DYNAMIC PURITY DETERMINATIONS. I.
LOCATION OF THE SOLIDUS BY NUCLEAR MAGNETIC RESONANCE

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The error in purity determinations by differential scanning calorimetry has been studied on two different kinds of systems, metallic and organic, the latter with different types of impurities added. The organic systems have been corrected for solid-solubility error by a nuclear magnetic resonance technique.

The impurities chosen for the organic systems were either quite dissimilar to the matrix or similar enough to render solid solution probable. This solid solution leads to deviations from the equation used for dynamic purity determinations. The nuclear magnetic resonance determination of the solidus establishes the proper starting temperature for area summation on a DSC curve.

Thermoanalytical techniques are so generally useful that it is not at all difficult to establish new applications or deduce relationships on the basis of some experimental data – then find that there is substantial limitation on that application or concept. This senior author (PDG) has sought, from time to time, to examine some concepts that have developed in thermal analysis or are testable by thermal analysis to prove or disprove [1 – 8] or to delineate their limits [9, 10, this work].

This program of research was undertaken to evaluate the potential error inherent in the purity determination methods which depend upon the assumption of ideal liquid solution but zero solid solution. Impurities are highly probable in real systems and in any real system the most probable impurities are materials closely related in chemical structure to the matrix material because of their origin or processing.

The well known effect of small amounts of impurities on melting behavior of crystalline compounds, i.e., lowering of their melting points, provides an excellent basis for purity determinations by various methods (time dependent and time independent). There are three main advantages of these methods: first, simplicity and speed of some of them, viz. the time dependent ones; second, sensitivity which is of such magnitude that it can be compared with the best methods known, for instance, high temperature mass spectrometric analysis [10]; third, a firm base upon thermodynamic principles which means that no reference materials need to be applied. Experimentally, in purity determinations based on lowering the melting point

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of a solvent by different solutes, a relation between two measurable variables is always established; the temperature (T) of solid and liquid phases coexisting in a state of thermodynamic equilibrium and the fraction in the liquid phase (F).

In order to extract all the information contained in this relation and particularly the total amount of impurities within the investigated system, various theories have been proposed [12, 15], each assuming an ideal system. The results of those theories have been summarized in Equations 1 − 4.

$$(T^0_{m_i} - T)^{-1} = \frac{\Delta H^0_{m_i}}{R(T^0_{m_i})^2} \cdot \frac{1}{x_j} \cdot F \tag{1}$$

$$(T^0_{m_i} - T)^{-1} = \frac{\Delta H^0_{m_i}}{R(T^0_{m_i})^2} \cdot \frac{1}{x_j} \cdot F - \frac{\Delta H^0_{m_i}}{R(T^0_{m_i})^2} \cdot \frac{1}{x_j} \cdot \frac{k}{1 - k} \tag{2}$$

$$(T^0_{m_i} - T)^{-1} = \frac{\Delta H^0_{m_i}}{R(T^0_{m_i})^2} \cdot \frac{1}{x_j} \cdot \frac{1}{1 - k} \cdot F^{(1-k)} \tag{3}$$

$$(T^0_{m_i} - T)^{-1} = (1/x_j - 2a) \frac{\Delta H^0_{m_i}}{R(T^0_{m_i})^2} \cdot F - 2a \frac{\Delta H^0_{m_i}}{\Delta(T^0_{m_i})^2} \cdot \tag{4}$$

Where

T = equilibrium temperature of the liquid with its solid, K
$T^0_{m_i}$ = melting temperature of the solvent, K
x_j = solute content in the solution, mole fraction
F = fraction melted
$H^0_{m_i}$ = molar enthalpy of melting of the solvent, cal mole^{-1}
R = gas constant, cal deg^{-1} · mole^{-1}
k = partition coefficient, dimensionless
a = parameter of equation (4) which magnitude depends on both solubility of components in the solid and deviations from ideality in the system, dimensionless

The discussion of assumptions upon which derivation of Equations 1−4 has been based is given elsewhere [15]. The assumptions of ideal liquid solution and zero solid solution are essential to the development of the relationships. All of them are semiempirical in nature because they contain a variable F that although a thermodynamic variable in definition is found empirically from fractional heat measurements. A general picture of Equations $(1-4)$ in $(T^0_{m_i} - T)^{-1}$ vs F coordinates is presented graphically in Figure 1.

Equation (4) takes into account more known experimental facts than the remaining equations. Equation (1) is a special case of Equation (4) $(a = 0)$, so the latter may be used as a measure of deviations from some ideal case, viz., Equation (1).

So far no single theory has been developed which describes the various experimental methods of purity determinations by DSC or DTA successfully. Generally the discrepancy between Equations $(1-4)$ and experimental results will arise from
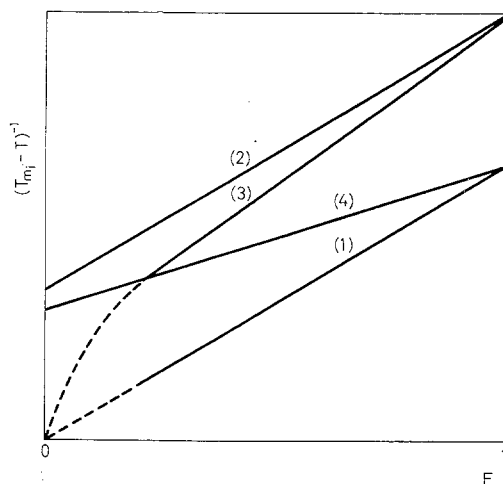
Fig. 1. Graphical presentation of Eqs 1—4 in $(T_{m_i}^0 - T)^{-1}$ vs F coordinates

the fact that the sample investigated fails to be in the state of thermodynamic equilibrium assumed in all these equations. A state of thermodynamic equilibrium consists of three kinds of interdependent states of equilibrium: mechanical, thermal and concentration equilibrium.

It is taken for granted that there is no pressure gradient within the sample, so the sample is in a state of mechanical equilibrium.

In all kinds of time dependent experiments there is a temperature gradient created within the sample. The sample cannot be in a state of thermal equilibrium but the temperature gradient can be made small or at least to appear to be small.

It is also widely believed that this lack of thermal equilibrium is the main reason for the mentioned above discrepancies [16, 17]. Because it is not easy to express the lack of thermal equilibrium in terms of measurable variables (T, x) different experimental techniques rather than modifications of equations have been proposed. These techniques are either time independent or less time dependent [16], for example, by allowing the temperature gradient within the sample to decay more or less rapidly.

It has also been noted [14, 15, 18, 19] that lack of concentration equilibrium (and homogeneity) within the sample may contribute greatly to the discrepancies between observed and calculated values. The principal phenomena contributing to the lack of concentration equilibrium are deviations from ideality in the liquid phase and solubility of minor components in the solid major component. A sample that has been wholly or partially melted will not have the predicted compositions in the first- and the last-solidified portions. These continually-varying compositions produce frozen-in concentration gradients in the solid sample. Usually not much can be done to wipe out these concentration gradients; at the same time it is not easy to express the lack of concentration equilibrium in terms of measurable vari-

ables T and x. The practical solution that has been used to bring theory and experiment into closer agreement is a redefinition of the state of equilibrium (the solid of the two phase systems containing the lesser component in veins or pockets) and stimulating experimentally the investigated system to conform with this state of quasi-equilibrium by quenching. This has been more or less explicitly expressed in several publications [14, 15, 18, 19].

In addition to the above limitations, which might be described as theoretical in nature, there are other possible reasons for discrepancies associated with technique or with instrumentation.

This study is intended to improve methods of purity determination by enabling avoidance or correction of error particularly in differential scanning calorimetry.

The specific aims are:

1. To generate cryoscopic data for different classes of compounds by differential scanning calorimetry and to correct them (where applicable) for instrumental errors by a nuclear magnetic resonance technique,

2. To ascertain whether or not these systems may be treated by the ideal-solution-without-solid-solubility method (Eq. (1)),

3. To develop methods for estimation and correction of error in nonideal systems (Eq. (4)).

Experimental

The types of systems chosen for purity determinations were pure tin, tin contaminated with 0.2, 0.5 and 1 at. % of lead and indium respectively; pure phenacetin, phenacetin contaminated with 0.5, 1.0 and 5.0 mole % benzamide, acetanilide and n-tetracosane respectively. All solutions have been prepared in relatively large amounts both to minimize the error due to weighing and to enable a number of tests on a homogeneous sample.

Weighed high purity grade components of the metallic systems have been melted together under an atmosphere of nitrogen, then quenched to obtain samples of uniform concentration.

A commercial phenacetin was purified by zone refining until the best fractions chosen did not show any visible differences in physical properties (by DSC heating curve or preparative liquid chromatography). Weighed amounts of the selected impurity were dissolved in weighed amounts of the molten principal component. After thorough homogenation, the samples were chilled quickly below the eutectic temperature by pouring the specimen onto a slab of aluminum. Homogeneity of composition has been preserved by not allowing time for crystallization and separation of the principal component.

The model DSC-2 differential scanning calorimeter was used as a principal tool for purity determinations. The instrumental line was carefully optimized in the regions of interest: $120-160°$ (phenacetin) and $215-245°$ (tin). The thermal resistance of this particular apparatus was determined and found to be equal to 0.12 deg s/mcal. The temperature and energy calibrations were checked. Samples of two to three milligrams were used. The heating rate ordinarily used was 1.25°/min.

A Varian A-60 Nuclear Magnetic Resonance apparatus was used for determining the relative amount of liquid in the solid-liquid system in the low liquid content region. The NMR apparatus has had improving modifications so that its signal-to-noise ratio is equal to that of later models. In principle, any peak in the NMR spectrum can be used. In practice, prominent peaks yield somewhat better resolution. It is probably advisable, however, not to use a methyl peak if the group is at the end of a side chain; the possibility of extra mobility while the "backbone" is still rigidly held in the crystal might impair resolution.

The manufacturer's heating equipment for the NMR has been improved so that a constancy of the temperature of 0.1 has been achieved. The equilibrium temperature has been measured by a differential copper vs constantan thermocouple.

The purities of the systems investigated have been established according to Eq. (4). $T_{m_j}^0$ may be evaluated by a trial-and-error procedure until the assumed straight line of the plot $(T_{m_j}^0 - T)^{-1}$ vs F is achieved. The slope of this line will be $(1/x_j - 2a) \Delta H_{m_j}^0 / R(T_{m_j}^0)^2$ and the intercept $2a\, RH_{m_j}^0 / R(T_{m_j}^0)^2$. Thus if $\Delta H_{m_j}^0$ is known we are able to calculate x_j.

Results and discussion

Pure samples of n-hexatriacontane, tin and phenacetin (two samples with almost identical masses) have been quenched down to a temperature about 50 degrees below the melting point. Two consecutive DSC runs have been performed at exactly the same conditions and the obtained curves have been superimposed.

From the superimposed curves one can see that the state to which we may refer conventionally as a quenched state of equilibrium is exactly reproducible in case of n-hexatriacontane and tin samples. In the case of phenacetin the reproducibility of the initial part of the curve is also good. This is in agreement with the observati on made by Smit [20]. The reproducibility of the next part of the curve deteriorates somewhat and is probably due to slight sublimation of the sample over the heating range.

On the other hand one can see that it is impractical to use the notion of a true state of equilibrium in purity measurements by time dependent methods. The DSC curve is changing gradually with the course of time during which the system is equilibrating. In fact, there is no definite state of equilibrium of this kind, i.e., a state when all processes due to diffusion come to an end. The diffusion in the solid phase is extremely slow, for example Tiller considered the growth of a crystal from an aqueous solution, and found that the diffusion coefficients in the solid and liquid phases are equal to 10^{-18} cm^2/s and 10^{-6} cm^2/s, respectively [21].

The metallic systems have been chosen mainly to elucidate the impact of thermal equilibrium on purity measurements by DSC. It has been reasoned that because of excellent thermal conductivity of those samples (three orders of magnitude higher than organics) the temperature gradient within the sample, during the time of the experiment, should be negligible. Thus, the sample could be considered to be in a state of thermal equilibrium. Now, if lack of thermal equilibrium within the sample

is the only reason for which the experimental data do not follow Eq. (1), then the results of measurements on these particular systems should obviously exhibit a straight line behavior when presented as T vs $1/F$. Figure 2 shows the cryoscopic curve of a pure tin sample in T vs $1/F$ coordinates obtained by DSC.

The character of this curve (slope and curvature) is similar to typical cryoscopic curves obtained for most organic compounds by different techniques, both static and dynamic [22, 23]. Qualitatively the picture is the same, there are only quantitative differences. This indicates that the lack of thermal equilibrium within the sample cannot be the only reason for which the experimental data do not follow Eq. (1). Other factors related to lack of concentration equilibrium as: solubility of components in the solid, partitioning in the solid, deviations from ideality in the solid and liquid phases are important, too. As an example Figure 3 shows the cryoscopic curves of tin contaminated with different amounts of indium.
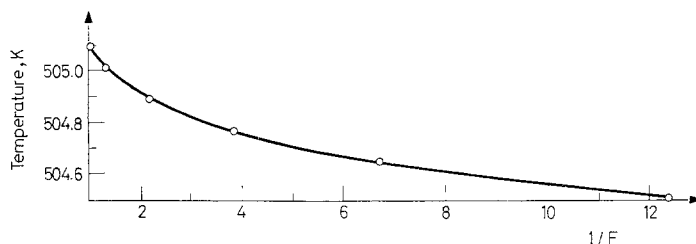

Fig. 2. A cryoscopic curve of a pure tin sample

It should be noted that it has not been possible to straighten the $(T_{mi}^0 - T)^{-1}$ vs F line by the trial-and-error procedure in the whole range of variable F. The range of variable F used in purity calculations is indicated in Figure 3.

Estimates of the accuracy of the purity evaluations on tin-and-contaminants samples are presented in Table 1. These data indicate that an accuracy to within 10% of the actual impurity can be anticipated in the 99−99.5% purity region.

Staub and Perron proposed a modification of the DSC method which involves stepwise melting of the sample by incremental increases in the temperature followed by decay to steady state heating instead of continuously scanning over the melting region [16]. It has not been possible to obtain meaningful data by this technique for samples of relatively high purity. This is simply because such samples melt over an extremely narrow range, say 0.1 deg, and the smallest increment available at the DSC-2 is 0.1 deg. So, the continuous and step scanning DSC techniques have been compared on samples of tin containing 1 at. % lead. The results are presented in Figure 4. It is seen that in the region from 100% to 40% of liquid in the sample both curves superimpose. This is another indication that lack of thermal equilibrium within the sample cannot be the only reason for the observed deviations from linearity in the T vs $1/F$ plot.
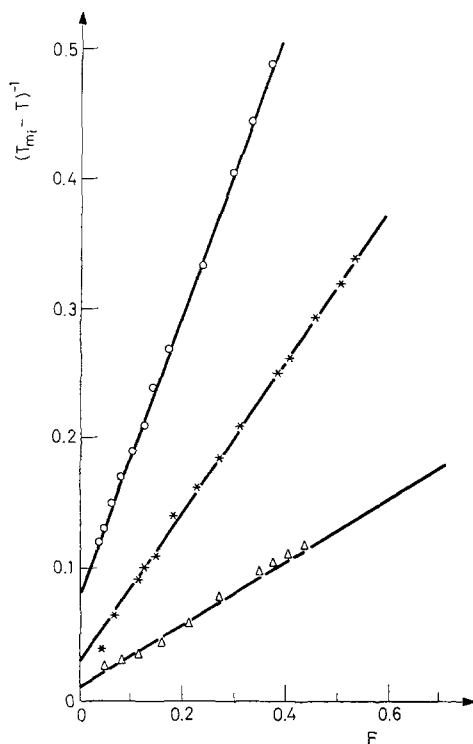
Fig. 3. Cryoscopic curves of tin contaminated with 0.2 (○), 0.5 (∗) and 1.0 at. % (△) indium

Table 1

Summary of purity measurements in a metal system and a non-metal system

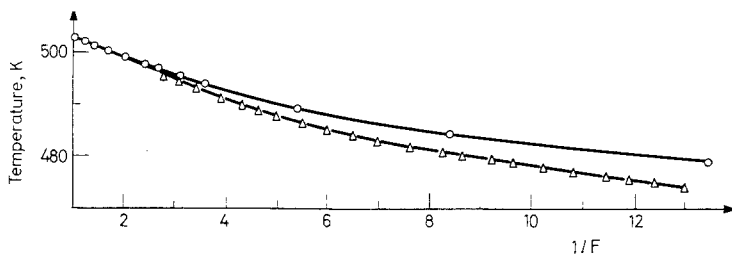| Components		Impurity		NMR corrected
		Added	Found	
Major	Minor	Mole percent		
Tin	Lead	0.20	0.22	
		0.50	0.48	
		1.00	0.96	
Tin	Indium	0.20	0.23	
		0.50	0.50	
		1.00	1.12	
Phenacetin	n-Tetracosane	0.50	0.08	0.08
		1.00	1.23	1.01
Phenacetin	Acetanilide	0.50	1.74	1.58
		1.00	1.31	1.17
		5.00	4.47	4.72
Phenacetin	Benzamide	0.50	0.07	0.05
		1.00	0.60	0.63
		5.00	6.33	5.87

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Fig. 4. Cryoscopic curves of tin contaminated with 1 at. % lead obtained by continuous (o) and stepwise (△) DSC techniques

The second class of systems investigated in this work, is phenacetin and some admixtures, viz, benzamide, acetanilide and tetracosane. Because of different chemical structures the phenacetin should form systems with benzamide or acetanilide that exhibit rather large deviations from ideality of the positive type (similar type of interaction prevails over the dissimilar type of interaction). The solubility gap of these systems is large because of slightly different crystalline structures of those systems [24].

On the other hand the system formed by phenacetin and n-tetracosane should exhibit almost no deviations from ideality because both compounds are neutral whereas the solubility gap should be substantially smaller because the chain-like molecule of the aliphatic hydrocarbon easily penetrates the crystalline structure of phenacetin.

As an example, cryoscopic curves of phenacetin contaminated with equal amounts of different admixtures are shown in Figure 5.
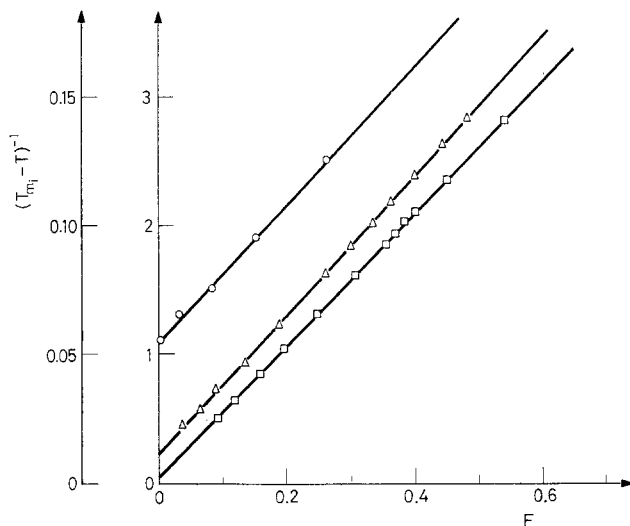

Fig. 5. Cryoscopic curves of pure phenacetin (o) and phenacetin contaminated with 1 mole % benzamide (△), acetanilide (□)

It is seen that neither are the T vs $1/F$ lines straight nor are they superimposed as they should be according to Eq. (1). This indicates that the assumptions upon which Eq. 1 has been derived, viz. no deviations from ideality in the liquid and solid and no solubility in the solid are inapplicable.

Estimates of the accuracy of the purity evaluations (according to Eq. 4) are presented in Table 1. It is seen that in this case this accuracy is much lower than in the case of metallic samples. This may be explained by following considerations.
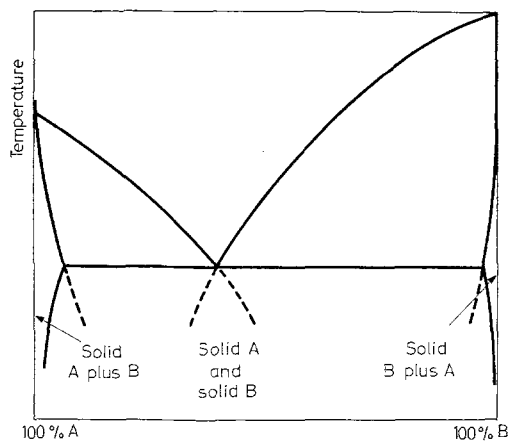

Fig. 6. Phase diagram for a binary system having limited solid solubilities

If the solid components of the investigated system are soluble in each other to some degree they will form a phase diagram shown in Figure 6, in which the existence of limits to the eutectic range can be seen. At either extreme some solid solutions exist. But these are the very regions of the phase diagram where purity determinations are used.

The DSC method depends upon measurement of fractional areas of the DSC peak. Accurate measurement would require a clearly defined departure from the baseline. Now, looking back at Figure 6 it is clear enough that the liquefaction begins at the solidus point, but in a material of say 99 % purity, the demand for heat of fusion represented by a deviation from the straight line heating, would be imperceptible at the start. That is, the deviation at the beginning is lost in the ordinary variability of the measurement. The variation of this first liquefaction is indicated by the slope of the solidus, dT/dx.

It is important to note that the measurement of a fractional area is affected more than the measurement of the total area by error in this initial portion of the peak. It has to be noted, too, that the slopes of the solidus at 1 % A and 1 % B are substantially different, so the error will depend upon which material is measured for purity.

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To solve these problems supplementary techniques should be introduced. Lawrenson has shown that nuclear magnetic resonance can be used directly for purity determinations [25] as well as for phase diagram measurements [16].

It must be stressed that there is no advantage for NMR over DSC in purity determinations. In comparison to DSC, NMR suffers greatly in point of instrument time, the accuracy of measurement of the fraction melted is no better and the temperature is generally much less accurately known in NMR than it is in DSC. On the other hand equipment costs, measurement time and simplicity of operation all favor the DSC method.
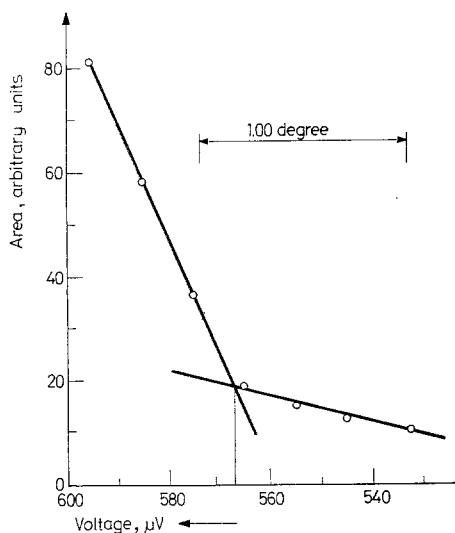

Fig. 7. Area under NMR peaks versus signal of the temperature sensor for phenacetin contaminated with 1.0 mole % tetracosane

The NMR technique has the advantage that it can detect the solidus far better than can DSC. It is that special capability which is being exploited in this work, using it to improve the accuracy of the DSC method.

Quenched phenacetin samples of mass ca. 2 g were inserted into a NMR cell and equilibrated at a temperature well below the region where the first trace of liquid appears. Then the temperature was raised by steps and after proper equilibration the NMR spectrum and the corresponding equilibrium temperature were recorded. Areas under NMR peaks versus equilibrium temperature constituted the basis for solidus point determinations. Figure 7 shows an example how the solidus point has been determined.

There is a broad and very weak NMR signal from the solid which changes slightly with temperature. The true solidus point is found by extrapolating the two parts of the curve shown in Figure 7. These two parts have different slopes.

After the true solidus points have been established the lower integration limits on the thermal curves are corrected and the purity calculations repeated according to new conditions. That is, the DSC data are used in the computation; the function of the NMR solidus determination is to establish accurately the starting point for integration, which is dependent upon both the *nature* and *amount* of impurity. This improvement is found because the detection of the start of melting is no longer by pre-set instrumental parameters, which must take into account all the electronic noise in setting the criterion for departure from the base line, nor by selection of a point-of-departure by laying a straight edge on the chart record, which is inherently subjective, but by a positive indication of the presence of liquid.

Conclusion

Because the most probable impurities in an organic material are either homologs or reactants used in its preparation, solid solubility in samples of real interest is almost certainly quite common. When solid solubility exists, the computation methods based on an ideal system fail both in principle and in practice.

The failure in practice is due to the inability to discern the solidus in the non-eutectic-forming compositions, that is, at low concentrations of impurity.

Nuclear magnetic resonance is very sensitive to liquid formation. Measurement of the temperature at which liquid first appears enables correction of the integration limits and better agreement of calculated and known concentrations. In those cases in which the NMR correction is significant (>0.03), the direction of change is toward the known concentration.

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ZUSAMMENFASSUNG — Der Fehler in Reinheitsbestimmungen mittels Differential-Scanning-kalorimetrie wurde an zwei verschiedenartigen Systemen untersucht, metallisch und organisch, wobei zu letzteren verschiedentliche Verunreinigungen zugefügt wurden. Der durch Feststoff-Feststofflöslichkeit verursachte Fehler in den organischen Systemen wurde mittels einer kern-magnetischen Resonanzmethode korrigiert.

Die für die organische Systeme gewählten Verunreinigungen waren entweder sehr ver-schieden von der Matrix, oder aber genügend ähnlich, um feste Lösungen wahrscheinlich zu machen. Diese festen Lösungen führen zu Abweichungen von der für dynamische Reinheits-bestimmungen angewendeten Gleichung. Die Bestimmung der kernmagnetischen Resonanz des Feststoffs ermöglicht die Bestimmung der richtigen Anfangstemperatur für die Flächen-summierung auf der DSC-Kurve.

Резюме — С помощью ДСК была изучена ошибка при определении чистоты двух раз-личных систем: металлической и органической. При этом последняя система изучалась с различного рода примесями. С помощью метода ЯМР для органических систем была учтена ошибка твердотельной растворимости. Примеси, взятые для органических сис-тем, или полностью отличались от исходного органисеского вещества, или же были в такой степени подобны, что могли образовывать твердый раствор. Твердый раствор вызывал отклонения от уравнения, исыользованного для динамического определения чистоть. Определение солидуса методом ЯМР позволило установить начальную темпе-ратуру для итоговой поверхноти ДСК-кривой.