

CALORIMETRIC TEST OF PURITY I.

ANALYSIS OF DESCRIPTIONS OF THE MELTING CURVE

$$\frac{dH}{dT} \text{ vs. } T$$

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Relationships of various levels for the thermodynamical description of two-component eutectic systems have been investigated. It has been established that the van't Hoff relationship describes the melting curve dH vs. T with satisfactory accuracy, but for its practical application a modification of the mathematical character, maintaining the physical content of the equation, is needed. The interpretation and the mode of application of the modified equation are given.

Symbols

1	Index, symbol of the main component
2	Index, symbol of the impurity
R	Gas constant, J/mol K
T	Equilibrium temperature of the system, K
T_i	Melting point of the i -th pure component, K
ΔH_i	Change in enthalpy of fusion of the i -th pure component, J/mol
ΔH_i^0	Change in enthalpy of fusion of the i -th pure component at the melt in point, J/mol
ΔC_i^0	Difference of specific heat in the solid and molten states of the i -th pure component at the melting point, J/mol K
x_i	Molar fraction of the i -th component in the melt phase
\bar{x}_i	Total molar fraction of the i -th component in the system
f_i	Activity coefficient of the i -th component in the melt phase
F	Molten fraction, mol/mol
W	Interaction energy between the two components J/mol
Δh	Change in enthalpy of fusion of the sample investigated up to temperature T , J
n	Quantity of sample investigated, mol

One of the important fields of application of the thermoanalytical methods QDTA and DSC, that is suitable for the quantitative measurement of the enthalpy change, is the purity determination based on the melting point depression phenomenon.

The pertinent literature and our own experimental experience directed our attention to the fact that practical application of the procedure suffers from several problems. For example, a survey of the literature reveals results with an improbably high accuracy, while on the other hand according to some reports only the order of magnitude of the impurity content can be established.

Papers published recently in this field consider that the problems stem from the simplifications used in the relationships describing the phenomenon, and also from experimental shortcomings.

This induced us to investigate the problem in a complex way, from several aspects.

The results are reported in two communications. Our present paper deals with the theoretical approach and partly with the problems of evaluation, while the next paper discusses the problems of the measuring techniques and data-processing.

Literature on the theoretical basis of the purity test

In an isobaric melting process, the thermodynamic equilibrium of a two-component, eutectic system is described by the following relationship:

$$\frac{\Delta H_1}{RT^2} dT = d \ln (f_1 x_1) \quad (1)$$

where ΔH_1 is a function of temperature, and a function of temperature and composition.

From this relationship, the van't Hoff equation described in the literature and used in practice is obtained under the following assumptions:

- I. $\Delta H_1 = \Delta H_1^0$
- II. $f_1 = 1$.

Substituting these into (1) and forming its integral function from T_1 constant to T variable, we obtain:

$$\frac{\Delta H_1^0}{R} \frac{T_1 - T}{T_1 T} = -\ln x_1 \quad (2)$$

Applying the following simplifications:

- III. $-\ln x_1 = x_2$
- IV. $T_1 T = T_1^2$

Eq. (2) is transformed into:

$$T_1 - T = x_2 \frac{RT_1^2}{\Delta H_1^0} \quad (3)$$

Using the material balance valid for simple eutectics, the van't Hoff equation is obtained:

$$T_1 - T = \frac{\bar{x}_2 RT_1^2}{F \Delta H_1^0} \quad (4)$$

Transposing the van't Hoff equation and differentiating with respect to temperature, the relationship describing the melting curve is obtained:

$$\frac{dH}{dT} = \Delta H_1^0 \frac{dF}{dT} = \bar{x}_2 R \frac{T_1^2}{(T_1 - T)^2} \quad (5)$$

The above derivation can also be found in the literature [1]. It must be mentioned in connection with the derivation [1, 2] that the simplifications made may cause such large differences from the actual situation that the van't Hoff equation is unsuitable for the description of the phenomenon from beginning to end.

Hence, the establishment and analysis of a relationship containing less limitations is needed. Equations of this kind have been published by Marti [1] and Kawalec [3]. Marti took the dependence of ΔH_1 on the temperature, and Kawalec that of f_1 on the composition into consideration.

In our present work, with the simultaneous use of these two approximations, we derive a more general model of the melting curve and compare it with that given by (5).

Formulation of the equation of the melting curve

Let us start from the relationships which take the dependence of ΔH_1 on temperature as of first order, and the dependence of f_1 on temperature and composition as the regularly assumed one:

$$\begin{aligned} \Delta H_1 &= \Delta H_1^0 + \Delta C_1^0(T - T_1) \\ f_1 &= e^{\frac{Wx_2^2}{RT}} \end{aligned} \quad (6)$$

Substituting the above two equations into (1):

$$\frac{\Delta H_1^0 + \Delta C_1^0(T - T_1)}{RT^2} dT = d \ln \left(e^{\frac{Wx_2^2}{RT}} (1 - x_2) \right) \quad (7)$$

Expanding the right-hand side of the expression:

$$\frac{\Delta H_1^0 + \Delta C_1^0(T - T_1)}{RT^2} dT = d \ln \left(e^{\frac{Wx_2^2}{RT}} + d \ln(1 - x_2) \right) \quad (8)$$

	Benzamide	Phenacetin
Melting point	400 K	407 K
ΔH°	20 400 J/mol	32 300 J/mol
ΔC°	52 J/mol K	55 J/mol K

Eutectic point: 372 K, 60.6% benzamide.

From the consideration that:

$$d \ln e^{\frac{Wx_2^2}{RT}} = \frac{2Wx_2}{RT} dx_2 + \frac{Wx_2^2}{RT^2} dT \quad (9)$$

$$d \ln (1 - x_2) = - \frac{dx_2}{1 - x_2}.$$

We may substitute (9) into (8) and reduce the expression, the equation describing the phase diagram thereby being obtained:

$$\frac{\Delta H_1^0 + \Delta C_1^0(T - T_1) + Wx_2^2}{RT^2} dT = \left(\frac{2Wx_2}{RT} - \frac{1}{1 - x_2} \right) dx_2. \quad (10)$$

The correctness of (10) has been checked on the system phenacetin-benzamide, data on which have often been reported in the literature. The data needed for the calculations were taken from [1, 4].

The value of the interaction energy W was established by trials aimed at the best approximation of the calculated and the theoretical eutectic points (Fig. 1). A value of about 400 J/mol was found for W . In addition to Eq. (10), the material balance valid for simple eutectics and the expression of the change of enthalpy of melting of two-component regular mixtures is also needed for the calculation of the melting curve:

$$F = \frac{\bar{x}_2}{x_2} \quad (11)$$

$$\Delta H_{1,2} = \Delta H_1^0 + \Delta C_1^0(T - T_1) + Wx_2^2. \quad (12)$$

From the available Eqs (10), (11) and (12), in contrast with earlier [5], the $\frac{dH}{dT}$ vs. T curve was calculated with the algorithm in the Appendix. This was then compared with the curve calculated with Eq. (5).

The results are shown in Figs 2 and 3.

Our experiments indicate that whether working with dynamic or with stepwise techniques, the uncertainty in the measured results is considerably more determin-

ing than the differences between the two models are equivalent from the practical point of view, but Eq. (5) is more advantageous, because it is easier to handle.

Moreover, our experiments showed that the above uncertainty is of particular importance in the initial section of melting. The reason for this is that the slope of the melting curve, which is a carrier of useful information, is very small, and its value can be changed substantially by a low noise.

In our further work a data-processing method will be described which does not require a knowledge of the whole melting range; the section of the curve with a greater slope, i.e. with a better signal/noise ration, is sufficient.

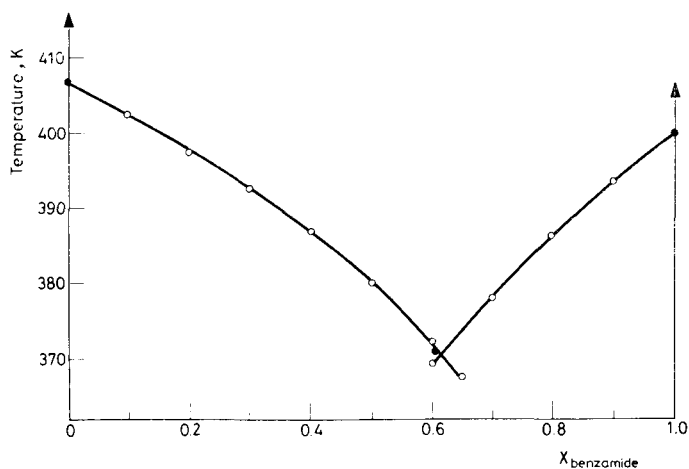


Fig. 1. Phase diagram of the system phenacetin-benzamide calculated on the basis of differential equation (10). Points marked with a circle are data in the literature of the pure substances and of the eutectic mixture

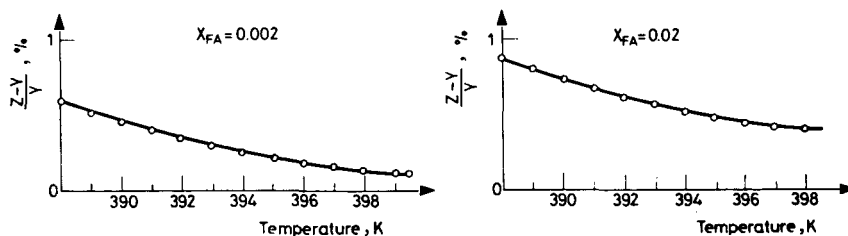


Fig. 2. Differences between the equations describing the melting curve of phenacetin at different benzamide impurities. $Y = \frac{dH}{dT}$, calculated with the algorithm; $Z = \frac{dH}{dT}$, calculated on the basis of Eq. (5)

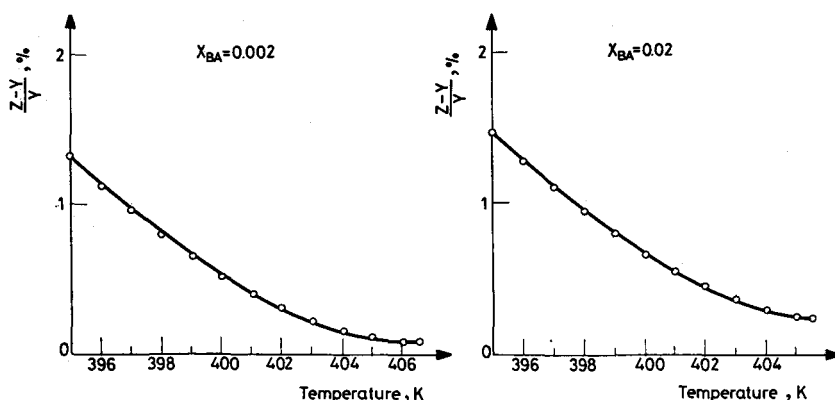


Fig. 3. Differences between the equations describing the melting curve of benzamide at different phenacetin impurities. $Y = \frac{dH}{dT}$, calculated with the algorithm; $Z = \frac{dH}{dT}$, calculated on the basis of Eq. (5)

Process for evaluation of the experimental results of the purity test

First, Eq. (4) is transformed:

$$T_1 - T = \bar{x}_2 RT_1^2 \frac{1}{\Delta H_1^0 F} \quad (13)$$

where $\Delta H_1^0 F$ is the change in enthalpy up to temperature T for 1 mole of the substance. This can be related to the change in enthalpy of the sample in the following way:

$$\Delta H_1^0 F = \Delta h/n. \quad (14)$$

Substituting (14) into (13), we obtain:

$$T_1 - T = \bar{x}_2 RT_1^2 \frac{n}{\Delta h}. \quad (15)$$

Let us now interpret our process with the aid of Fig. 4. Let T_s be the temperature at which the slope of the melting curve rises above the increment arising from noise. The fundamental idea of the determination of T_s is as follows. It is known that the melting curve (5) and its derivatives are strictly monotonously increasing functions of temperature. Accordingly, the derivative of the continuous curve measured with the dynamic technique and the differences of the peak areas measured with the stepwise technique must also increase strictly monotonously.

Thus, experimental data are analyzed first from this aspect, T_s is indicated where the strictly monotonous increase is already true. Let χ be the theoretical enthalpy change before T_s , and $\phi(T)$ the enthalpy change measured between T_s and T arising from melting. Thus:

$$\Delta h = \chi + \phi(T). \quad (16)$$

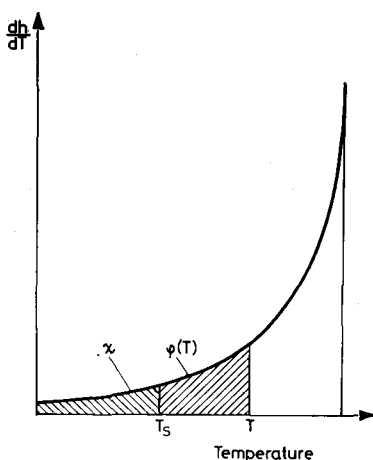


Fig. 4. Explanatory figure for the evaluation of the melting curve

Substituting (16) into (15), we have:

$$T_1 - T = \bar{x}_2 RT_1^2 \frac{n}{\chi + \phi(T)}. \quad (17)$$

In this equation T_1 , χ and \bar{x}_2 are unknown, and we have the related $\phi(T)$ and T experimental data. The unknown values can be estimated by the least squares method:

$$\min \sum_{\chi, T_1, x_2} \left(T_1 - T_i - x_2 n R T_1^2 \frac{1}{\chi + \phi(T_i)} \right)^2.$$

The search for the minimum by iteration with respect to χ can easily be performed on a computer. In our next paper an example of the application of the process will be given.

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RÉSUMÉ — On a examiné diverses corrélations pour décrire des systèmes eutectiques à deux composants. On a établi que la relation de van't Hoff décrit la courbe de fusion $\frac{dH}{dT} - T$ avec une exactitude satisfaisante. Cependant, son application pratique exige une modification de caractère mathématique mais celle-ci ne porte pas sur le contenu physique de l'équation. On donne l'interprétation et le mode d'application de l'équation modifiée.

ZUSAMMENFASSUNG — Verschiedene Zusammenhänge zur thermodynamischen Beschreibung eutektischer Zweikomponentensysteme wurden untersucht. Es wurde festgestellt, daß der van't Hoff-sche Zusammenhang die Schmelzkurve $\frac{dH}{dT} - T$ mit befriedigender Genauigkeit beschreibt, daß jedoch ihre praktische Anwendung eine Abänderung mathematischen Charakters benötigt, wobei der physikalische Inhalt der Gleichung erhalten bleibt. Deutung und Anwendungsmethode der modifizierten Gleichung werden angegeben.

Резюме — Исследованы взаимосвязи различного уровня для термодинамического описания двухкомпонентных эвтектических систем. Установлено, что соотношение Вант-Гоффа с удовлетворительной точностью описывает кривую плавления $\frac{dH}{dT} - T$, но для практического применения требуется видоизменение его математического характера, сохраняя при этом физическое содержание уравнения. Представлена интерпретация и метод применения этого видоизмененного уравнения.

APPENDIX

