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THE SKAU'S DYNAMIC CRYOMETRY DETERMINATION OF ADVANCE IN THE SOLID–LIQUID PHASE TRANSITION

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ABSTRACT

The inadequacy of methods described so far for establishing the T_j-line which limits from above the surface corresponding to the advancing solid–liquid phase transition in the Skau's cryometric technique has been emphasized.

A new method has been presented which makes it possible to ascertain the T_j-line and to find the corrected T_j'-line which allows us to distinguish between the heat effect connected with the phase transition and the heat effect corresponding to the temperature growth of the sample investigated, at any point in the melting curve.

INTRODUCTION

Skau's kinetic cryometry serves to determine the equilibrium temperature T between the solid and liquid phases as a function of the melted fraction F or its reciprocal: $T = f(1/F)$ [1]. The knowledge of this pair of values enables us to determine other quantities occurring in cryometric equations. Sample temperature is recorded experimentally over a time period Z within which a programmed heating-block temperature T_b is being raised linearly. A representative diagram obtained by Skau's technique is reproduced in Fig. 1. The phase transition area is bounded by the curves T_p and T_p^0. The T_p^0-line is obtained as an approximation of the T_p-line and simulates the course of the T_p-line for the situation when no phase transition takes place. The degree of phase transition corresponding to successive points in the T_p-curve is determined by the heat balance involving an adopted simplified heat-transfer model.

(i) Heat is assumed to be transferred by conduction exclusively and, in agreement with Newton's law of cooling, the quantity of heat transferred through a unit surface area is assumed to be proportional to the temperature difference of the surfaces between which this heat is exchanged.

$$q_p = \alpha(T_j - T_p) \tag{1}$$

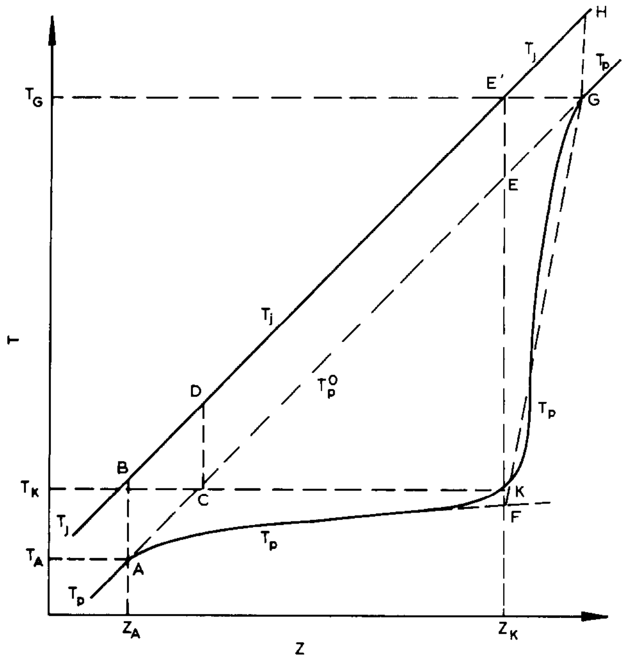

Fig. 1. Typical curve illustrating results obtained by the Skau method, with points used for limiting the fields adopted by Lyashkevitch [2] and Cisse and Clechet [4].

where q_p is the thermal flux density to the surface, α is the heat-transfer coefficient, T_j is the temperature of the heating surface (environment) and T_p is the temperature of the surface examined.

The total thermal effect Q, heat transferred through the surface during the time period Z_1 to Z_2

$$Q = \alpha s \int_{Z_1}^{Z_2} \left(T_j(Z) - T_p(Z)\right) \mathrm{d}Z \tag{2}$$

(*ii*) The influence of the change of the surface of contact of the sample with the cell wall during melting is neglected and the heat transfer coefficient α is assumed to be constant. Then $\alpha s = k =$ constant.

(*iii*) Any heat capacity involved is taken as temperature independent over the temperature range of interest and the difference in the heat capacities of the solid and liquid is neglected.

Actually, Skau's apparatus is built up from various materials differing in thermal conductivity and heat capacity which, in addition, are temperature dependent; during the melting process the temperature difference $(T_j - T_p)$ between the sample and the heating surface varies and so do other temperature gradients in the apparatus. Therefore, the heat exchange course is quite complicated and the adopted heat transfer model is only justified as long as it is verified by experimentation, i.e., when the assumption is borne out by practical Skau's technique applications.

The Skau method assumes that at any temperature T_m between temperature T_A (the liquid appearance temperature, Fig. 1) and T_K (the temperature at the point assumed to represent the end of melting, Fig. 1) the liquid phase fraction may be expressed as

$$F = \frac{\int_{Z_A}^{Z_m} (T_J - T_p) \mathrm{d}Z}{\int_{Z_A}^{Z_K} (T_J - T_p) \mathrm{d}Z} \tag{3}$$

No heat term occurs in eqn. (3) and the partial and overall heat effects are expressed in arbitrary units, e.g. surface units on the T–Z diagram. Since sample temperature $T_p(Z)$ is measured directly, the quantity that remains to be determined [to solve eqns. (2) and (3)] is the ambient temperature $T_J(Z)$ with respect to which the difference $(T_J - T_p)$ has been established.

A number of methods have been reported for the determination of the T_J-line, often referred to as the evaluation of the correction for heat losses, which reflects the assumption that if there was no uncontrolled heat exchange between the measuring instruments and the environment, the T_J-line which could be adopted would be the line for the programmer-controlled linearly raised temperature T_b of the heating block.

In practice, the line T_J is determined by analyzing the sample temperature increase. While considering the T_p-curve section extending from point K, at which the phase transition may be approximately assumed to have been completed, to point G, at which the sample temperature may be assumed to have achieved a rate of growth corresponding to the programmed linear increase of the environment temperature, Lyashkevich [2] has pointed out that with the adopted heat-exchange model the area KEE′HG (Fig. 1), representing the heat required to warm the sample from T_K to T_G, should equal the area CDHG which represents the heat of warming the sample from $T_C = T_K$ to T_G along the T_p^0-curve in the case when no phase transition takes place. Since the EE′HG area is common to both the KEE′HG and the CDHG areas, experimental determination of the KEG area allows us to place the T_J-line in the diagram so that the area CDE′E equals the KEG area.

Such a procedure, though formally correct, does not justify using the T_J temperature line thus determined to follow the advance in the melting process on the basis of the heat balance over the area ABDE′K, where, in addition to the phase transition, the sample temperature has increased. Hence the Lyashkevich correction (known as Correction 1) introduces a considerable systematic error which may be partially compensated for only by ignoring other corrections, especially that for the liquid phase content at the temperature adopted as the melting start point [3]. Cisse and Clechet [4] have formally eliminated this error by suggesting an additional correction which eliminates from the calculations a part of the ABDC area representing the heat of warming of the sample. This correction, although essentially correct, suggests the area corresponding to the thermal effect due to the phase transition to be bounded by a broken line ACDE′ which no longer has the physical meaning attributed to the T_j-line.

It is the purpose of this work to ascertain a corrected T_j-line, named T'_j, which would allow us to distinguish at any point in the T_p-line the thermal effects associated with the warming of the sample from those of the solid–liquid phase transition and would thus provide a basis for a more correct evaluation of advance in this transition than the heating curve determined by Skau's technique.

THEORETICAL

The total thermal effect Q, given by eqn. (2) may be split up into two parts: Q_m, the heat associated with the phase transition and Q_h, the heat required to raise the system temperature. Evidently

$$dQ_m = \Delta H_m n dF \tag{4}$$

where ΔH_m is the molar heat of melting, n is number of moles, and

$$dQ_h = C_p^s dT \tag{5}$$

where C_p^s is the heat capacity of the system incorporating the sample, sample cell, thermocouple, etc. The actual heat absorbed by the system within the time period Z_A to Z_G is $Q = Q_m + Q_h$. The AKGA area (cf., Fig. 1) represents only Q_m and the area ABHGA represents Q_h.

Since the overall heat effect per unit time is proportional to the temperature difference $(T_j - T_p)$ which drives the heat transfer

$$dQ/dZ = dQ_m/dZ + dQ_h/dZ = k(T_j - T_p) \tag{6}$$

where either of the terms may be ascribed a suitable temperature difference.

$$dQ_m/dZ = k(T_j' - T_p) \tag{7}$$

$$dQ_h/dZ = k(T_j'' - T_p) \tag{8}$$

From eqns. (6), (7) and (8) follows

$$(T_j - T_p) = (T_j' - T_p) + (T_j'' - T_p)$$

or

$$(T_j'' - T_p) = (T_j - T_j') \tag{9}$$

Equation (9) allows us to eliminate T_j'' from eqn. (8) to give

$$dQ_h/dZ = k(T_j - T'_j) \tag{10}$$

Integration of eqn. (7) over an interval Z_A to Z_G allows us to write the heat balance of melting of the sample

$$Q_m = k\int_{Z_A}^{Z_G}(T'_J - T_p)\mathrm{d}Z \tag{11}$$

Similarly, to correctly evaluate the liquid phase fraction F, T_J in eqn. (3) should be replaced by T'_J. To integrate eqn. (11) and for suitable terms of eqn. (3) it is necessary to know the temperature difference $(T'_J - T_p)$ as a function of time, i.e., to determine $T'_J = T'_J(Z)$.

Following the assumptions underlying the Skau technique, the heating block temperature T_b is a linear function of time; therefore, T_J and T_p^0 should, also, be straight lines parallel to T_b.

In the region where no phase transition occurs, $Q_m = 0$ and, from eqns. (7) and (11) $T'_J = T_p$, the two lines coinciding with T_p^0 to form a straight line parallel to T_J.

At any point in the warming curve the rate of sample temperature increase is given as

$$\partial T_p/\partial Z = \tan\alpha_p \tag{12}$$

the angle α being that of the tangent to the curve at this point with the Z-axis. Then $\mathrm{d}T_p = \tan\alpha_p\,\mathrm{d}Z$.

Similarly, the programmer-enforced rate of increase of the environment temperature along the T_J-line is given as $\tan\alpha_J$ and, in agreement with the assumptions of Skau's technique, is constant.

$$\partial T_J/\partial Z = \tan\alpha_J = \text{const.} \tag{13}$$

In the region where no phase transition takes place and the line $T_p = T_p^0 = T'_J$ is parallel to T_J, $\tan\alpha_p = \tan\alpha_p^0 = \tan\alpha_J$.

If an absolutely pure substance is melted, the sample temperature T_p remains constant as long as the conditions of thermodynamic equilibrium in the solid–liquid phase transition are preserved. Since $\mathrm{d}T_p = 0$, $\tan\alpha_p = 0$ and by eqn. (5), $\mathrm{d}Q_h = 0$ and the heat supplied to the sample is used only for melting of the substance

$$\mathrm{d}Q_h/\mathrm{d}Z = 0 \text{ (melting of pure substance)}$$

and, by eqn. (11),

$$T'_J = T_J \tag{14}$$

In practice we never have absolutely pure substances and, as a result, melting occurs over a certain temperature range, the extent of which is related to the nature of the major component and to impurity content. Within the equilibrium melting region the sample temperature rises, i.e., $\mathrm{d}Q_h \neq 0$, $\tan\alpha_p \neq 0$, $T_J > T'_J > T_p^0$ and thus the line which bounds from above the area that represents the thermal effect associated with the phase transition will occupy in the Skau diagram an intermediate position between the lines T_J and T_p^0.

To determine the position of this curve (T_j') we may consider the relation of the temperature difference ($T_j' - T_p^0$) or ($T_j - T_j'$) to the difference or the ratio of the rate of growth of the sample temperature (tan α_p) to that of the environment temperature (tan α_j).

As already pointed out, the temperature difference ($T_j' - T_p^0$) of interest to us may vary from zero (when no phase transition occurs) to ($T_j - T_p^0$) when a pure substance melts and the corresponding difference in the rates of growth of sample temperature (tan α_j − tan α_p) may vary from zero to tan α_j. If we assume the temperature difference ($T_j' - T_p^0$) to be directly proportional to the difference (tan α_j − tan α_p) we have

$$\left(T_j' - T_p^0\right) = \left(T_j - T_p^0\right) - \left(T_j - T_j'\right) = a\left(\tan \alpha_j - \tan \alpha_p\right) \tag{15}$$

This equation should hold true over the whole experimental range, and may be considered in conjuction with the boundary conditions, i.e., the above-mentioned extreme cases: (*1*) tan α_p = tan α_p^0 = tan α_j or (*2*) tan $\alpha_p = 0$. The second boundary condition together with eqn. (14) allows us to evaluate the proportionality coefficient a as

$$a = \left(T_j - T_p^0\right)/\tan \alpha_j \tag{16}$$

then

$$T_j' - T_p^0 = \left(\tan \alpha_j - \tan \alpha_p\right)\frac{T_j - T_p^0}{\tan \alpha_j} \tag{17}$$

In the model adopted, the difference ($T_j - T_p^0$) is constant in a given experiment; we denote it by ΔT^0. The solution of this equation for T_j' is

$$T_j' = T_j - \Delta T^0\left(\tan \alpha_p/\tan \alpha_j\right) \tag{18}$$

Another approach to establishing T_j' is to consider the relationships of Q_h and Q_m with tan α_j and tan α_p. When no phase transition occurs, the entire heat is used to warm the sample, $\mathrm{d}Q_h/\mathrm{d}Z$ reaches the maximum value and the temperature difference in eqn. (10) amounts to ($T_j - T_p^0$), (T_j' coincides with T_p^0). This corresponds to the rate of growth of the sample temperature determined by tan α_p = tan α_j.

When the phase transition takes place, the heat used to warm the sample is proportional to the temperature difference ($T_j - T_j'$) and the rate of growth of the sample temperature is given by tan α_p. The remaining heat, proportional to the temperature difference ($T_j' - T_p$), is used for the phase transition. The ratio of the heat $\mathrm{d}Q_h/\mathrm{d}Z$ used to warm the sample at any point to the maximum values $\mathrm{d}Q_{h_{max}}/\mathrm{d}Z$ is given by the ratio of temperature difference $(T_j - T_j')/(T_j - T_p^0)$ and should be proportional to the quotient (tan α_p/tan α_j)

$$\left(T_j - T_j'\right)/\left(T_j - T_p^0\right) = b\left(\tan \alpha_p/\tan \alpha_j\right) \tag{19}$$

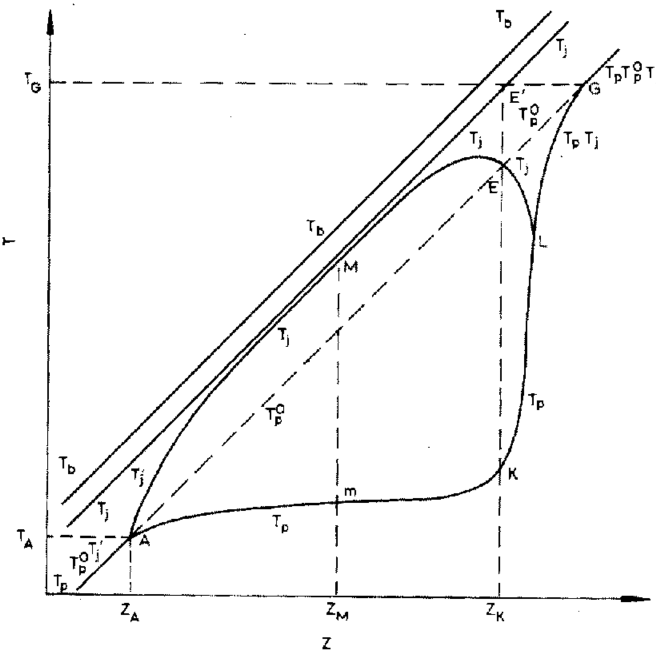

Fig. 2. Plot for the same experiment as in Fig. 1, with T_j' line.

where b is the net proportionality coefficient. Using the first boundary condition $\tan \alpha_p = \tan \alpha_j$ we find $b = 1$ whereby eqn. (19) becomes eqn. (18).

To facilitate the graphical interpretation, it is useful to plot Skau's technique data points in such a scale that $\tan \alpha_j = \tan \alpha_p^0$ is always unity in every experiment. Then all the straight lines T_j and T_p^0 are inclined at an angle of 45° to the z-axis.

Equation (18) then becomes

$$T_j' = T_j - \Delta T^0 \tan \alpha_p \tag{20}$$

and eqn. (19) may be written

$$T_j' = T_p^0 + \Delta T^0 (1 - \tan \alpha_p) \tag{21}$$

A schematic course of the T_j'-line is presented in Fig. 2 which shows a typical melting curve diagram obtained by the Skau technique.

As is evident from Fig. 2, the T_j' curve coincides with the T_p^0 curve in the regions beneath temperature T_A and above T_G and intersects the T_p^0-curve at point E. This point corresponds to point K located in a non-equilibrium portion in the T_p curve, the sample containing a small quantity of crystals in a superheated liquid. The tangent to the T_p-curve at this point is parallel to the T_j and T_p^0 line. Approximately, the Z_K value corresponding to this might be identified with the $Z_K(Z)$ value adopted in the literature [2] as the end of the melting process but for the occurrence of the superheating phenomenon (cf., Fig. 1) above the point K, the rate of growth of the sample temperature expressed by tan α_p continues to increase and attains a maximum at the inflection point L, in which presumably the last crystals disappear and the curve follows an exponential course tending to the straight T_p^0-line.

In agreement with the model adopted for heat transfer, the T_j' curve should reach the T_p curve at point L and continue to follow coincidentally.

Determination of the T$_j$*-line*

To use the present method for establishing the T_j'-line, it is necessary to know the course of the T_j-line or the difference $(T_j - T_p^0) = \Delta T^0$ (eqn. 19). The T_j-line may be evaluated as reported in the literature [2] and described in the Introduction to this study. The line may also be ascertained by using the method applied above to find the T'_j-line. For this purpose we consider the end section of the melting curve between points L and G as corresponding to the heating of the completely molten sample.

From eqns. (5) and (11) we can write

$$C_p^s \mathrm{d}T/\mathrm{d}Z = k(T_j - T_j') \tag{22}$$

or

$$\mathrm{d}T/\mathrm{d}Z = k'(T_j - T_j') \text{ where } k' = \frac{k}{C_p^s} \tag{23}$$

In the region from L to G (and above G), when no phase transition occurs line T_j' coincides with T_p. Then

$$\tan \alpha_p = k'(T_j - T_p) \tag{24}$$

Writing this equation for any two points on the T_p curve we can eliminate k' and find T_j and ΔT^0. Taking one point between L and G and another above G when T_p coincides with T_p^0 we find

$$\Delta T^0 = \frac{\tan \alpha_p^0 (T_p^0 - T_p)}{\tan \alpha_p - \tan \alpha_p^0} \tag{25}$$

Determination of the melted fraction F

The surface bounded by the T_p- and T_j'-lines from point A to L corresponds to the total heat S_c utilized to melt the sample from temperature T_A adopted as the melting start point (Fig. 2).

Therefore, the melted fraction F at any point m in the melting curve between A and L may be evaluated as the ratio of the surface S_m = AmMA to the total surface (S_c). If, as usual, the sample, at temperature T_A, is already partially molten, the corresponding surface S_A may be evaluated as described before [3]. In this case, the fraction F at point m (F_m) is

$$F_m = \frac{S_A + S_m}{S_A + S_c} \tag{26}$$

where

$$S_m = \int_{Z_A}^{Z_m} (T_j' - T_p) \mathrm{d}Z \tag{27}$$

and

$$S_c = \int_{Z_A}^{Z_L} (T_j' - T_p) \mathrm{d}Z \tag{28}$$

If we assume that S_A is given by one of the equations proposed previously [3], e.g.

$$S_A = \frac{(T_3 - T_2) S_2 S_3}{(T_2 - T_A) S_3 - (T_3 - T_A) S_2}$$

then

$$S_A = \frac{(T_3 - T_2) \int_{Z_A}^{Z_2} (T_j' - T_p) \mathrm{d}Z \int_{Z_A}^{Z_3} (T_j' - T_p) \mathrm{d}Z}{(T_2 - T_A) \int_{Z_A}^{Z_3} (T_j' - T_p) \mathrm{d}Z - (T_3 - T_A) \int_{Z_A}^{Z_2} (T_j' - T_p) \mathrm{d}Z} \tag{29}$$

Thus the fraction melted F_m at the temperature T_m may be determined from the course of $T_p(Z)$ and $T_p^0(Z)$ lines using eqns. (25) and (18) after the points $(T_A Z_A)$, $(T_L Z_L)$ and $(T_G Z_G)$ were fixed and the points (T_2, Z_2) and (T_3, Z_3) on the T_p curve were selected at the equilibrium section of the melting curve AL.

EXPERIMENTAL AND CALCULATIONS

Determination of a tan α_p value for any T_p in eqn. (25) requires that the experimental $T_p(Z)$ curve above should be well established. A numerical method of smoothing the $T_p(Z)$ curve and then of computation of ΔT^0 has been proposed.

The eqn. (25) has been treated as a differential equation in which time is accepted as an independent variable Z and T_p as a dependent variable y. Then tan $\alpha_p = y'$, tan α_p^0 and ΔT^0 should have constant values: tan $\alpha_p^0 = a$, $T_p^0 = aZ + b$ and $\Delta T^0 = d$.

After rearrangement and integration we receive for $y(Z)$ above the L point

$$y = aZ + b - c \exp\left[-\frac{a}{d}(Z - Z_0) \right] \tag{29}$$

The method was checked on the melting curves recorded by the Skau technique for several organic substances.

The apparatus and the procedure were as described in the preceding paper [5]. The temperature-rise programme generates linear increase of the Copper-Constantan thermocouple used for the temperature controlling voltage. The voltage of a similar thermocouple placed in the sample was used as a measure of temperature. The values of the constants *a* and *b* were determined from the straight line section of the experimental curve $T_p(Z)$ above the G point (cf., Fig. 2).

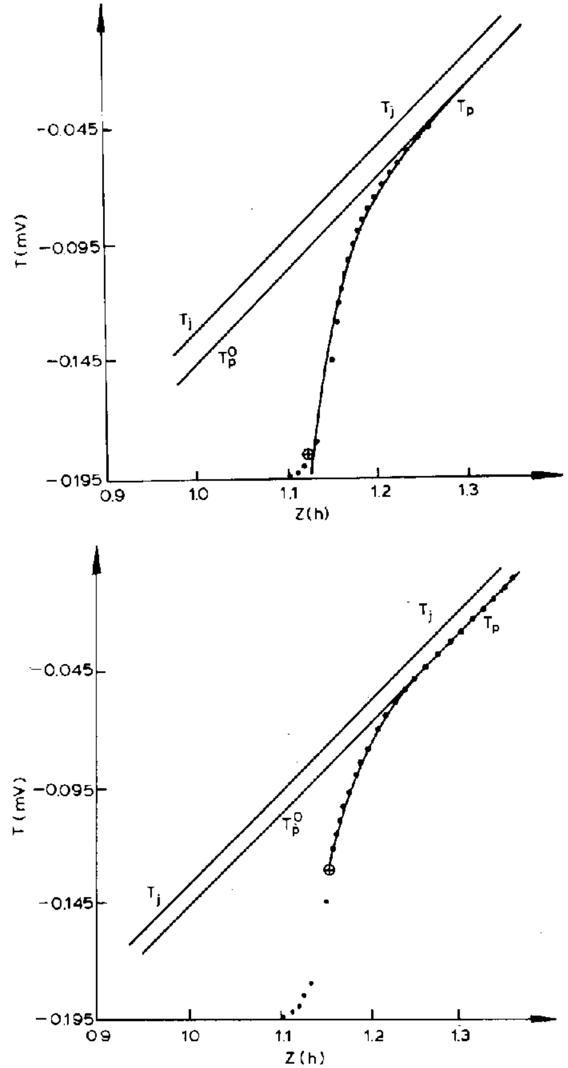

Fig. 3a and 3b. Graphs illustrating the influence of choosing point Z_0 on the fitting precision of the computed curve to the experimental data in the LG area. ······, experimental points $T_p(Z)$ for 2,6-lutidine sample of 99.86 mol% purity; ———, curves $T_p(Z)$ and $T_j(Z)$ computed from eqn. 29; ⊕, point Z_0 adopted for computation.

The choice of Z_0 point value presented some difficulties. As it is evident that it should be located above the assumed inflection point L, the computation was performed for several experimental points lying above point L and the first point for which the fitting of the curve given by eqn. (29) to the experimental curve was satisfactory was selected.

The choice of Z_0 determined the value of c. For $Z = Z_0$ we have

$y_0 = aZ_0 + b - c$ and $c = aZ_0 + b - y_0$

and c is equivalent to the difference $(T_p^0 - T_p)$ for $Z = Z_0$ (cf., Fig. 2).

After the values of a, b and c were computed we were able to find the value of $d = \Delta T^0$. Our computation started from the linearization of eqn. (29) but the results were unsatisfactory. Then we adopted the FLM procedure which minimizes the sum of squares by

$$\mathrm{SS} = \sum \left(T_{\mathrm{p}_i} - aZ_i + c\,\exp\left[-\frac{a}{d}(Z_i - Z_0) \right] \right)^2 \qquad (30)$$

by the use of Levenberg–Marquardt [6] algorithm. The deviations have diminished to less than 1%.

The influence of appropriate choice of the Z_0 point on the description of the experimental data $T_p(Z)$ in the region LG by means of eqn. (29) is shown in Fig. 3a and 3b, which represent the last part of the melting curve of a 99.86 mol% pure 2,6-lutidine sample.

The choice of the Z_0 point below the inflection point L leads to great discrepancy; when the Z_0 point is selected in the region of the exponential course of the T_p–Z curve the calculated curve agrees well with the experimental data.

The numerical calculation of the T_j and T_j' curves allows us to eliminate the corrections applied so far, which were found graphically and facilitates the automation of computation of the degree of purity of the samples examined by Skau's method.

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