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# PURITY DETERMINATION BY CALORIMETRY. AN ANALYSIS OF RELATIONSHIPS DESCRIBING SOLID-LIQUID EQUILIBRIA IN EUTECTIC SYSTEMS

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Various formulations of the material balance in solid-liquid equilibria have been discussed. It has been established that the melt fraction, as usually defined, is related to the corresponding fractional heat of melting in an approximate way only.

By expressing the material balance in terms of a more appropriate melt fraction, relationships for the thermodynamic description of two-component eutectic systems have been derived, and their correctness checked on the system benzoic acid-naphthalene.

## Symbols

| | |
|---|---|
| 1 | Index, symbol of the main component (solvent) |
| 2 | Index, symbol of the impurity |
| $R$ | Gas constant, J/(mol deg) |
| $T$ | Equilibrium temperature of the system, K |
| $T_1$ | Melting point of the solvent, K |
| $\Delta H_1^0$ | Enthalpy of fusion of the solvent at the melting point, J/mol |
| $\Delta C_1^0$ | Difference in molar heat capacity in the solid and liquid states of the solvent at the melting point, J/(mol deg) |
| $M_i$ | Molecular weight of the $i$-th component |
| $x_i$ | 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 |
| $\tilde{x}_i$ | Molar fraction of the $i$-th component in the eutectic mixture |
| $n_s$ | Number of moles of sample in the solid phase |

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| | |
|---|---|
| $n_l$ | Number of moles of sample in the liquid phase |
| $\bar{n}_i$ | Total number of moles of the $i$-th component |
| $\tilde{n}_i$ | Number of moles of the $i$-th component in the eutectic mixture |
| $F$ | Molten fraction referred to total number of moles of sample |
| $F_1$ | Molten fraction referred to total number of moles of solvent |
| $f_1$ | Molten fraction referred to number of moles of solvent not present in the eutectic mixture |
| $W$ | Interaction energy between the two components, J/mol |
| $\Delta H_1$ | Integral heat of melting of solvent from the eutectic to the final melting point, J/mol |
| $\Delta h_1$ | Integral heat of melting of solvent from the eutectic to a partial melting point, J/mol |

Since the first procedure was proposed [1, 2], most work on purity determination by DSC has been based upon the equation derived from the Van't Hoff law:

$$T = T_1 - K_1 x_2 \tag{1}$$

where, for brevity, $K_1 = RT_1^2/\Delta H_1^0$ and $x_2$ is expressed by the material balance equation:

$$x_2 = \bar{x}_2/F \tag{2}$$

$F$ being defined as $F = n_l/(n_l + n_s)$.

Whereas the relationship between $T$ and $1/F$ should be linear, as predicted by Eqs (1) and (2), this is not generally the practical case. The absence of thermodynamic equilibrium in a dynamic experiment, the inability of DSC to detect early melting and the influence of thermal gradients all have to be considered as possible instrumental causes of non-linearity. In order to eliminate this non-linearity, several methods have been proposed, where an appropriate "$x$ correction" is added to both the partial areas and the total area of the melting curve [1–8]. Calculated impurity values are found, however, to depend strongly upon the chosen limits of $1/F$. The application of stepwise melting has been claimed to remove the above mentioned causes of non-linearity [9], but nevertheless, some controversy still exists as to the need to linearize experimental data in stepwise measurements, as well [8–11].

On the other hand, curvature in the $T = f(1/F)$ function has been ascribed by several authors to theoretical rather than to instrumental causes. Relationships less approximate than Eq. (1) have been investigated [6, 12–14], but the results reported are rather discordant as regards the utility of such improvements.

Further, some modified forms of Eq. (2) have been adopted. The material balance taking into account solid solution formation was proposed by Mastrangelo and Dornte [15]:

$$x_2 = \bar{x}_2/[k+F(1-k)] \tag{3}$$

where $k$ represents the partition coefficient of the minor component between the solid and liquid phases. Applications of Eq. (3) have been found, generally, to lead to considerable improvements in the assessment of purity values [3, 13, 16, 17]. The intrinsic inconsistency of the same has been emphasized, however, owing to its inability to handle systems forming true solid solutions [3, 6, 16].

Another modified form of Eq. (2) has been proposed [18] in order to take into account both the solubility in the solid phase and the departure of liquid and solid solutions from ideality:

$$x_2 = \bar{x}_2/[F+2a\bar{x}_2(1-F)] \tag{4}$$

where $a$ is a fitting parameter assumed to relate the solute content in the solid to its content in the liquid.

In the present work, it will be shown that, even in the case of simple eutectic systems, modifications of Eq. (2) very similar to Eqs (3) and (4) are obtained when the material balance is expressed in terms of molten fractions more appropriate than $F$ for DSC measurements.

On this basis, a general model describing solid-liquid equilibria in eutectic systems will be derived and checked on a real system.

## Material balance in eutectic systems

As far as is known, Eq. (2) has been systematically used to express the material balance in eutectic systems. However, whereas $F$ represents the melted fraction of the total sample, experimental molten fractions are obtained as fractional heats of melting of the main component only. A relation between $F$ and the melted fraction of the main component $F_1$ is found by expressing the material balance in the form

$$\text{I.}\quad \begin{aligned} n_l &= \bar{n}_2+F_1\bar{n}_1 \\ n_s &= \bar{n}_1(1-F_1) \end{aligned}$$

where it is taken into account that, after the eutectic transition, all the minor component is present in the molten phase. From I, we obtain:

$$\text{II.}\quad F = \bar{x}_2+F_1(1-\bar{x}_2)$$

Substitution of II into Eq. (2) allows us to express $x_2$ as a function of $F_1$:

$$x_2 = \bar{x}_2/[\bar{x}_2+F_1(1-\bar{x}_2)] \tag{5}$$

A comparison of Eq. (5) and Eq. (3) is of interest. By taking into account that the same experimental values are substituted either for $F$ or for $F_1$, the two relationships appear identical, provided that the partition coefficient in Eq. (5) is identified with $\tilde{x}_2$. This may not perhaps be a mere coincidence, on account of some findings concerning calculated values of $k$, where variations in the latter as large as the impurity molar fraction itself have been observed [17].

It is even possible to go one step further in defining a melt fraction more suitable than $F_1$. Determination of this latter requires in fact a knowledge of the eutectic heat of melting of the major component, which is usually not obtainable from the melting curve. If the area due to the eutectic melting is included in the calculation of $F_1$, as done by some workers [9, 19], values larger than the true ones are obtained owing to inclusion of the eutectic heat of melting of the minor component too. An implicit "$x$ correction" is applied, therefore, this being the larger, the more impure the sample is.

If fractional heat measurements are limited to the portion of the melting curve after the eutectic event, as is usually done, the corresponding melt fractions $f_1$ are related to $F_1$ by the relationship

III. $F_1\bar{n}_1 = \tilde{n}_1 + f_1 n_1$

where $n_1 = n_1 - \tilde{n}_1$.

After division by $n_1$ and rearrangement, we obtain

IV. $F_1 = (f_1 + \tilde{n}_1/n_1)/(1 + \tilde{n}_1/n_1)$

The ratio $\tilde{n}_1/n_1$ can be expressed in terms of the system composition:

V. $\tilde{n}_1/n_1 = \tilde{x}_1\bar{x}_2/(\tilde{x}_2 - \bar{x}_2)$

the term $\bar{x}_2/(\tilde{x}_2 - \bar{x}_2)$ being, by the lever rule, the ratio of the number of moles of eutectic to the number of moles of component 1.

By combining V with IV and II, we obtain

VI. $F = f_1 + (1 - f_1)\bar{x}_2/\tilde{x}_2$

Finally, substitution of VI into Eq. (2) yields

$$x_2 = \bar{x}_2/[f_1 + (1 - f_1)\bar{x}_2/\tilde{x}_2] \tag{6}$$

Equation (6) gives the required relationship between $x_2$ and $f_1$ from the eutectic to the clear melting point.

Once again, a comparison is of value by taking into account that the same experimental values are substituted either for $F$ or for $f_1$. Although derived under very different assumptions, Eq. (6) and Eq. (4) become identical provided that $1/\tilde{x}_2$ is identified with $2a$.

Relationship (6) will be adopted as the working one in the following. However, a limitation implicit in calorimetric measurements must still be considered. Molten fractions, though defined in terms of mole fractions, are determined as fractional heats by assuming direct proportionality between the heat of fusion and the number of moles melted. Strictly speaking, such an assumption is valid only for 100% pure samples, since for impure samples the dependence of the heat of melting on temperature and on composition must be taken into account. In order to express such a dependence, a relationship describing solid-liquid equilibria in eutectic systems is needed.

## Formulation of equations describing the melting equilibrium in eutectic systems

By assuming a first-order dependence of the enthalpy of melting on temperature and the regular behaviour of the melt phase, the following equation holds, as long as $\theta/T_1 < 1$:

$$-\ln x_1 - Wx_2^2/RT = A^{-1} \sum_{n=1}^{\infty} [1 - B(1-1/n)](\theta/T_1)^n \tag{7}$$

where $\theta = T_1 - T$, $A = RT_1/\Delta H_1^0$ and $B = \Delta C_1^0 T_1/\Delta H_1^0$.

From the consideration that, for $\theta/T_1 < 1$

$$T^{-1} = T_1^{-1} \sum_{n=0}^{\infty} (\theta/T_1)^n$$

the term $Wx_2^2/RT$ can be expressed as

$$Wx_2^2/RT = Cx_2^2 + Cx_2^2 \sum_{n=1}^{\infty} (\theta/T_1)^n$$

where $C = W/RT_1$.

Substitution into Eq. (7) yields, after rearrangement

$$-(\ln x_1 + Cx_2^2)/(1+ACx_2^2) = A^{-1} \sum_{n=1}^{\infty} [1 - B(1-1/n)/(1+ACx_2^2)](\theta/T_1)^n \tag{8}$$

Since $AC$ can be estimated to be less than 0.1, an approximation is made by neglecting the corresponding term on the right-hand side of Eq. (8), so that terms in $\theta$ become separated from terms in $x_2$. At the same time, the approximation is partially compensated by amending the left-hand side:

$$(1 - ACx_2^2) \cong (1 + ACx_2^2)^{-1}$$

We obtain, therefore

$$-(\ln x_1 + Cx_2^2)(1 - ACx_2) \cong A^{-1} \sum_{n=1}^{\infty} [1 - B(1 - 1/n)](\theta/T_1)^n \tag{9}$$

If $\ln x_1$ is expressed in the form of a power series, Eq. (10) is obtained:

$$\sum_{n=1}^{\infty} b_n x_2^n \cong \sum_{n=1}^{\infty} c_n(\theta/K_1)^n \tag{10}$$

where $c_n = A^{(n-1)}[1 - B(1 - 1/n)]$ and the coefficients $b_n$ are determined by the product of the terms on the left-hand side of Eq. (9). By expressing the explicit dependence of $\theta$ on $x_2$ in the form

$$\theta/K_1 \cong \sum_n a_n x_2^n \tag{11}$$

the coefficients $a_n$ can be determined by substituting Eq. (11) into Eq. (10) and then applying the principle of the identity of polynomials. The coefficients thus determined take the form

$$a_n = 1/n - \sum_{j=1}^{n} a_{n,j} A^{(j-1)}$$

where $a_{1,1} = 0$, $a_{2,1} = C$ and successive terms $a_{n,j}$ are expressions containing both $B$ and $C$. A relationship similar to (11) has already been applied to DSC purity measurements [20].

In order to obtain a relation between the partial heat of melting and the corresponding molten fraction, let us start from the expression of the differential enthalpy of fusion of two-component regular mixtures:

$$\mathrm{d}(\Delta H_1)/\mathrm{d}f_1 = \Delta H_1^0 - \Delta C_1^0 \theta + Wx_2^2 \tag{12}$$

From Eq. (6), we have

$$\begin{aligned} f_1 &= (\bar{x}_2/x_2)(\tilde{x}_2 - x_2)/(\tilde{x}_2 - \bar{x}_2) \\ \mathrm{d}f_1 &= -x_2^{-2}[\tilde{x}_2\bar{x}_2/(\tilde{x}_2 - \bar{x}_2)]\,\mathrm{d}x_2 \end{aligned} \tag{13}$$

Substitution of Eqs (11) and (13) into (12) yields, after integration between 0 and $f_1$

$$\Delta h_1/f_1 = \Delta H_1^0 - \Delta C_1^0 K_1 \Phi(x_2) + W\tilde{x}_2 x_2 \tag{14}$$

where

$$\Phi(x_2) = [\tilde{x}_2 x_2/(\tilde{x}_2 - x_2)][\ln(\tilde{x}_2/x_2) + \sum_n a_{n+1}(\tilde{x}_2^n - x_2^n)/n]$$

For $f_1 = 1$, Eq. (14) becomes

$$\Delta H_1 = \Delta H_1^0 - \Delta C_1^0 K_1 \Phi(\bar{x}_2) + W\tilde{x}_2\bar{x}_2 \tag{15}$$

It is seen that the function $\Phi(\bar{x}_2)$ takes into account both the melting point depression related to $\bar{x}_2$ and the range of melting related to $\tilde{x}_2 - \bar{x}_2$. Calculation of its boundary values yields

$$\Phi(\bar{x}_2) = 0 : (\bar{x}_2 \to 0)$$

$$\Phi(\bar{x}_2) = \sum_n a_n \tilde{x}_2^n = \theta(\tilde{x}_2)/K_1 : (\bar{x}_2 \to \tilde{x}_2)$$

These values, when substituted into Eq. (15), determine the range of variability of $\Delta H_1$ as a function of $\bar{x}_2$:

$$\Delta H_1^0 - \Delta C_1^0 \theta(\tilde{x}_2) + W\tilde{x}_2^2 < \Delta H_1 < \Delta H_1^0$$

Finally, a relationship between the molten fraction and the fractional heat is obtained by combining Eqs (14) and (15):

$$f_1 = \frac{\Delta h_1}{\Delta H_1} \frac{1 - [\Delta C_1^0 K_1 \Phi(\bar{x}_2) + W\tilde{x}_2\bar{x}_2]/\Delta H_1^0}{1 - [\Delta C_1^0 K_1 \Phi(x_2) + W\tilde{x}_2 x_2]/\Delta H_1^0} \tag{16}$$

The dependence of $\Delta h_1/\Delta H_1$ on $f_1$ appears to be rather complex. Owing to the conditions

$$\bar{x}_2 \leqslant x_2 < \tilde{x}_2 : \Phi(\bar{x}_2) \leqslant \Phi(x_2) < \Phi(\tilde{x}_2)$$

it can be said, as a general rule, that the ratio $f_1 \Delta H_1/\Delta h_1$ will always be greater than unity, its value being the higher, the lower the fraction melted is, and to a degree depending on the purity of the sample.

In order to check the correcteness of the above relationships, the benzoic acid-naphthalene system was chosen; this system has been investigated elsewhere and recognized to follow the behaviour of a eutectic system. However, owing to substantially different reports concerning the eutectic composition, the system has been reinvestigated in this work.

## Experimental

All calorimetric measurements were carried out with a Perkin–Elmer Model DSC 1–B differential scanning calorimeter. The calorimetric output was connected to a Linseis L2041 potentiometric recorder and to a Linseis system consisting of a μV amplifier and a digital integrator with analog output. The overall precision of the system was better than 1% with the voltage threshold level set at 10 μV. The output of the integrating system was recorded together with the DSC signal. In addition, the analog output of the temperature read-out was converted into a digital domain with a nominal correspondence of 0.03 deg per digit.

The calorimeter was calibrated as previously reported [21]. The value of 3.28 kJ/mol [22, 23] was chosen as the heat of fusion of indium for the calibration of the power axis. A quadratic polynomial was used to express the temperature correction calibration curve, with a standard deviation of 0.11 deg for seven data points.

Various amounts of benzoic acid and naphthalene (both Carlo Erba thermometric standards) were weighed directly into volatile sample pans: between 4 and 6 mg, to an accuracy of 5 μg. The pans were then sealed following the procedure suggested by Kennedy and Carr [24]. In this way, a high reproducibility was observed after one or two premelts.

Calorimetric measurements were carried out in the stepwise mode to avoid thermal lag effects and loss of resolution. For the sake of comparison, however, dynamic measurements of the total heat of melting were carried out, as well. Peak areas were measured as the heights of the integrated signal, corrected, if necessary, for the different slopes of the initial and final isotherms. The partial areas between the eutectic and the clear melting point were summed after subtraction of the respective background values. Background interpolation was performed according to [25]. This iterative procedure was found necessary because of the appreciable difference between the initial and final background values.

All calculations were carried out on a microcomputer with ten-digit accuracy.

## Results and discussion

### *Thermodynamic properties of the benzoic acid-naphthalene system*

The values of thermodynamic quantities needed for calculations are reported in Table 1. The heats of fusion and the specific heats of the two components, though

**Table 1** Thermodynamic data on the system benzoic acid-naphthalene

| Quantity | Benzoic acid | Naphthalene |
|---|---|---|
| $T_1$, K | 395.5 | 353.3 |
| $\Delta H_1^0$, J/mol | 17100 | 18800 |
| $\Delta C_1^0$, J/mol | 63 | 22 |

Eutectic point: 341.4 K, 64.5 mole% naphthalene. Interaction energy: 2.0 kJ/mol

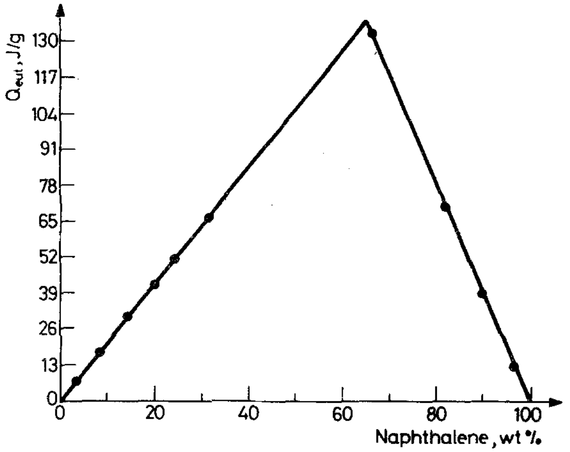

**Fig. 1** Eutectic heat of fusion *vs.* composition for the benzoic acid-naphthalene system: ■ experimental points, —— regression lines

often reported in the literature, were determined by DSC analysis on the actual pure components in order to get a consistent set of data. The values of these quantities, however, appear to be in good agreement with most literature data. The melting points of the pure components, which were used as calibrants of the temperature correction curve, are those reported by the manufacturer [26]. The eutectic composition was determined by plotting the heat of fusion of the eutectic *vs.* composition [27], as reported in Fig. 1. The two straight lines that pass through 0% and 100% and intersect at the eutectic composition are in accordance with the behaviour of a eutectic system with no solid solubility. The eutectic composition thus determined is in fair agreement with the value reported by Shilov and coworkers [28].

The value of the interaction energy $W$ was established through trials aimed at the best approximation of the experimental eutectic point and that calculated from Eq. (7) by taking $n=5$ as the upper limit of the summation in the right-hand member. In order to obtain consistent values of $W$ on both sides of the eutectic composition, dimerization of benzoic acid was assumed in calculations of molar fractions with naphthalene as the solvent. This assumption is in accordance with findings from X-ray analysis [28].

### *Comparison of formulated equations and experimental data*

The accordance between Eq. (7) with $n=5$ as the upper limit of the summation and Eq. (11) with $n=8$ as the upper limit of the summation was found to be within ±0.05 deg over the whole melting range of the components of the two systems:

benzoic acid-naphthalene and phenacetine-benzamide. The data needed for calculations on the latter system were taken from [12]. However, since Eq. (7) required an iterative procedure for calculating $\theta$, Eq. (11) was preferred as the working one.

Only samples with benzoic acid as the main component were analysed, in order to avoid the considerable interference of the eutectic peak with subsequent melting. No significant difference was found between dynamic and stepwise techniques in measurements of total melting areas. The accuracy of measurements for both techniques was found to be essentially limited by the accuracy of background evaluation. For the analyzed samples which melted over a range of about 40–50 K, a precision limit of 3% was reached by applying the iterative method for baseline interpolation.

An experimental check of Eq. (15) was performed by determining $\Delta H_1$ as the ratio of the experimental heat of fusion $Q_1$ (measured from the eutectic to the final melting point) to the number of moles $n_1$ of benzoic acid in the sample. The value of $n_1$ was determined from the weighed amount of sample $m$ by means of the relationship

$$n_1 = \bar{x}_1 m/(\bar{x}_1 M_1 + \bar{x}_2 M_2) - \tilde{n}_1$$

which, combined with $V$, becomes

$$n_1 = (m/\tilde{x}_2)(\tilde{x}_2 - \bar{x}_2)/(\bar{x}_1 M_1 + \bar{x}_2 M_2)$$

Substitution into Eq. (15) yields

$$\Delta H_1^0 = (Q_1 \tilde{x}_2/m)(\bar{x}_1 M_1 + \bar{x}_2 M_2)/(\tilde{x}_2 - \bar{x}_2) + \Delta C_1^0 K_1 \Phi(\bar{x}_2) - W \tilde{x}_2 \bar{x}_2 \quad (17)$$

Equation (17) allows an indirect determination of the heat of fusion of the pure main component from the melting curves of impure samples. Values determined for various samples, by using impurity molar fractions calculated from weighed

**Table 2** Values of heat of fusion of benzoic acid calculated from experimental heats of fusion of impure samples

| Mole fraction of naphthalene | Heat of fusion | |
|---|---|---|
| | experimental, J/g | calculated, kJ/mol |
| 0.028 | 129.6 | 17.0 |
| 0.086 | 112.4 | 16.7 |
| 0.141 | 103.2 | 17.4 |
| 0.198 | 87.4 | 16.9 |
| 0.242 | 79.8 | 17.3 |
| 0.315 | 66.5 | 17.8 |

amounts, are reported in Table 2 and appear in satisfactory agreement with the heat of fusion of the pure component reported in Tale 1. The results indicate, moreover, no substantial loss of melting area with the adopted procedure.

Equation (11) combined with Eq. (6), allows the calculation of simulated $T = F(1/f_1)$ curves. A comparison between simulated and experimental curves is reported in Fig. 2 for three samples representing the range of purity investigated.

The temperature readings were corrected according to the calibration curve, while fractional heats were converted into the corresponding $f_1$ values by applying an iterative procedure to Eq. (16). It appears from Fig. 2 that the proposed model allows a correct description of the experimental behaviour over a wide range of $x_2$ values.

Indeed, for all the samples investigated, the standard deviation of the experimental temperature from that calculated via Eqs (6) and (11) ranged from 0.22 deg to 0.56 deg, with no significant dependence on the impurity level. These values, although larger, are seen to be of the same order of magnitude as that determined from the fitting of the correction calibration curve (0.11 deg).

Since additional errors are introduced when calculating the values of temperature, due to uncertainties both in the measurement of molten fractions and in the determination of the values of the parameters, the validity of the relationships employed is supported by the above comparison.

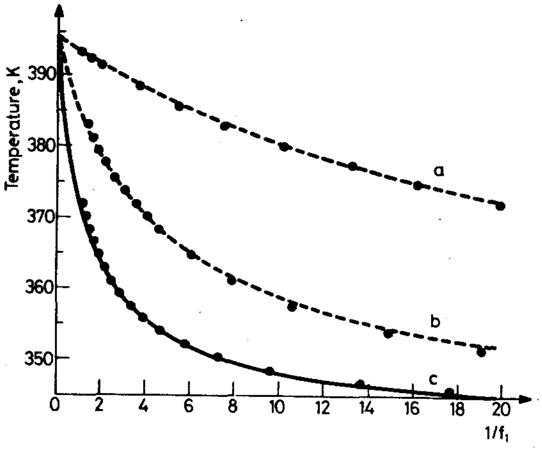

**Fig. 2** Comparison of experimental points and calculated $T = F(1/f_1)$ curves for benzoic acid as main component and naphthalene as impurity. Impurity molar fractions: a, 0.028, b, 0.141, c, 0.315; ● experimental points

## Conclusion

The results obtained indicate a reasonable accordance of theoretical relationships with experimental data when previously determined values of the parameters are utilized. The more important question remains, however, of how accurately such values can be determined by fitting the above relationships to experimental data. This problem will be dealt with in a subsequent paper.

**Zusammenfassung** — Es wurden zahlreiche Darstellungsarten von Stoffbilanzen bei Festkörper-Flüssigkeitsgleichgewichten diskutiert. Es wurde festgestellt, daß die auf gewohnte Weise definierte Schmelzenfraktion nur annähernd mit der korrespondierenden Schmelzwärme für diese Fraktion in Beziehung steht. Durch Formulieren der Stoffbilanz, ausgehend von einer geeigneteren Schmelzenfraktion konnten Beziehungen für eine thermodynamische Beschreibung von Zweikomponenten-Eutektika-Systemen erhalten werden. Deren Richtigkeit wurde am System Benzoesäure-Naphthalin überprüft.

**Резюме** — Обсуждены различные формулировки при составлении вещественного баланса для равновесия типа твердое тело—жидкость. Установлено, что доля расплава, связанная с дробной теплотой плавления, обозначается только приблизительно. Выразив вещественный баланс на основе более подходящей доли расплава, были выведены соотношения для термодинамического описания двухкомпонентных систем и справедливость которых была проверена на системе бензойная кислота-нафталин.