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Application of the "shape-factors method" to purity analysis of compounds by thermal methods

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Abstract

The shape-factors method may be applied to the determination of phase diagrams by thermal methods. In this paper, its applicability to purity evaluation of compounds (organic and inorganic) is discussed. It is a rapid and easy method which can be applied either to impurities which form a eutectic phase diagram with the main component or to impurities miscible in the solid state with the compound to be purified.

INTRODUCTION

Groups at the Universities of Barcelona, Bordeaux and Utrecht work together on the measurement and theoretical interpretation of phase-diagrams of binary systems composed of organic compounds. These systems are generally of importance for the storage of energy and they all offer an opportunity to study the molecular interactions between the constituent compounds. This international cooperation is called REALM, which stands for Réseau Européen sur les Alliages Moléculaires. One of the ways of studying the phase diagrams is by thermal methods. We use the DSC (differential scanning calorimetry) and DTA (differential thermal analysis) techniques. In order to obtain the characteristic temperatures and, in particular, the solidus and liquidus temperatures from the experimental signals, we correct for the convolution of the apparatus and the thermal effect by introducing the shape-factors method [1–3].

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Our series of measurements gives us the opportunity to apply the shape-factors method to the problem of the influence of impurities on the shape of the experimental signals, not only for eutectic systems but also for systems which show solid solution behaviour, i.e. not only for systems where impurity B is insoluble in the compound A, but also when B is soluble in it.

The literature on the subject of purity determination by thermal methods is extensive. In general, we think that the methods based on the Van't Hoff equation have proved to be useful for detecting impurities which form eutectic systems with the main component [4,5].

However, if the impurity dissolves not only in the liquid state but also in the solid state, the matter of detecting the impurity level is not so straightforward. Some models had been proposed in the literature, i.e. Mastrangelo and Dornte [6], and Van Wijk and Smit [7], but there is no easy method for the rapid detection of this kind of impurity.

We feel that the proposed shape-factors method can be applied to purity analysis for soluble impurities as well as for eutectic ones. Moreover the method can be of use to check the result of a purification process.

PRINCIPLE OF THE METHOD

The fundamental bases of the proposed method are those of the shape-factors method which were analysed through an experimental study of the main parameters which influence the shape of a thermal signal [2]. In the case of an isothermal phenomenon (for instance the melting of a pure material at a temperature T), the thermal signal (Fig. 1) appears to begin effectively at $T = T_0$ (onset temperature); its summit is at T_s and it finishes at T_{fin}.

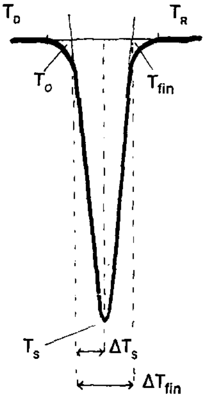

Fig. 1. Melting of a pure compound. Thermal analysis signal.

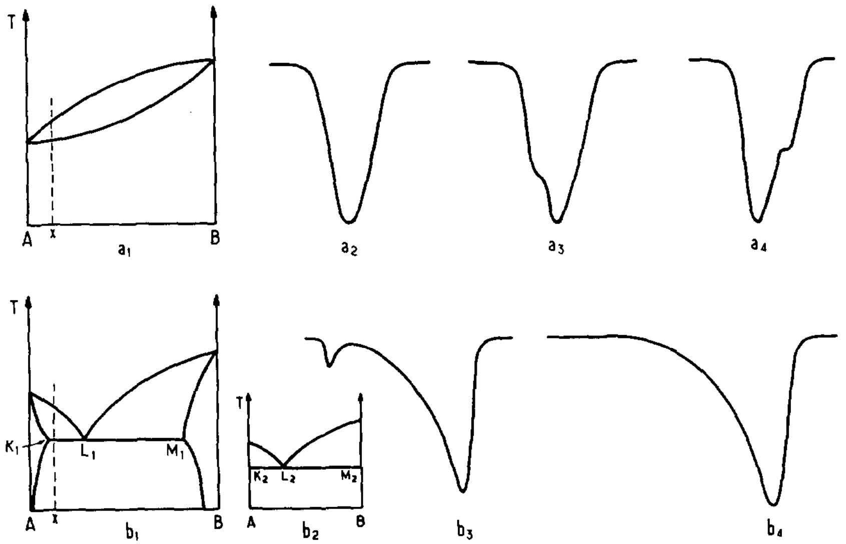

Fig. 2. Phase diagrams for total (a) and partial (b) miscibility and melting signals for a given x composition (b_2 is the limit case of b_1).

$\Delta T_s = T_s - T_o$ and $\Delta T_{fin} = T_{fin} - T_o$ are two shape factors. The authors have shown that ΔT_s and ΔT_{fin} can be considered quasi-identical for all the compounds of a given family provided that all the experimental conditions remain the same, i.e. device, mass, measurement cells, atmosphere, heating speed, etc. Therefore the temperature of the phenomenon can be obtained from

$$T \equiv T_o \equiv T_s - (\Delta T_s)^{\ominus} \equiv T_{fin} - (\Delta T_{fin})^{\ominus}$$

where $(\Delta T_s)^{\ominus}$ and $(\Delta T_{fin})^{\ominus}$ are characteristic values of the series.

Let us consider now the melting of an impure compound, the mole fraction of the second component, i.e. the impurity, being x; the composition is given by $(1-x)A + xB$. In this case, the melting is no longer isothermal; the form of the signal observed in thermal analysis is related to the involved phase diagram A–B. Two main types (a and b) can be distinguished. (For more examples see ref. 2). Figure 2(a) shows the case of total miscibility in the solid state (alloy) and some possible configurations (a_2, a_3, a_4) of the melting signal for a particular x. Figure 2(b) shows the case of partial miscibility in the solid state and some possible corresponding configurations (b_3, b_4) for the melting signal for a particular composition x (b_2 is the limit case of b_1; there]K2 M2[is the eutectic invariant). In neither case are we dealing with an isothermal phenomenon. Melting starts at $T_{solidus}$, the temperature at which the first drop of liquid appears. It continues with the coexistence of the liquid and the solid until the $T_{liquidus}$ temperature is reached where the last solid particle disappears.

In refs. 1 and 2, the authors have shown how to use $(\Delta T_s)^{\ominus}$ and $(\Delta T_{\mathrm{fin}})^{\ominus}$ to determine the actual characteristic temperatures T_{solidus} and T_{liquidus} from the experimental signal:

$$T_{\mathrm{sol}} = (T_o)_x$$

$$T_{\mathrm{liq}} = (T_s)_x - (\Delta T_s)^{\ominus} = (T_{\mathrm{fin}})_x - (\Delta T_{\mathrm{fin}})^{\ominus}$$

where $(\Delta T_s)^{\ominus}$ and $(\Delta T_{\mathrm{fin}})^{\ominus}$ are taken to be similar to the pure compounds values. When the pure compound is not available they can be determined by analogy with the other members of the family.

In this paper, the purpose is to use $(\Delta T_s)^{\ominus}$ and particularly $(\Delta T_{\mathrm{fin}})^{\ominus}$ to indicate the presence of an impurity in a sample (samp). Indeed, one can see (Fig. 2) that the shapes of the thermal signals for pure and impure samples can be very similar (especially when B is soluble in A) but they differ from one another in width. The presence of an impurity in a sample may induce some anomaly in the shape of the experimental signal but in every case, the melting phenomenon is no longer isothermal and the signal width increases. The apparent width of the signal can be estimated by

$$(\Delta T_{\mathrm{fin}})_{\mathrm{samp}} = (T_{\mathrm{fin}})_{\mathrm{samp}} - (T_o)_{\mathrm{samp}}$$

The actual width of the melting domain being, of course

$$l = T_{\mathrm{liquidus}} - T_{\mathrm{solidus}}$$

i.e.

$$l = \left[(T_{\mathrm{fin}})_{\mathrm{samp}} - (\Delta T_{\mathrm{fin}})^{\ominus}\right] - (T_o)_{\mathrm{samp}}$$

$$l = (\Delta T_{\mathrm{fin}})_{\mathrm{samp}} - (\Delta T_{\mathrm{fin}})^{\ominus}$$

In other words, if the sample is not pure, l is no longer equal to zero and $(\Delta T_{\mathrm{fin}})_{\mathrm{samp}} > (\Delta T_{\mathrm{fin}})^{\ominus}$.

We will illustrate how to use this property by reporting our measurements relative to two experimental cases, one with a soluble impurity in the solid state, the other with an insoluble one. In each case we started with pure materials and then we introduced small known amounts of a second compound (considered as the impurity B) in order to follow the enrichment in the impurity but also, reciprocally, to simulate the measurements to be expected in a purification process. In the first case, A will be 2-methylnaphthalene and B, 2-chloronaphthalene. In the second case, A will be *para*-bromochlorobenzene and B, naphthalene.

EXPERIMENTAL

The measurements were performed with two kinds of equipment: a Du Pont de Nemours DSC 910-990 and a Perkin–Elmer DSC 4. In all cases,

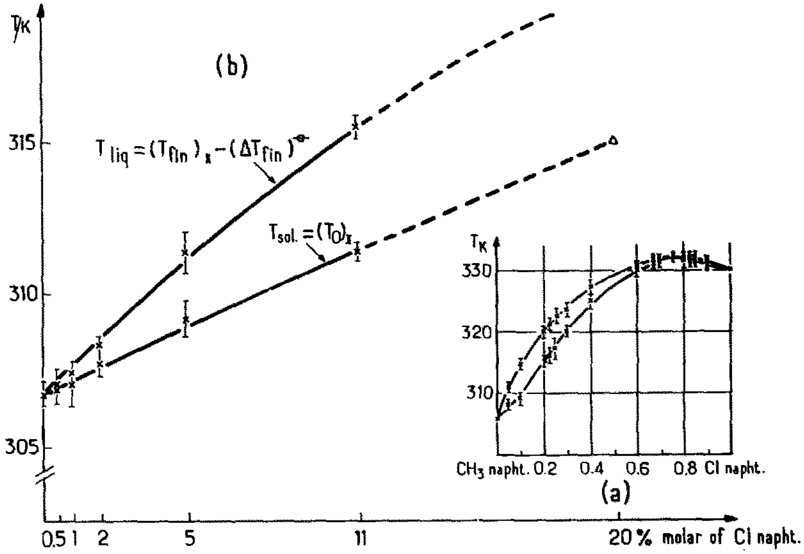

Fig. 3. Case of a soluble impurity. (a) General features of the 2-methylnaphthalene–2-chloronaphthalene system according to ref. 8. (b) Effects of small amounts of impurity on the solidus and liquidus curves.

samples of 2–3 mg were weighed into capsules which were closed hermetically.

The components used were obtained from Eastman Kodak (2-methylnaphthalene), Fluka (2-chloronaphthalene), Aldrich (*para*-bromochlorobenzene) and NPL (naphthalene). All the compounds were purified by repeated sublimation; purity was checked by gas chromatography and mass spectroscopy. No purity levels less than 99.99% were found.

The mixtures were prepared by co-crystallization from a solvent. The pure components A and B were both dissolved in suitable proportion. The solvent was evaporated at a controlled temperature (T) under a light stream of nitrogen. This method enables the stable phase or phases at temperature T to be formed.

RESULTS AND DISCUSSION

First case: soluble impurity

We are dealing here with the 2-methylnaphthalene–2-chloronaphthalene system; its general features are given in Fig. 3(a). The miscibility is total, i.e. one obtains a molecular alloy whatever the respective amounts of the two compounds.

We have chosen this case because the addition of the impurity (2-chloronaphthalene) increases the melting temperature. Usually, especially in purity determination, one expects a decrease in melting temperature when

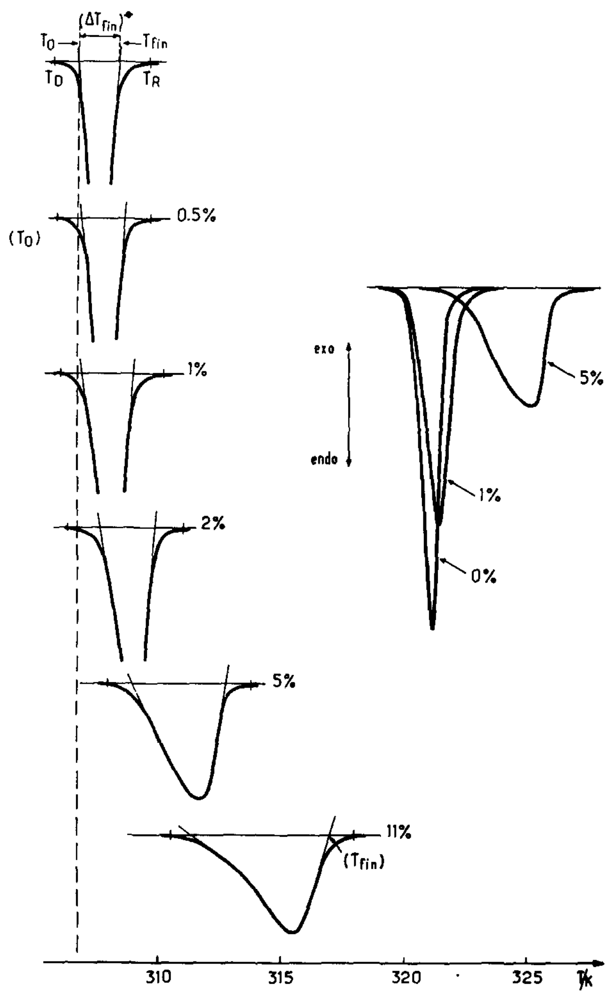

Fig. 4. Thermogram evolution of samples of 2-methylnaphthalene containing increasing molar amounts of 2-chloronaphthalene.

the impurity level is increased. It is important to keep in mind that this is not always the case so that an increase in the melting temperature is not a criterion of an increase in the purity.

Measurements were performed with high concentrations of 2-methylnaphthalene and increasing amounts of 2-chloronaphthalene.

The shape of the thermograms changes gradually with the impurity levels (Fig. 4). We have analysed each of these thermograms in measuring $(T_o)_{samp}$, $(T_s)_{samp}$ and $(T_{fin})_{samp}$ (for n independent experiments in order to estimate the precision by the student's method). Then, using the shape-factors method, we have determined $T_{solidus}$, $T_{liquidus}$, $(\Delta T_s)_{samp}$ and $(\Delta T_{fin})_{samp}$. All these values are reported in Table 1.

TABLE 1

Experimental values of the melting temperatures (K) and the shape factors for the system 2-methylnaphthalene–2-chloronaphthalene

2-Clnaphth. (mol.%)	n	T_{solidus}	T_{liquidus}	$(\Delta T_s)_{\text{samp}}$	$(\Delta T_{\text{fin}})_{\text{samp}}$
0	15	306.8 ± 0.4	–	0.62 ± 0.07	1.58 ± 0.07
0.5	4	306.8 ± 0.4	307.0 ± 0.6	0.98 ± 0.28	1.86 ± 0.40
1.0	6	307.0 ± 0.7	307.4 ± 0.6	0.98 ± 0.17	1.94 ± 0.24
2.0	4	307.7 ± 0.4	308.3 ± 0.3	1.24 ± 0.20	2.18 ± 0.10
5.0	4	309.2 ± 0.6	311.4 ± 0.7	2.82 ± 0.43	3.76 ± 0.40
11.0	4	311.4 ± 0.3	315.5 ± 0.4	4.22 ± 0.11	5.73 ± 0.11

The variations of T_{solidus} and T_{liquidus} versus the impurity level are given in Fig. 3 and those of $(\Delta T_s)_{\text{samp}}$ and $(\Delta T_{\text{fin}})_{\text{samp}}$ are illustrated in Fig. 5.

It is recommended to use the variations of T_{solidus} and, especially, of T_{liquidus} (the slight cryoscopic decrease which here is an increasing one) to test the purity of an experimental sample but it is easier and more successful to compare $(\Delta T_{\text{fin}})_{\text{samp}}$ with $(\Delta T_{\text{fin}})^{\ominus}$.

Moreover, from Fig. 5, one can deduce that if the phase diagram of a binary system is known, the shape-factors concept can help to make quantitative statements about the amount of the impurity; this can be particularly helpful if one wants to follow the result of a purification process by thermal analysis.

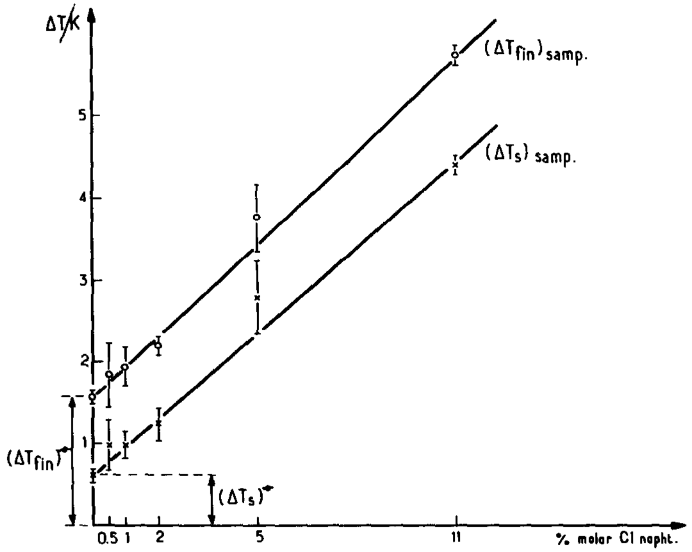

Fig. 5. Influence of the amount of impurity (2-chloronaphthalene) on the shape factors $(\Delta T_s)_{\text{samp}}$ and $(\Delta T_{\text{fin}})_{\text{samp}}$ of 2-methylnaphthalene samples.

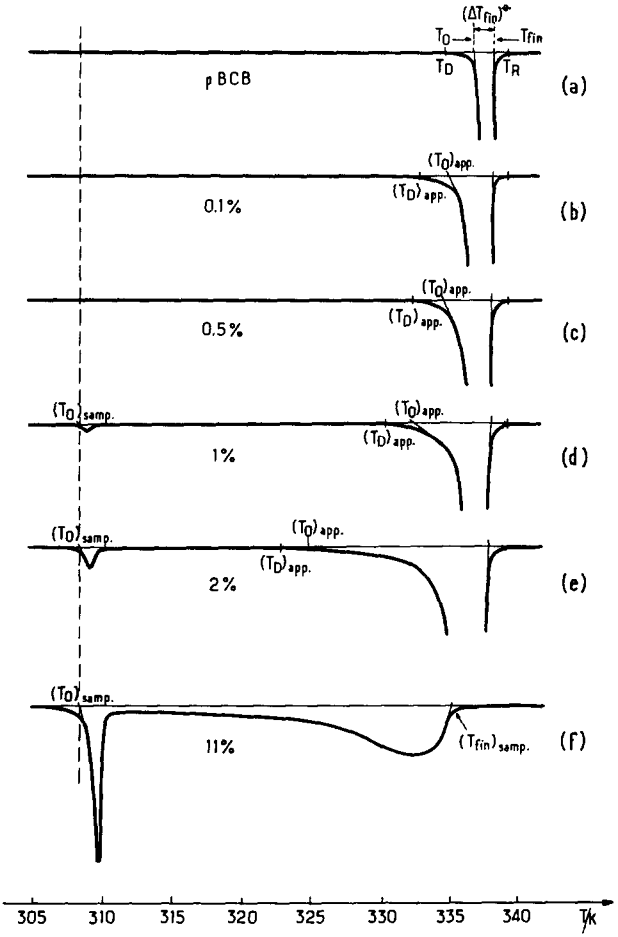

Fig. 6. Thermogram evolution of samples of *para*-bromochlorobenzene containing increasing amounts of naphthalene.

Second case: insoluble impurity

In this example we chose increasing amounts of naphthalene as the impurity in *para*-bromochlorobenzene. The corresponding thermograms are given in Fig. 6. One can see that there are two sorts of experimental signals: some of them (Fig. 6, curves d, e and f) are unambiguous representations of a eutectic melting. Let us consider, for example, the sample with 11 mol.% impurity (case f). The signal begins at $(T_o)_{\text{samp}}$ with a very sharp first part corresponding to the eutectic invariant; it continues over a large range of temperature; the end of the melting process occurs at T_{liquidus}, i.e. at $T_{\text{fin}} - (\Delta T_{\text{fin}})^{\ominus}$. For both cases d and e, we are dealing with the same situation; the melting process is still a continuum running from $T_{\text{solidus}} = (T_o)_{\text{sample}}$ to $T_{\text{liquidus}} = T_{\text{fin}} - (\Delta T_{\text{fin}})^{\ominus}$ but the proportion of eutectic fusion

TABLE 2

Experimental values (K) of samples in the *para*-bromochlorobenzene–naphthalene system

Naphth. (mol.%)	n	$(T_o)_{samp}$	$(T_o)_{app}$	$(T_{fin})_{samp}$	$(\Delta T_{fin})_{app}$	$(\Delta T_{fin})_{samp}$	$T_{liq} = (T_{fin})_{samp} - 1.46$
0.1	6	–	335.0	338.6	3.6	–	337.1 ± 0.5
0.5	6	–	334.5	338.3	3.8	–	336.8 ± 0.5
1.0	6	308.6 ± 0.6	332.1	337.9	5.8	29.3 ± 0.5	336.4 ± 0.6
2.0	6	308.5 ± 0.6	325.1	337.4	12.3	28.9 ± 0.5	335.9 ± 0.5
11.0	6	308.6 ± 0.6	–	334.7	–	26.1 ± 0.6	333.2 ± 0.5

For pure *p*-BCB, we found ($n = 40$) $T = 337.1 \pm 0.3$ K and $(\Delta T_{fin})^{\ominus} = 1.46 \pm 0.09$ K.

vanishes as the proportion of impurity decreases. Because of this, the curve seems to return to the base line after the crossing of the eutectic invariant so that the experimental DSC trace appears to consist of two distinct signals, the temperature at which the second begins being $(T_o)_{apparent}$. In determining $(T_o)_{app}$ it is possible to make use of another shape factor, ΔT_D, the definition of which is $(\Delta T_D)^{\ominus} = |T_D - T_o|^{\ominus}$ (Fig. 6, curve a) so that $(T_o)_{app} = (T_D)_{app} + (\Delta T_D)^{\ominus}$.

The interpretation of the other cases (b and c) is not so straightforward: it is difficult to decide if the observed signal (beginning at $(T_o)_{app}$) corresponds to the second part of a continuum of melting or if it actually represents an entire phenomenon of fusion, i.e. whether we are dealing with the b_2 or the b_1 case, Fig. 2. As a matter of fact, the actual problem here is not to establish the phase diagram but to determine whether the

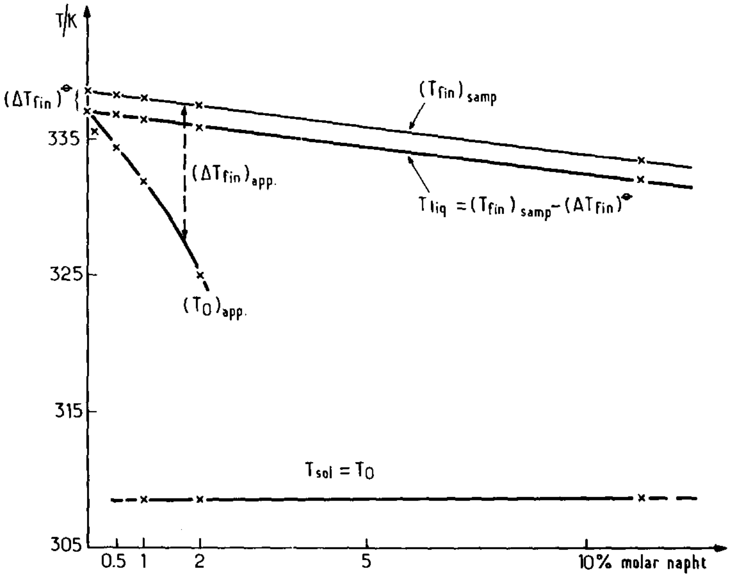

Fig. 7. Influence of the amount of impurity (naphthalene) on T_{liq}, T_{sol} and $(T_o)_{app}$.

sample is pure. This is quite possible whatever the form of the phase diagram, by determining the difference $(\Delta T_{\text{fin}})_{\text{app}} - (\Delta T_{\text{fin}})^{\ominus}$, where $(\Delta T_{\text{fin}})_{\text{app}} = (\Delta T_{\text{fin}})_{\text{samp}} - (T_{\text{o}})_{\text{app}}$. If the result is significantly higher than zero, the sample is not pure.

We have analysed each of the thermograms presented in Fig. 6 by measuring $(T_{\text{o}})_{\text{samp}}$, $(T_{\text{o}})_{\text{app}}$ and $(T_{\text{fin}})_{\text{samp}}$. All these values are reported in Table 2 with the determined values of $(T_{\text{fin}})_{\text{samp}}$, $(\Delta T_{\text{fin}})_{\text{samp}}$ and T_{sol}. The variation of the main values versus the impurity level are given in Fig. 7. It is clear that the decrease of $(\Delta T_{\text{fin}})_{\text{app}}$ is a very sensitive indicator of the decrease in the impurity level, whereas the slight cryoscopic decrease (T_{liq}) is not a significant indicator.

In conclusion, we feel that the shape-factors method can be of assistance, not only for the determination of phase diagrams but also for determining purity levels and for the control of purification processes. This method is also applicable in the case of solid-solution formation, whether the melting point is decreased or increased by the impurity. The method is expected to give better, more reliable results because no absolute values of temperature are included; only temperature differences are taken into account.

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