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CALORIMETRIC DETERMINATION OF PURITY BY SIMULATION OF DSC CURVES 2

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This paper presents further results of the purity determinations by simulated DSC curves. The instrumental parameters of a heat-flux DSC are now determined at two temperatures whereby the accuracy of the results is improved. In addition the calorimeter model is adapted to another calorimeter. The method also allows a more exact determination of fusion temperature.

Van't Hoff's law is a considerably simplified description of the coexistence curves in a eutectic phase diagram. A detailed error analysis of the five simplifications leading to this law shows that the relative total error introduced is proportional to the impurity concentration and is of same magnitude as the latter.

Introduction

The rapid development of microcomputers in the recent past has facilitated simulation of the heat flux behaviour in calorimeters. Since one can expect an increase in computational speed and in storage capacity by a factor of 5-10 within the next few years, simulation of natural and technical processes will generally become more and more attractive <1>.

This work presents further results obtained with a simple method first described in our previous article <2>. In this calorimetric purity determination method we compare experimental DSC-curves with calculated ones using a suitable calorimeter model. Since van't Hoff's law of freezing temperature depression is the basis for the conventional purity determina-

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tion method, the resulting errors of the five mathematical and physical simplifications in the derivation of this law are assessed first.

Assessment of the Errors of the Simplifications Leading to van´t Hoff´s Law

In the following derivation of van´t Hoff´s law of freezing temperature depression the relative error $Re_i = (X_2-X_2')/X_2'$ (Re_i = (approximate quantity - true quantity) / true quantity) is calculated for each step of simplification. Such an assessment is necessary for a statement of the accuracy of purities determined in using van´t Hoff´s law.

Ideal eutectic systems show complete miscibility in the liquid and immiscibility in the solid phase(s). For equilibrium at constant pressure the following equation describes the coexistence between melt and crystal between eutectic and fusion temperatures <3>:

$$\ln a_1 = \frac{H_1^E - \Delta_{fus}H + \Delta C_p * T_{fus}}{R} * \frac{\Delta T}{T * T_{fus}} - \frac{\Delta C_p}{R} * \ln \frac{T_{fus}}{T} \tag{1}$$

1st simplification: The temperature dependence of the activity coefficient is neglected. Thus the differential enthalpy of dilution H_1^E is taken as zero: $H_1^E = 0$.

$$\ln a_1 = \frac{-\Delta_{fus}H + \Delta C_p * T_{fus}}{R} * \frac{\Delta T}{T * T_{fus}} - \frac{\Delta C_p}{R} * \ln \frac{T_{fus}}{T} \tag{2}$$

$\mathbf{Re_1} = (X_2-X_2')/X_2' \approx (\ln a_1 - \ln a_1')/\ln a_1' \approx$
$(\ln a_1 - \ln a_1')/(-\Delta_{fus}H*\Delta T/(R*T*T_{fus})) = \mathbf{H_1^E/\Delta_{fus}H}$

2nd simplification: The temperature dependence of the enthalpy of fusion is neglected. This implies $\Delta C_p = 0$ (because of Planck´s equation: $(d\Delta_{fus}H(T)/dT)_{koex} = \Delta C_p + \Delta_{fus}H/T -$

$\Delta_{fus}H*(\delta \ln V/\delta T)_p)$.

$$\ln a_1 = -\frac{\Delta_{fus}H*\Delta T}{R*T*T_{fus}} \quad (3)$$

Re_2 $= (X_2-X_2')/X_2' \approx (\ln a_1-\ln a_1')/\ln a_1' \approx \Delta C_p*\Delta T/(2*\Delta_{fus}H) \approx$ **$\Delta C_p*R*T_{fus}^2/(2*\Delta_{fus}H^2)*X_2$**

3rd simplification: Instead of activities concentrations are used: $a_1 = X_1*f_1 \approx X_1$; $(f_1 := 1)$.

$$\ln(1-X_2) = -\frac{\Delta_{fus}H*\Delta T}{R*T*T_{fus}} \quad (4)$$

Re_3 $= (X_2-X_2')/X_2' \approx [-\ln(1-X_2) + \ln(1-X_2')]/X_2' =$ $-\ln f_1/X_2' \approx$ **$-\ln f_1/X_2$** $= -C*X_2$

4th simplification: The logarithm is approximated: $\ln(1-X_2) \approx -X_2$.

$$X_2 = \frac{\Delta_{fus}H*\Delta T}{R*T*T_{fus}} \quad (5)$$

Re_4 $= (X_2-X_2')/X_2' = (X_2-X_2+1/2*X_2^2)/X_2' \approx$ **$1/2*X_2$**

5th simplification: The freezing temperature of the pure substance T_{fus} is substituted for the lowered freezing temperature T: $T*T_{fus} \approx T_{fus}^2$.

$$X_2 = \frac{\Delta_{fus}H*\Delta T}{R*T_{fus}^2} \quad \text{(van't Hoff's law)} \quad (6)$$

Re_5 $= (X_2-X_2')/X_2' = -\Delta T/T_{fus} \approx$ **$-R*T_{fus}/\Delta_{fus}H*X_2$**

The total error Re_{tot} is the sum of the individual errors Re_1 to Re_5. Table 1 compiles the analytical expressions for the five errors. Several systems of organic substances have been used to demonstrate the typical ranges of errors involved.

Table 1 Relative errors Re_1 to Re_5
(* 5 systems: benzene-cyclohexane <4>, benzene-acetone <5>, acetone-benzene <5>, acetone-water <5>, water-acetone <5>; ** 4 substances: benzene, toluene, naphthalene, trans-azobenzene, <6>, <7>, <8>; *** 3 systems: benzene-cyclohexane <4>, methylal-carbondisulfide <9>, carbondisulfide-methylal <9>; **** 8 substances: benzene, toluene, naphthalene, trans-azobenzene, carbon tetrachloride, water, tin, sulphur, <4>, <10>)

	Analytical expression	Simplification	Range of error
Re_1	$\frac{H_1^E}{\Delta_{fus}H}$ or $C'*X_2$	$f_1(T) \approx f_1$	-2.37...0.44 *
Re_2	$\frac{\Delta C_p*R*T_{fus}^2}{2*\Delta_{fus}H^2} * X_2$	$\Delta_{fus}H(T) \approx \Delta_{fus}H$	0.006..0.13 **
Re_3	$-\frac{\ln f_1}{X_2}$ or $-C*X_2$	$a_1 \approx X_1$	-0.48..-0.32 ***
Re_4	$1/2*X_2$	$\ln(1-X_2) \approx -X_2$	0.5
Re_5	$-\frac{R*T_{fus}}{\Delta_{fus}H} * X_2$	$T_{fus}*T \approx T^2$	-1.87..-0.13 ****

For small concentrations of impurities ($X_2 < 0.05$) all five errors can be expressed as being proportional to X_2. Re_1 and Re_3 depend on the properties of both components of the mixture, Re_2 and Re_5 only on those of the main component and Re_4 does not depend on substance properties. Except for Re_2 the order of magnitude for all errors is about 0.5 to 1, Re_2 is smaller by a factor of 10. Owing to different sign, the errors partly cancel. As an example the total error for the system benzene-cyclohexane is $Re_{tot} = (0.32 + 0.01 - 0.46 + 0.50 - 0.23) * X_2 = 0.14 * X_2$.

To control the results obtained, for all of the five estimations both X_2 and X_2' are calculated by the equations (2) to (6) respectively (1) to (5). The left side of the approximations $(X_2-X_2')/X_2'$ is then compared with the analytical expression on the right side, whereby the data for the system benzene-cyclohexane have been used. For all simplifications in the five assessments the errors were less than ±5%. In summary, the following statement can be made:

The amount of the relative total error involved in van't Hoff's law is approximately of the same size as the impurity concentration: $|Re_{tot}| \approx X_2$.

This applies for impurities in the concentration range 0...0.05. Example: $X_2' = 0{,}05$, $Re_{tot} \approx \pm 0.05$, $X_2 = 0.05 \pm 0.0025$.

In the following model calculations the description of eutectic systems will be based on equation (4), thus in contrast to standard procedures of purity determination the errors Re_4 and Re_5 are avoided. It is hardly possible to use the more exact equations (1), (2) or (3), because in the case of the impurity being unknown, nothing can be said about the activity coefficient and the enthalpy of mixing.

Modelling a Heat-flux Calorimeter

Fig. 1 shows the R-C-model of a heat-flux calorimeter developed in <2>, which is based on an analysis of the heat-flux behaviour in the Heraeus TA 500 calorimeter (Heraeus GmbH, Hanau, F.R.G.)

In <2> we have described how the equipment parameters R_1, R_2, R_4, C_1 and C_2 can be derived from two heat capacity measurements. Table 2 lists these parameters for the Heraeus TA 500 calorimeter for the temperatures 50 and 200°C. The difference to those given in <2> arise from a new calorimeter head being installed. Γ_1 is the time constant between oven and measuring head.

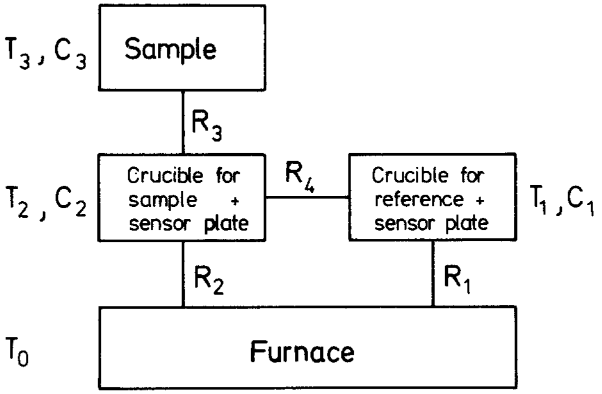


Fig. 1 R-C-modell of the heat-flux calorimeters used <2>

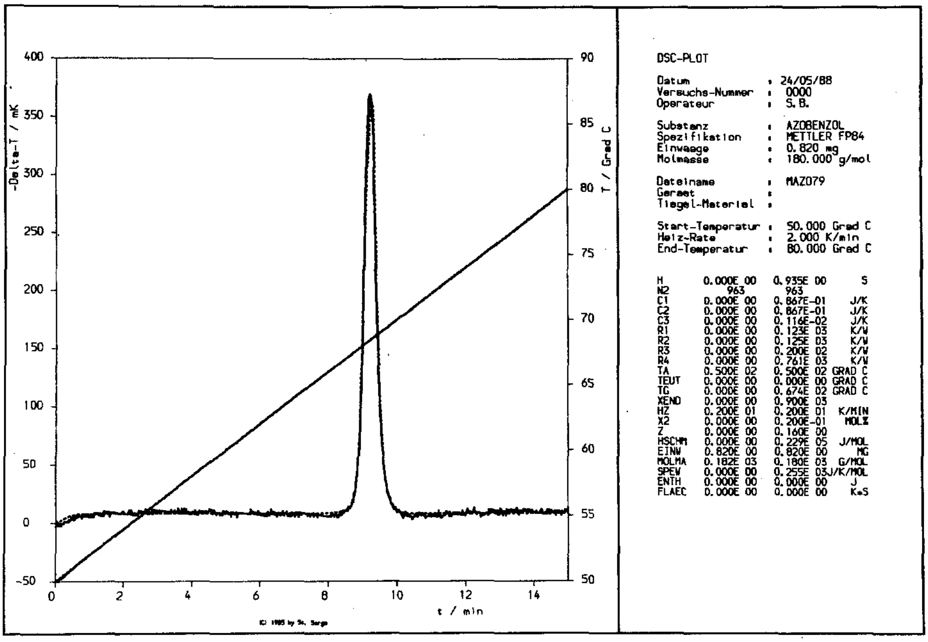
Table 2 Parameters of the calorimeters Heraeus TA 500 and Mettler FP 84

ϑ / °C	$R_1=R_2$ / $K*W^{-1}$	R_4 / $K*W^{-1}$	$C_1=C_2$ / $J*K^{-1}$	Γ_1 / s
Heraeus TA 500				
50	240.4	80.9	0.219	52.61
200	131.5	102.8	0.365	47.81
Mettler FP 84				
70	≈123	≈761	≈0.087	≈10.7

One can see in Fig. 3 and 4 that the fit of calculated to experimental curves using the new temperature dependent parameters is even better than in <2>.

Since the model presented is relatively simple, it can be easily adapted to other heat-flux calorimeters. Table 2 also gives the parameters for the calorimeter Mettler FP 84 at ϑ = 70°C. In the Heraeus TA 500 calorimeter the temperature T_2 is measured below the sample container. In the Mettler calorimeter, however, only the oven temperature T_0 is recorded. Thus with the FP 84, the temperature differences necessary for the derivation of instrument parameters (see equations (21)-(23) in <2>) can only be determined indirectly. Therefore the parameters for the Mettler FP 84 are only approximate values.

Fig. 2 shows the fusion curve of zone purified trans-azobenzene obtained with the Mettler FP 84 at a heating rate of 2 K*min^{-1} and the calculated optimal fit with X_2(sim) = 0.02 mol%.



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DSC-PLOT

Datum              : 24/05/88
Versuchs-Nummer    :  0000
Operateur          :  S.B.

Substanz           :  AZOBENZOL
Spezifikation      :  METTLER FP84
Einwaage           :  0.820 mg
Molmasse           :  180.000 g/mol

Dateiname          :  MAZ079
Geraet             :
Tiegel-Material    :

Start-Temperatur   :  50.000 Grad C
Heiz-Rate          :  2.000 K/min
End-Temperatur     :  80.000 Grad C

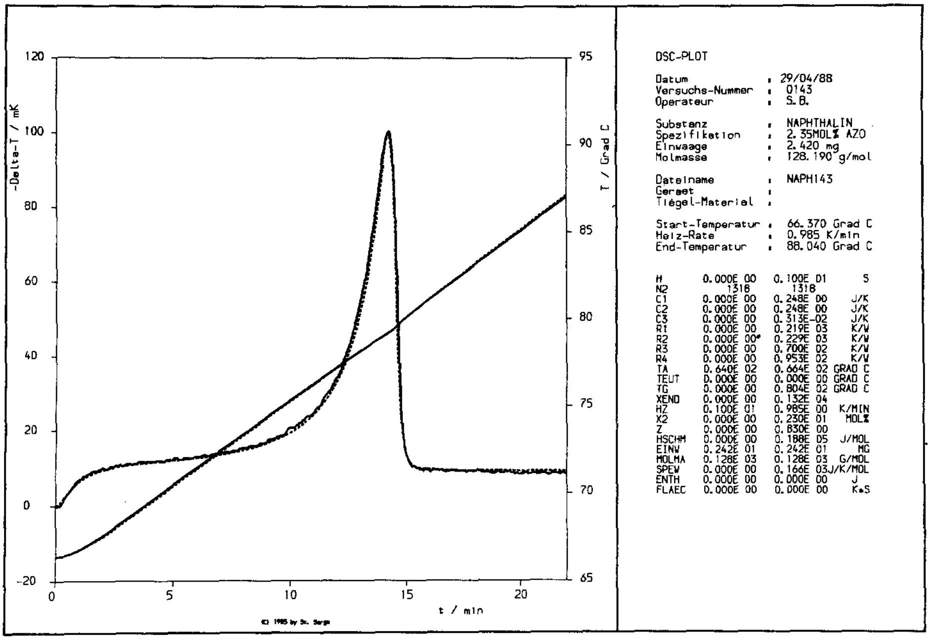
H       0.000E 00   0.935E 00       S
N2         963         963
C1      0.000E 00   0.867E-01     J/K
C2      0.000E 00   0.867E-01     J/K
C3      0.000E 00   0.116E-02     J/K
R1      0.000E 00   0.123E 03     K/W
R2      0.000E 00   0.125E 03     K/W
R3      0.000E 00   0.200E 02     K/W
R4      0.000E 00   0.761E 03     K/W
TA      0.500E 02   0.500E 02  GRAD C
TEUT    0.000E 00   0.000E 00  GRAD C
TG      0.000E 00   0.674E 02  GRAD C
XEND    0.000E 00   0.900E 03
HZ      0.200E 01   0.200E 01   K/MIN
X2      0.000E 00   0.200E-01    MOL%
Z       0.000E 00   0.160E 00
HSCHM   0.000E 00   0.229E 05   J/MOL
EINW    0.820E 00   0.820E 00      MG
MOLMA   0.182E 03   0.180E 03   G/MOL
SPEW    0.000E 00   0.255E 03J/K/MOL
ENTH    0.000E 00   0.000E 00       J
FLAEC   0.000E 00   0.000E 00     K*S
```

Fig. 2 Fusion curve of trans-azobenzene, ——, Mettler FP 84, heating rate 2 K/min; and simulated curve, ····, with X_2(sim) = 0.02 mol%.

Purity Determination by Simulation of DSC Curves

In the DSC purity determination method by simulation of DSC curves the experimental (real) and the calculated fusion curve are plotted in one diagram and compared. The property aimed at - the total impurity concentration - is varied together with the fusion temperature until an optimal fit between experimental and calculated curve is obtained.

The results shown in Fig. 3 and 4 have been obtained in the following manner. A mixture of zone purified naphthalene with 2.36 mol% trans-azobenzene (also zone purified) was prepared



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DSC-PLOT

Datum               : 29/04/88
Versuchs-Nummer     :  0143
Operateur           :  S.B.

Substanz            :  NAPHTHALIN
Spezifikation       :  2.35MOL% AZO
Einwaage            :  2.420 mg
Molmasse            :  128.190 g/mol

Dateiname           :  NAPH143
Geraet              :
Tiegel-Material     :

Start-Temperatur    :  66.370 Grad C
Heiz-Rate           :  0.985 K/min
End-Temperatur      :  88.040 Grad C

H       0.000E 00   0.100E 01        S
N2         1318        1318
C1      0.000E 00   0.248E 00      J/K
C2      0.000E 00   0.248E 00      J/K
C3      0.000E 00   0.313E-02      J/K
R1      0.000E 00   0.219E 03      K/W
R2      0.000E 00   0.229E 03      K/W
R3      0.000E 00   0.700E 02      K/W
R4      0.000E 00   0.953E 02      K/W
TA      0.640E 02   0.664E 02 GRAD C
TEUT    0.000E 00   0.000E 00 GRAD C
TG      0.000E 00   0.804E 02 GRAD C
XEND    0.000E 00   0.132E 04
HZ      0.100E 01   0.985E 00  K/MIN
X2      0.000E 00   0.230E 01     MOL%
Z       0.000E 00   0.830E 00
HSCHM   0.000E 00   0.188E 05  J/MOL
EINW    0.242E 01   0.242E 01       MG
MOLMA   0.128E 03   0.128E 03  G/MOL
SPEW    0.000E 00   0.166E 03J/K/MOL
ENTH    0.000E 00   0.000E 00        J
FLAEC   0.000E 00   0.000E 00      K*S
```
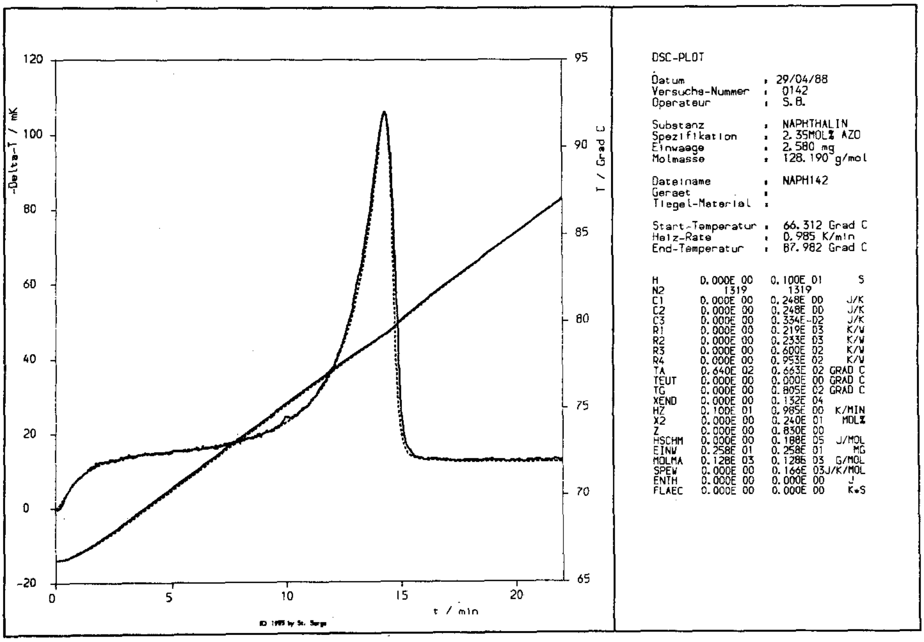

Fig. 3 Fusion curve of naphthalene, ——, X_2(exp) = 2.36 mol%; simulated curve, ····, X_2(sim) = 2.30 mol%.



```
DSC-PLOT

Datum               : 29/04/88
Versuchs-Nummer     :  0142
Operateur           :  S.B.

Substanz            :  NAPHTHALIN
Spezifikation       :  2.35MOL% AZO
Einwaage            :  2.580 mg
Molmasse            :  128.190 g/mol

Dateiname           :  NAPH142
Geraet              :
Tiegel-Material     :

Start-Temperatur    :  66.312 Grad C
Heiz-Rate           :  0.985 K/min
End-Temperatur      :  87.982 Grad C

H       0.000E 00   0.100E 01        S
N2         1319        1319
C1      0.000E 00   0.248E 00      J/K
C2      0.000E 00   0.248E 00      J/K
C3      0.000E 00   0.334E-02      J/K
R1      0.000E 00   0.219E 03      K/W
R2      0.000E 00   0.233E 03      K/W
R3      0.000E 00   0.600E 02      K/W
R4      0.000E 00   0.953E 02      K/W
TA      0.640E 02   0.663E 02 GRAD C
TEUT    0.000E 00   0.000E 00 GRAD C
TG      0.000E 00   0.805E 02 GRAD C
XEND    0.000E 00   0.132E 04
HZ      0.100E 01   0.985E 00  K/MIN
X2      0.000E 00   0.240E 01     MOL%
Z       0.000E 00   0.830E 00
HSCHM   0.000E 00   0.188E 05  J/MOL
EINW    0.258E 01   0.258E 01       MG
MOLMA   0.128E 03   0.128E 03  G/MOL
SPEW    0.000E 00   0.166E 03J/K/MOL
ENTH    0.000E 00   0.000E 00        J
FLAEC   0.000E 00   0.000E 00      K*S
```

Fig. 4 Fusion curve of naphthalene, ——, X_2(exp) = 2.36 mol%; simulated curve, ····, X_2(sim) = 2.40 mol%.

as a physical mixture. Even mixing of the components azobenzene (red) and naphthalene (white) results in an even colour distribution in the mixture. To check the homogeneity of the mixture and the reproducibility of the technique two samples of 2.420 mg and 2.580 mg mass are weighed into aluminium crucibles. Fig. 3 and 4 show the fusion curves and their optimal fit. The impurity concentrations were determined as 2.30 mol% and 2.40 mol%; this corresponds to a deviation of -3% and +2% respectively.

The column on the right side within the figures contains all data pertinent to the substance and instrument used in a specific case.

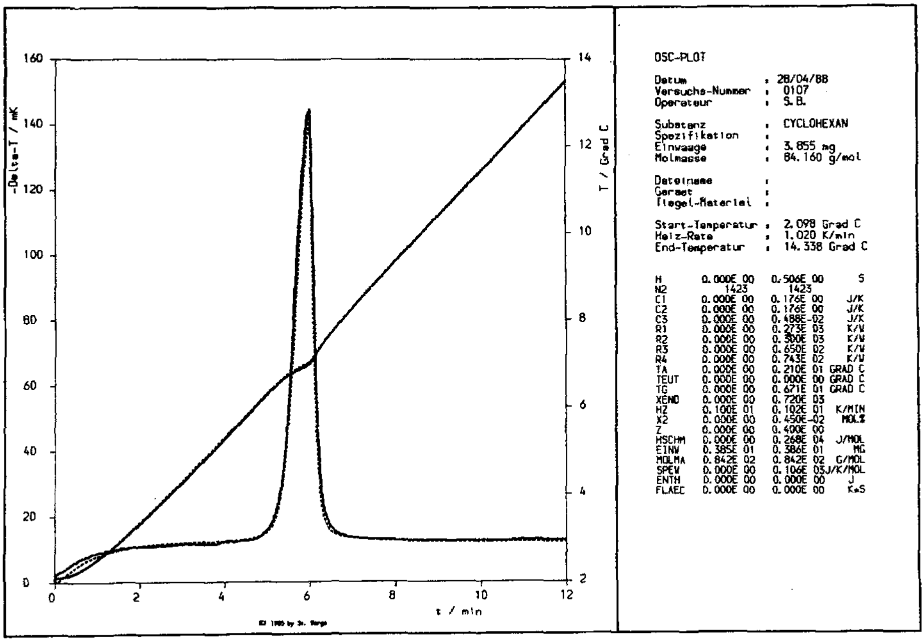
Fig. 5 and 6 demonstrate the applicability of the method also for small impurity concentrations and for different temperature regions. One recognizes in Fig. 5 that the fit for cyclohexane with X_2 = 0.0045 mol% at the relatively low temperature ϑ_{fus} = 6.71°C is very reasonable. As shown in Fig. 6 the fit for indium in the falling part of the fusion curve is not as good. In the increasing part of the curve, however, which is the one important for the impurity assessment, the fit is good and the impurity content derived as X_2(sim) = 0.0001 mol% is the same as given by the manufacturer.

The experiments shown in Fig. 3 to 6 were performed at the same heating rate, 1 K*min^{-1}. The figures demonstrate well the qualitative differences in peak form and peak height with increasing purity of the main component.

In Table 3 the results of the fits of this and the prece-

Table 3 Compilation of the different fitting results in this paper and <2> together with R_3 and X_2

Substance	R_3 / K*W^{-1}	X_2(exp) / mol%	X_2(sim) / mol%	Error
Heraeus TA 500				
Naphthalene	60	0.98	0.8	-18%
Naphthalene	80	5.01	5.4	+ 8%
Naphthalene	70	2.36	2.30	- 3%
Naphthalene	60	2.36	2.40	+ 2%
Indium	90	< 0.0001	0.0001	> 0%
Cyclohexane	65	unknown	0.0045	-
Mettler FP 84				
Azobenzene	20	unknown	0.020	-



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DSC-PLOT

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Versuchs-Nummer     :  0107
Operateur           :  S.B.

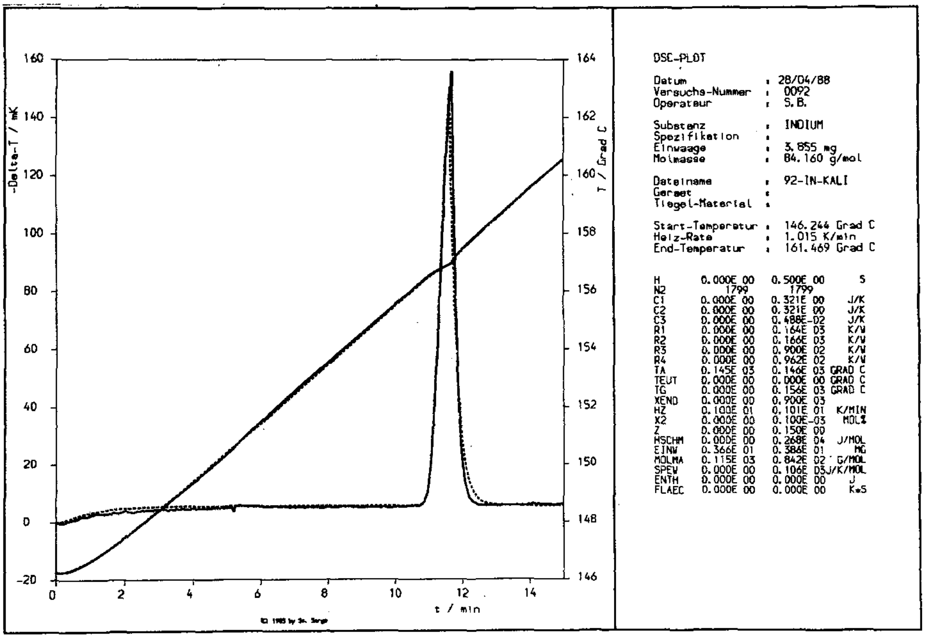
Substanz            :  CYCLOHEXAN
Spezifikation       :
Einwaage            :  3.855 mg
Molmasse            :  84.160 g/mol

Dateiname           :
Geraet              :
Tiegel-Material     :

Start-Temperatur    :  2.098 Grad C
Heiz-Rate           :  1.020 K/min
End-Temperatur      :  14.338 Grad C

H        0.000E 00    0.506E 00        S
N2         1423         1423
C1       0.000E 00    0.176E 00      J/K
C2       0.000E 00    0.176E 00      J/K
C3       0.000E 00    0.488E-02      J/K
R1       0.000E 00    0.273E 03      K/W
R2       0.000E 00    0.300E 03      K/W
R3       0.000E 00    0.650E 02      K/W
R4       0.000E 00    0.743E 02      K/W
TA       0.000E 00    0.210E 01  GRAD C
TEUT     0.000E 00    0.000E 00  GRAD C
TG       0.000E 00    0.671E 01  GRAD C
XEND     0.000E 00    0.720E 03
HZ       0.100E 01    0.102E 01    K/MIN
X2       0.000E 00    0.450E-02     MOL%
Z        0.000E 00    0.400E 00
HSCHM    0.000E 00    0.268E 04    J/MOL
EINW     0.385E 01    0.386E 01       MG
MOLMA    0.842E 02    0.842E 02    G/MOL
SPEW     0.000E 00    0.106E 03J/K/MOL
ENTH     0.000E 00    0.000E 00        J
FLAEC    0.000E 00    0.000E 00      K*S
```

Fig. 5 Fusion curve of cyclohexane, ——; simulated curve, ····, $X_2(\mathrm{sim}) = 0.0045$ mol%.



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DSC-PLOT

Datum               : 28/04/88
Versuchs-Nummer     :  0092
Operateur           :  S.B.

Substanz            :  INDIUM
Spezifikation       :
Einwaage            :  3.855 mg
Molmasse            :  84.160 g/mol

Dateiname           :  92-IN-KALI
Geraet              :
Tiegel-Material     :

Start-Temperatur    :  146.244 Grad C
Heiz-Rate           :  1.015 K/min
End-Temperatur      :  161.469 Grad C

H        0.000E 00    0.500E 00        S
N2         1799         1799
C1       0.000E 00    0.321E 00      J/K
C2       0.000E 00    0.321E 00      J/K
C3       0.000E 00    0.488E-02      J/K
R1       0.000E 00    0.164E 03      K/W
R2       0.000E 00    0.166E 03      K/W
R3       0.000E 00    0.900E 02      K/W
R4       0.000E 00    0.962E 02      K/W
TA       0.145E 03    0.146E 03  GRAD C
TEUT     0.000E 00    0.000E 00  GRAD C
TG       0.000E 00    0.156E 03  GRAD C
XEND     0.000E 00    0.900E 03
HZ       0.100E 01    0.101E 01    K/MIN
X2       0.000E 00    0.100E-03     MOL%
Z        0.000E 00    0.150E 00
HSCHM    0.000E 00    0.268E 04    J/MOL
EINW     0.366E 01    0.386E 01       MG
MOLMA    0.115E 03    0.842E 02    G/MOL
SPEW     0.000E 00    0.106E 03J/K/MOL
ENTH     0.000E 00    0.000E 00        J
FLAEC    0.000E 00    0.000E 00      K*S
```

Fig. 6 Fusion curve of pure indium, ——; simulated curve, ···· $X_2(\mathrm{sim}) = 0.0001$ mol%.

ding paper <2> are compiled. The second column contains the heat resistance R_3 between sample and sample support, which is not a pure instrument parameter, but depends to some extent on the substance. For the Heraeus TA 500 calorimeter a mean value of $R_3 = 70\ K*W^{-1}$ is obtained. This value is in good accord with that determined in <11> from the slope of the fusion peaks of several pure reference materials for temperature and enthalpy calibration, viz. 80 $K*W^{-1}$.

Determination of Fusion Temperatures by Simulation of DSC Curves

The extrapolated onset-temperature of a fusion peak is usually taken as the temperature of fusion. This onset-temperature depends on calorimeter and substance parameters, e.g. heating rate, sample mass, and purity of the sample. The influence of these parameters can be easily studied in varying their magnitude in the simulation of DSC curves. Using the set of parameters given in Fig. 3 (but at $X_2 = 0.3$ mol%) a variation in sample mass by a factor of 2 results in a shift of 0.1 K for the temperature of fusion. Since in fitting of calculated curves to the experimental DSC curves instrument and substance parameters are taken into consideration, this method offers a more exact determination of fusion temperatures.

Furthermore, comparison of calculated with experimental DSC-curves gives hints about correct function of the calorimeter and about the phase transformation (e.g. ideal eutectic behaviour). Thus it became evident during measurements that the actual heating rate of the Heraeus TA 500 calorimeter may differ by ±2% from the set value, (see also the legends in Fig. 3-6, parameter HZ). These deviations may especially affect those techniques, which depend on the heating rate, e.g. measurements of heat capacity or kinetic parameters.

List of Symbols

a_i	activity of component i
C, C'	constants
C_i	heat capacity of zone i
ΔC_p	difference in molar heat capacities
f_i	activity coefficient of component i
H_1^E	differential enthalpy of dilution
$\Delta_{fus}H$	molar enthalpy of fusion
R	universal gas constant
R_i	heat resistance of path i
Re_i	relative error i
T	absolute temperature
T_{fus}	fusion temperature of pure substance
ΔT	temperature difference
t	time
ϑ	temperature in degrees centigrade
x_i	mol fraction of component i
Γ_1	time constant between oven and sensor

References

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Zusammenfassung

Weitere Ergebnisse zur Methode der Reinheitsbestimmung durch simulierte DSC-Kurven werden vorgestellt. Die Geräteparameter eines Wärmeflußkalorimeters werden für zwei Temperaturen berechnet, womit genauere Ergebnisse erzielt werden können. Das Kalorimetermodell wird an ein weiteres Wärmeflußkalorimeter angepaßt. Die Methode bietet aufgrund der Berücksichtigung von Geräte- und Substanzeigenschaften auch die Möglichkeit einer genaueren Schmelztemperaturbestimmung.

Weiterhin wird eine Fehlerabschätzung zum van't Hoffschen Gesetz durchgeführt, welches eine vereinfachte Beschreibung der Koexistenzkurven eines eutektischen Phasensystems und damit der Gefrierpunktserniedrigung darstellt. Dabei ergibt sich, daß der relative Gesamtfehler proportional zur Verunreinigungskonzentration ist und in der gleichen Größenordnung wie diese liegt.

Резюме - Представлены дальнейшие результаты по определению чистоты с помощью модельных кривых ДСК. Инструментальные параметры для ДСК с тепловым потоком были определены при двух температурах, вследствии чего улучшена точность получаемых результатов. Дополнительно к этому, данная модель калориметра приспособлена к другому калориметру. Метод также позволяет более точное определение температуры плавления. Закон Вант-Гоффа значительно упрощенно описывает сосуществование кривых на эвтектической фазовой диаграмме. Детальный анализ ошибок пяти упрощений привел к тому, что закон показал, что введенная относительная общая ошибка пропорциональна концентрации примеси и является такой величиной, как и сама концентрация.