

EQUILIBRIUM AND NON-EQUILIBRIUM PHASE TRANSITIONS STUDIED BY ADIABATIC CALORIMETRY

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Abstract

An adiabatic calorimetry was used for some investigations of equilibrium and non-equilibrium phase transitions. For one of the substances studied (4,4'-di-*n*-heptyloxyazoxybenzene) it was possible to determine temperature dependence of an order parameter and number of clusters of high temperature phase in a region of a phase transition. For another substance (liquid 3,4 dimethylpyridine) an anomaly on the specific heat curves was interpreted as being responsible for a decay of molecules' clusters.

Non-equilibrium phase transitions were investigated for some liquid crystal substances. The process of transformation between metastable and stable phases was described quantitatively. The conclusions obtained concern the stability of metastable phases.

Keywords: adiabatic calorimetry, phase transitions

Introduction

An adiabatic calorimetry as an equilibrium method allows some thermodynamic values characterizing phase transitions in various substances to be determined precisely. On the other hand the analysis of specific heat anomaly shape gives information about nucleation processes pretransitional effects, some parameters characterizing an investigated substance such as order parameter.

The investigations presented in the work deal with anomalies in solid phases. On the other hand a similar, but smaller anomaly was observed in one of liquids. The question: what process is responsible for the anomaly – seems to be answered in the present work.

The work deals also with non-equilibrium processes, and their dependence on various factors. The problem is discussed using as an example a metastable – stable phase transitions in liquid crystal systems.

Equilibrium phase transitions

a) A comparison of some calorimetric results for monohydrate of perchloric acid and its deuterated form.

One of the many examples of equilibrium phase transitions is a phase transition in solid H_3OClO_4 and in D_3OClO_4 . The results of specific heat vs. temperature [1] show one phase transition in H_3OClO_4 at 248.4 ± 0.1 K and two phase transitions in D_3OClO_4 : at 245.5 ± 0.1 K and at 251.9 ± 0.2 K. On the other hand the dependence ΣQ vs. T (Figs 1 and 2) shows, in the case of H_3OClO_4 addi-

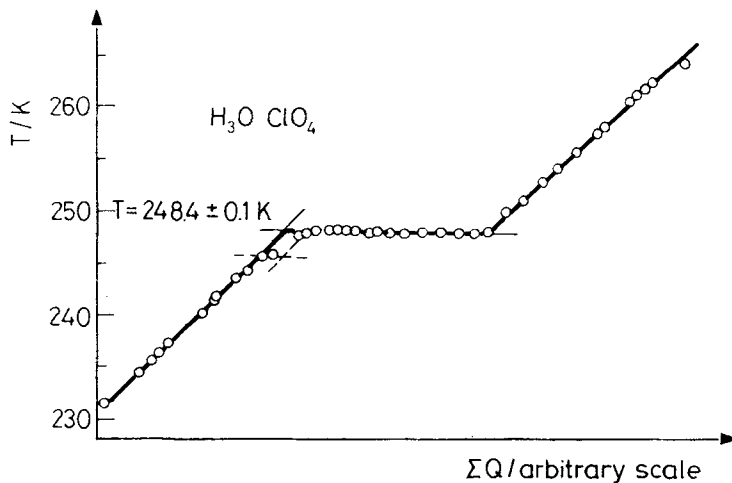


Fig. 1 T vs. ΣQ dependence for H_3OClO_4 [1]

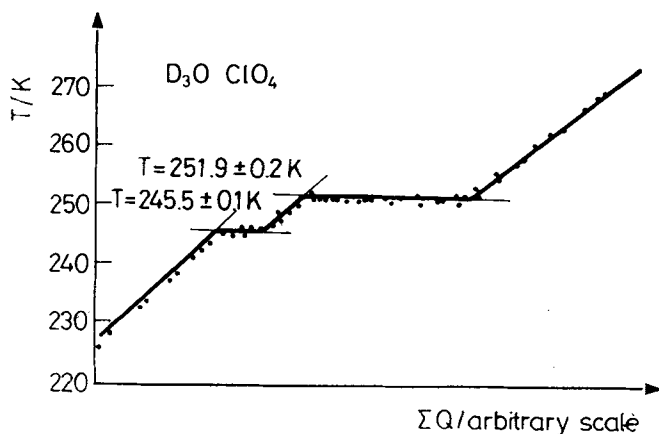


Fig. 2 T vs. ΣQ dependence for D_3OClO_4 [1]

tionally a trace of a small anomaly at ca. 246 K, which is distinctly detectable for D_3OCIO_4 . Figures 1 and 2 allow to determine ΔH and ΔS of those phase transitions. At the temperature of those phase transitions the two phases a low and a high temperature one, are in equilibrium, therefore $\Delta G=0$ and $\Delta S=\Delta H/T$. Taking into account the estimated here entropy value $\Delta H=21.97$ J/mol·K and the fact that in the low temperature phase there is one configuration of H_3O^+ [2] one could calculate the number of configurations of H_3O^+ in the high temperature phase as equal to 8 (caused by a double minimum potential existing in each hydrogen bond). Such interpretation was confirmed by the results obtained for D_3OCIO_4 . The evidence of the smaller anomaly at 245.5 K and the distinctly showed shift of the large anomaly for the substance in comparison with the corresponding anomaly of H_3OCIO_4 confirms the important role of H_3O or D_3O groups in the phase transition discussed. The sum of ΔS for the two phase transitions in D_3OCIO_4 is equal to 24.73 ± 1.51 J/mol·K which is comparable with the value of 21.97 ± 0.50 J/mol·K for H_3OCIO_4 .

b/ The analysis of the shape of an anomaly on the specific heat curve used for determination of the nematic order parameter η vs. temperature.

In the theoretical investigations of phase transitions, the phenomenological method of describing them is very common. The analytical behavior of free enthalpy near the phase transition is investigated here. The good example for it is the Landau theory. On its basis the dependence $\eta(T)$ was calculated with the use of the experimental dependence of the specific heat on temperature for HOAB (4,4'-di-*n*-heptyloxy-azoxy-benzene). η means here the parameter of the nematic order. Using the Landau's assumption, that in the phase transition region the thermodynamic potential can be expanded into a series, we get

$$G(p, T, \eta(p, T)) = G_0 + \alpha\eta + \frac{1}{2}A\eta^2 - \frac{1}{3}B\eta^3 + \frac{1}{4}C\eta^4 + \dots \quad (1)$$

$$\text{where } A = a(T - T^*); \quad (2)$$

a – a constant; T^* – temperature equal to or slightly lower than the phase transition temperature.

Additionally, taking into account the dependence of S on C_p and G , one could fit the theoretical values of C_p to the experimental ones in the region of the anomaly and then subsequently calculate $\eta = \eta(T)$ values. The dependence compared with the results obtained from other methods is showed in Fig. 3. It is seen here that the changes in η at T_k are consistent in the three methods. It is also evident, that our values are greater than those obtained by other techniques

for the nematic phase, especially in the temperature range far from the clearing point. This can be associated with the invalidity of the Landau theory in temperature ranges far from T_k as had already been observed in [6].

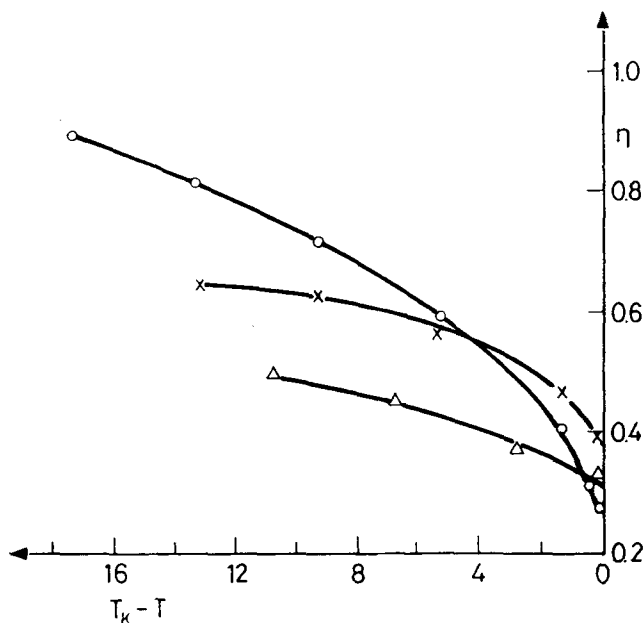


Fig. 3 η vs. $T_k - T$, T_k being the clearing temperature for HOAB determined by the NMR (T_{k1}) [4] and IR (T_{k2}) [5] methods and in this study (T_{k3}) [3]; o - results of [3], x - IR results, Δ - NMR results

c/ The analysis of the specific heat anomaly used to the estimation of nucleation's character of the new phase

The problem is discussed on the example of specific heat results for $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ (Fig. 4). For that substance the evidence of the two phase transitions was obtained, during heating of the sample: at 197 K (for the phase transition III - II) as a small anomaly and at ca. 247 K (phase II - phase I transition) as a large anomaly. The first anomaly is characterized by the large hysteresis found in [7, 8] and the other one by a small hysteresis of just several degrees. In the calorimetric measurements, it was found, that the temperature of the phase transition connected with the small anomaly is between 99.1 and 116.2 K on cooling. In Fig. 4 which presents the results of all experimental runs, we can see that in the region of the small anomaly there is relatively large scattering of experimental points, larger than that usually observed (0.6% at most). On the other hand in particular experimental runs the scattering of ex-

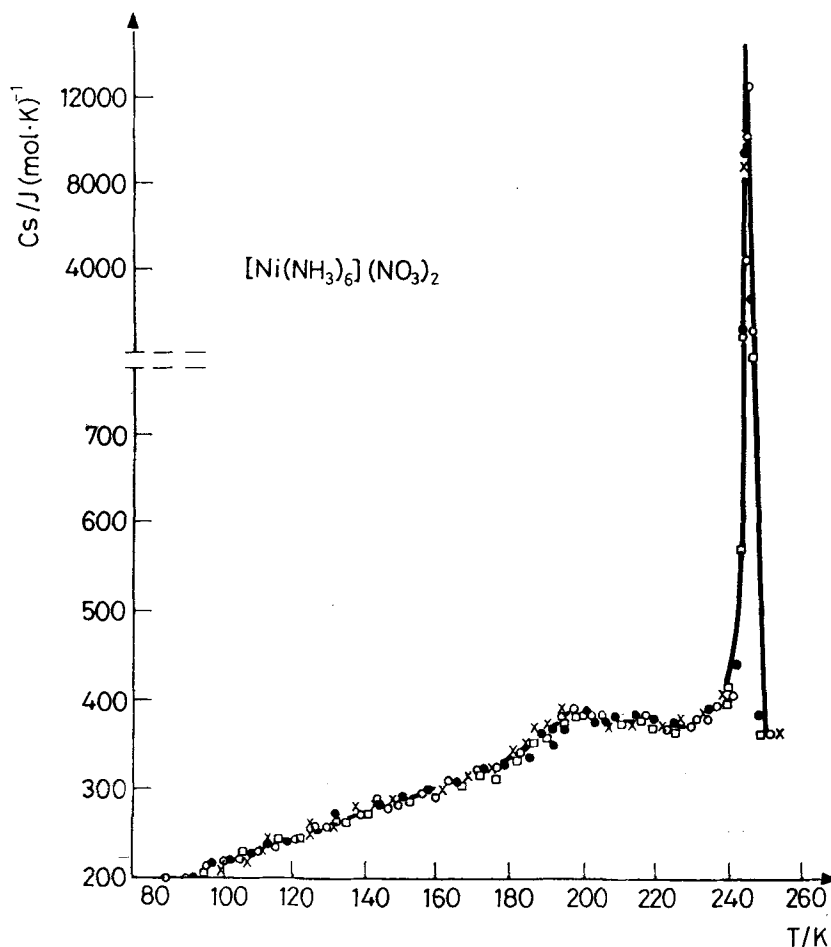


Fig. 4 Specific heat vs. temperature for $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$; \times - II run, \circ - IV run, \bullet - V run, \square - 2 run [7]

perimental points is much smaller but the shape of the anomaly is slightly different from run to run. It is interesting to analyze the experimental data, namely the enthalpy change ΔH of a whole system: calorimeter + sample in the temperature region of the small anomaly (Table 1) and the enthalpy change in the much larger temperature region (Table 2). Looking at Table 1 we can see that ΔH decreases if the number of run increases. If we take into account a larger temperature region (Table 2) the situation becomes different. In this case ΔH remains constant within the limit of error. The reason of it can be following. Namely, it seems that for the phase transition connected with the small anomaly the nucleation region covers practically whole low temperature part of the spe-

Table 1 ΔH calculated from various runs for the small anomaly of $[\text{Ni}(\text{NH}_3)_6] (\text{NO}_3)_2$

No. of experimental run	T region in which ΔH was calculated / K	$\Delta H/\text{J}\cdot\text{mol}^{-1}$	T at which the appropriate experimental run starts
II	170–230	9209±8	96.7 K
IV	170–230	9176±8	81.3 K
V	170–230	9155±8	88.3 K

Table 2 ΔH calculated for the same experimental runs as in Table 1 but in wider temperature range

No. of experimental run	T region in which ΔH was calculated / K	$\Delta H/\text{J}\cdot\text{mol}^{-1}$
II	115–230	16205±13
IV	115–230	16200±13
V	115–230	16184±13

cific heat curve with the small anomaly included. Thus the last set of ΔH values shows that one gets the same values of ΔH for subsequent runs only if ΔH is calculated in wide temperature range. In other words phase III- phase II transition takes place in a wide temperature region. The good confirmation of the hypothesis can be found taking into account the results of [8].

d/ The influence of high temperature phase formation in the pretransitional region on the shape of specific heat anomaly illustrated by melting peak for HOAB.

On the basis of NMR results [9] one can assume, that in the substance a formation of the new phase takes place already in region of several degrees before the melting temperature. The substance melts at 347.75 K [3]. The specific heat result for HOAB show that the anomaly display a distinct pretransitional effect on the low temperature side in a range of several Kelvin. The fact shows up also on the T vs. ΣQ dependence (Fig. 5). One can distinguish three segments here:

- 1/ connected with the pretransitional region
- 2/ connected with the very phase transition
- 3/ connected with the region above the phase transition.

One can see that in the case 1/ the straight line character is distinctly deformed by the mentioned effect. The value of the deformation is a measure of the amount of the new phase which is completely formed at 347.75 K. In the pretransitional region at certain temperature the ratio of a segment parallel to

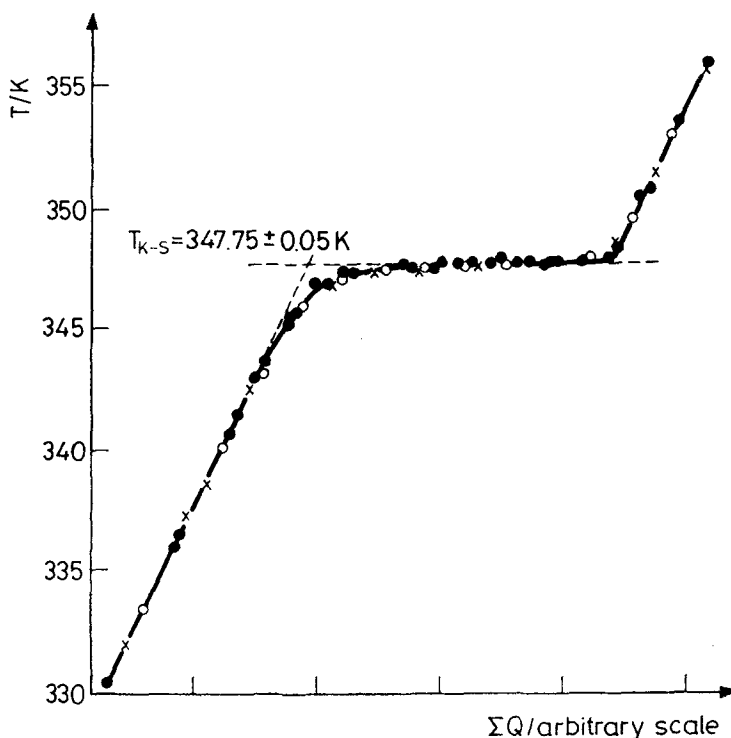


Fig. 5 T vs. ΣQ for crystal - smectic C phase transition in HOAB [3]

the ΣQ axis to the corresponding segment at the melting point gives the melted substance fractions at various temperatures. Knowing the total mass of the sample and assuming the number of molecules in a liquid - crystalline cluster to be of the order 10^5 [10] the number of liquid crystalline clusters was estimated as a function of temperature (Fig. 6).

e/ Specific heat anomalies in liquids

Some liquids, as for example 3,4 dimethylpyridine (3,4 lutidine), are characterized by not only one dependence on temperature of transport or relaxation coefficient [11, 12]:

$$A_T = A_0 \exp(E_A/kT) \quad (3)$$

where A_0 - const., E_A - energy of activation, R - the gas constant. It means, that we can say here about at least two various E_A . For liquid 3,4 lutidine investigated in the adiabatic calorimetry in the region 265-370 K a small anomaly on the specific heat curve was discovered at 293.5 K with $\Delta S = 0.16 \pm 0.02 \text{ J/mol}\cdot\text{K}$

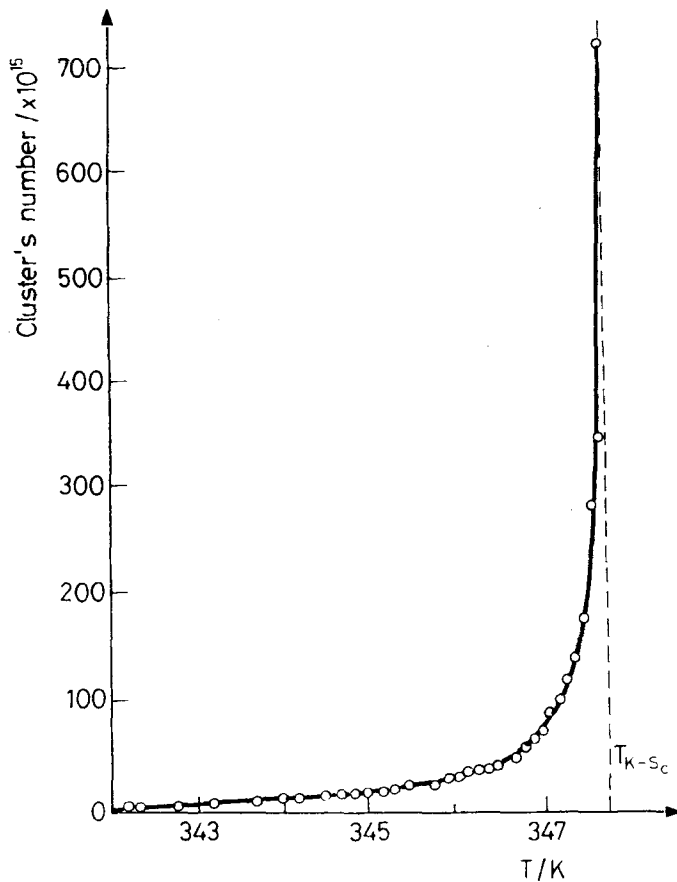


Fig. 6 Temperature dependence of the number of liquid - crystalline clusters in the premelting region [3]

and $\Delta H = 65.6 \pm 9.8$ J/mol. On the basis of [13] one can distinguish two reasons which could be responsible for the anomaly;

- 1/ the decay of molecular clusters
- 2/ partial or total release of molecular degrees of freedom of rotation.

If we assume [14] that the decay of molecular clusters is connected with energy E_d and the number of disintegrating clusters is described by the Boltzmann distribution

$$N_d = N \exp(-E_d/kT), \text{ where } N - \text{ the Avogadro number} \quad (4)$$

the full energy connected with the process is equal to $E_d N \exp(-E_d/kT)$. Hence the contribution to the specific heat from the process is described by:

$$\frac{d(E_d N_d)}{dT} = \frac{NE_d^2}{kT^2} \exp(-E_d/kT) \quad (5)$$

After finding the logarithm of (5) we get:

$$\ln \Delta CT^2 = \ln E_d^2/k \exp(-E_d/kt) = \ln E_d^2/k - E_d/kT = a - b/T \quad (6)$$

From the graphic analysis of the last equation applied to the anomaly of specific heat in Fig. 7, we get for E_d a value of $208 \pm 42 \text{ kJ} \cdot \text{mol}^{-1}$. The value seems to be 10 times too large if the breaking of hydrogen bonds responsible for the existence of the clusters is connected with the process of their decay. Therefore one should either assume another model of clusters which in view of [15–21] is less probable or suppose that the specific heat anomaly is connected with partial or total release of molecular degrees of freedom of rotation.

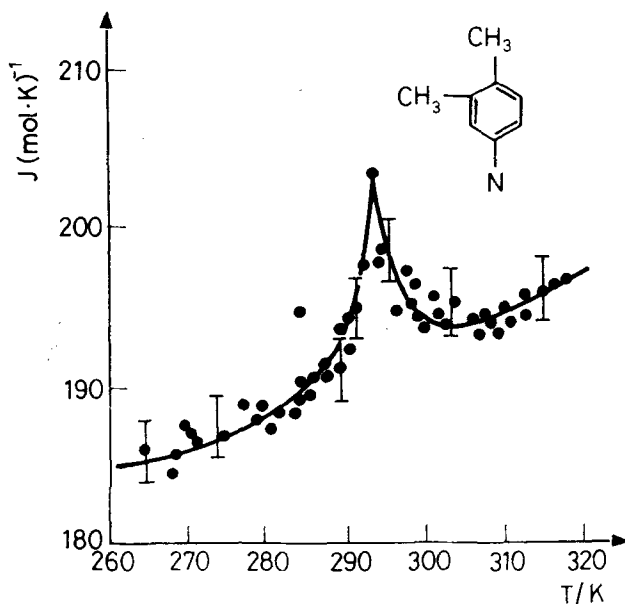


Fig. 7 Specific heat vs. temperature for 3,4 lutidine in the temperature region 265–320 K [13]

Non equilibrium phase transition on the example of the metastable – stable phase transition in HOAB

The so-called liquid crystal substances produce a metastable phase during fast cooling of the melted sample. The phase obtained in this way transforms to

a stable modification at a temperature dependent on the type of substance and on its thermal history. In an adiabatic calorimeter the process of transition from a metastable phase to stable one can be easily observed because one can register a continuous increase of temperature connected with passage of molecules from local minimum of energy (the metastable state) to the absolute minimum of energy (stable state). The process can be described by the equation:

$$T(\infty) - T(t) = B (\exp - t/\tau), \text{ or by} \quad (7)$$

$$\ln(T(\infty) - T(t)) = \text{const.} - t/\tau \quad (8)$$

where $T(t)$ means the temperature at a moment of transition, $T(\infty)$ means the temperature after the transition, t – time, τ denotes the time in which the temperature increase in moment t is equal to $1/e$ of the total temperature increase.

Table 3 The characteristic parameters for the metastable phase–stable phase transition in HOAB

Transition	Average temperature of transition / K	τ / min
metastable phase I – metastable phase II	339.5	232±25
metastable phase II – stable phase	343.7	670±65
metastable phase I – metastable phase II	335.8	594±34
metastable phase II – stable phase	344.4	5192±1144

Table 4 The dependence of τ on the thermal history of NPOB

Experiment No.	T down to which the sample was cooled / K	Time of storage of sample at given T / h	Average T of transition / K	τ / min
1	150.0	23	295.2	149±16
2	150.8	1	295.2	160±27
3	104.5	1	295.2	96±18
4	103.5	23	295.1	96±18

For HOAB one could get the evidence of two metastable phases. The obtained τ are set in Table 3 where the last row is ‘distinguished’. One can see in this

case the large value of τ although the temperature of transition is practically the same as in rows 2 or 4. This behavior can be related to the fact that the thermal histories were different. The similar effect of the influence of thermal history on τ value was observed also for 4-nitrophenyl 4'-octyloxybenzoate (NPOB) (Table 4). The dependence of $\ln(T(\infty)-T(t))$ on time shows that experimental points which follow the straight line at the beginning of the transition deviate (downwards) from the line as the end of the transition is approached and the effect exceeds experimental errors. Such behavior seems to reflect more than one relaxation process responsible for the metastable - stable phase transition.

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Zusammenfassung — Adiabatische Kalorimetrie wurde zur Untersuchung von Gleichgewichts- und Nichtgleichgewichts-Phasenumwandlungen eingesetzt. Bei einer der untersuchten Substanzen (4,4'-Di-n-heptyloxyazoxybenzol) war es möglich, die Temperaturabhängigkeit eines Ordnungsparameters und einer Anzahl von Clustern von Hochtemperaturphasen in einem Bereich der Phasenumwandlung zu bestimmen. Bei einer anderen Substanz (flüssiges 3,4-Dimethylpyridin) wurde eine Anomalie der Kurve für die spezifischen Wärme als Grund für die Abnahme der Molekül-Cluster verantwortlich gemacht. Für einige Flüssigkeitskristallsubstanzen wurden Nichtgleichgewichts-Phasenumwandlungen untersucht. Der Prozeß der Umwandlung zwischen metastabiler und stabiler Phase wurde quantitativ beschrieben. Die gezogenen Schlußfolgerungen betreffen die Stabilität der metastabilen Phasen.