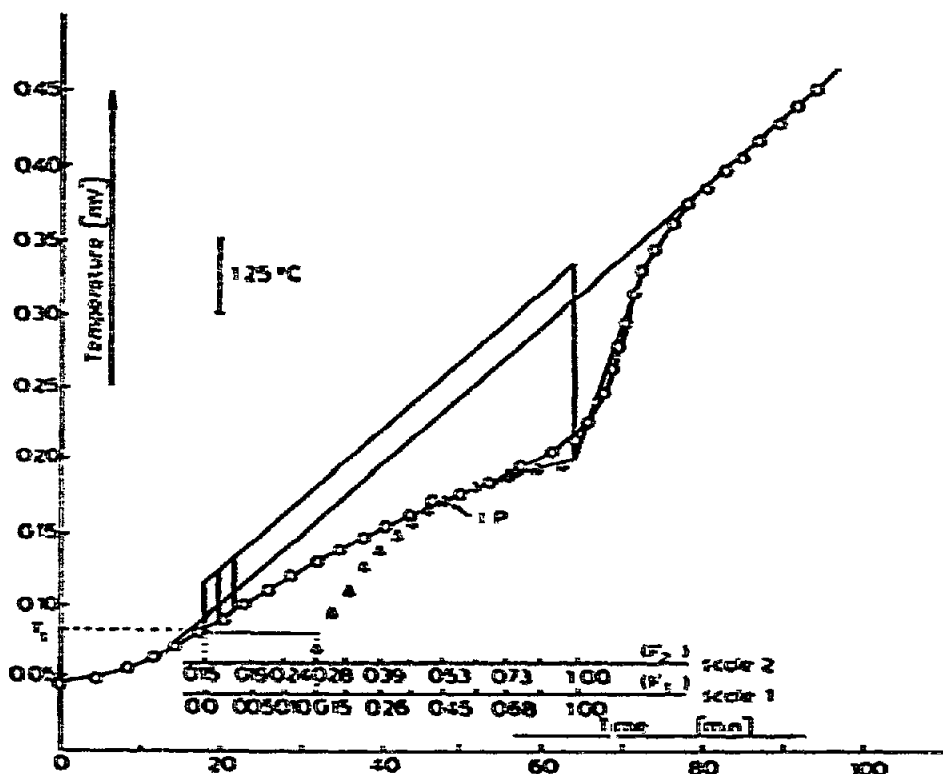
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Fig. 5. Illustration of the influence of the correction including liquid existence at temperature T_1, on the value of fraction melted (F) for various stages of the melting process. ○, experimental point; △, "ideal" melting curve reconstructed on the basis of the cryometric curve in accordance with scale 1. Displacement of "ideal" melting curve after making allowances for correction including liquid existence at temperature T_1 (scale 2), represented by the arrow.

The cryometric curve $T = f(F)$ which, in agreement with eqn. (1) forms an equilateral hyperbola, becomes distorted in the $T = f(z)$ plot because the time scale in this plot is inconsistent with the F-value scale (as indicated by Fig. 5). However, if the F- and T-values were correctly evaluated, the theoretical melting curve should coincide with the experimental curve. As evident from Fig. 5, such a coincidence is achieved in only a small region of the melting curve.

Two regions exhibiting diverse deviations may be distinguished. (1) In the initial melting range the theoretical melting curve follows a course beneath the experimental curve and makes a strong bend downward. (2) Starting with a certain point the experimental curve straightens and then makes a bend upwards.

The departure of the theoretical from the experimental curve in the final melting stage is suggestive of thermal disequilibrium and progressive superheating of the liquid phase. It is thus evident that extrapolation of the final melting curve section along the straight line up to the intersection with the straight line P–F (Fig. 1), as often practiced[5], to determine the sample melting point (T_i), is incorrect. Extrapolation of the melting curve beyond the equilibrium range up to $F = 1$ is justified along the hyperbolic type curve. However, the analytical form of this curve cannot

be determined until after the x_2^0/A value and the relation between the time scale, z, and the F-scale in the melting curve are known, i.e. after the relationship $F = f(z)$ has been established: therefore, the extrapolation and also the determination of T_f in the Skau technique directly from the melting curve may be only approximate in nature.

Figure 5 shows that the section $[1(F)] = 1$ to 2 as suggested in the literature for the determination of the cryometric depression is unsupported and still less justified is the extrapolation of the cryometric curve from $(1/F) = 1$ to 0.

The characteristic point in the melting curve (Fig. 5, point 1) at which melting begins to proceed under the increasingly high thermal disequilibrium conditions, is the inflection point. Therefore, for purposes of cryometric analysis it appears justified to consider only the points lying below this point within the low F-value range.

Since at the initial melting stage superheating may be ruled out as a possibility, deviations in this range of the experimental from the theoretical curve appear to be due to errors inherent in the determination of the liquid-phase mole fraction, F rather than to those arising from thermal disequilibrium.

The liquid phase present at the moment adopted at the start of the melting process is of consequence, a fact hitherto underrated. When impurities form eutectics with the major component, the liquid phase appears at the melting point of a binary or a multicomponent eutectic, which is usually much less than the melting point of the major component and also below the temperature range involved in the measurement. Therefore, as evident from Fig. 5, the greatest differences between the courses of the theoretical and experimental curves occur within the range accepted as the initial melting region in the melting curve where the measured F-values are burdened with largest errors.

For example, for the Skau melting curve (Fig. 5) of a sample containing 1 mole % of n-heptane as impurity, the liquid-phase mole fraction at temperature T_1 adopted as the melting start-point and determined from the phase diagram is ~15%. A suitable correction adopted for the F-value allows good agreement in the courses of the theoretical with experimental curves (Fig. 5, scale 2).

It remains open how to formulate the correction for fraction F of a substance with an unknown impurity content, a commonplace situation in cryometric measurements of purity. This problem has been discussed at greater length in our following paper.

For a substance of unknown impurity content and type and an unknown correction to be applied to the liquid phase, it appears to be most reasonable to rely upon the equilibrium melting curve section closely adjacent to the inflection point for the evaluation of impurity content. In the cryometric curves in Fig. 3 the points are marked, corresponding to the inflection points in the experimental melting curves obtained by the Skau technique.

The slopes of the straight lines drawn through these points and through the lower experimental points (toward higher $(1/F)$-values) were adopted as a basis for

TABLE 3

IMPURITY DATA EVALUATED FOR STANDARD BENZENE SAMPLES WITH THE AID OF THE INFLECTION POINT IN THE MELTING CURVE, AND CORRECTION OF THE LIQUID PHASE AT THE TEMPERATURE (T_1) ADOPTED AS THE MELTING START-POINT

No.	x_2 (mole %)		Absolute error (mole %)	Relative error (%)	Standard deviation $(100 \times S_x)$
	Actual	Observed			
1	0.119	0.109	−0.010	− 0.9	1.13
2	0.291	0.300	÷0.009	÷ 3.1	1.46
3	0.531	0.530	−0.041	− 7.7	2.26
4	0.501	0.520	÷0.019	÷ 2.4	2.55
5	1.031	0.930	−0.101	− 9.8	3.63
6	1.141	1.010	−0.131	−11.5	3.00
7	1.781	1.608	−0.173	− 9.7	2.18

the determination of x_2-values in the individual samples. Results are presented in Table 2.

As evident from Table 2 the relative error is held within the limits of 15%. The standard deviation, S_x, characteristic of the repeatability of the measurements performed, exhibits no considerable variation with the impurity concentration and maintains itself within the limits of 0.01 to 0.03 mole % in harmony with the precision obtained by other investigators.

Results obtained with the aid of the inflection point in the melting curve and correction on the liquid-phase presented in the temperature (T_1) adopted as the melting start-point are shown in Table 3.

As is evident from this Table the relative error is held within the limits of 10% and is smaller then that obtained without consideration of the liquid-phase presented at the temperature T_1 at the beginning of the experiment.

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