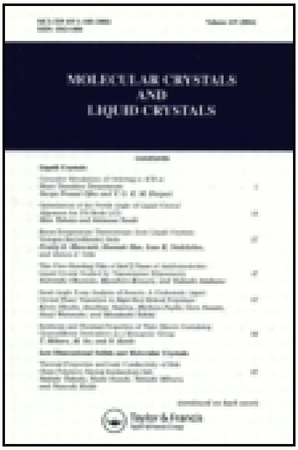

Molecular Crystals and Liquid Crystals

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Use of the Tables

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Use of the Tables

GENERAL REMARKS

This book does not claim to be complete but it provides a useful guide to existing literature containing thermodynamic data on mesogens. The subject continues to expand, and developments (for example, those relative to discogens) are now rapid. We have voluntarily restricted our investigations to pure compounds, in particular there are no data concern the polymers or the lyotropic mixtures. The tables are not critically evaluated, but we feel that this collection of dispersed data can help the users; sometimes we give different values and the corresponding sources.

Because of the supercooling* phenomenons, we have mainly selected transition values obtained by heating including data concerning transitions between monotropic phases. If results are measured only on cooling we mention this by footnote. Sometimes the melting data are dispersed, they can concern different solid phases. Of course, the most stable in the list is not necessarily the most possible stable solid state of the studied compound. Some authors give no indication of the purity of the studied samples, however, the phase change physical studies (particularly the calorimetric measurements) are generally good purity criterions except for the enantiomers forming perfect solutions.[2] If the racemic mixture exhibits a mesophase with a possible twist the texture observation is a good test for the optical purity. A doubt exists only for the optical purity of the enantiomers. Occasionally at the clearing temperature noticeable thermal decomposition occurs, this phenomenon is mentioned by footnote.

ORDER OF THE COMPOUNDS

For the calamitic mesogens the tables are organized in chemical series in an order resembling the well-known transition temperatures book.[3] The

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*Exceptionally for reentrant mesophases the organization can increase by increasing temperature and superheating can be observed.[1]

numbers of the compounds in this table are given here in the first columns of the second part in order to give quick access for references to further properties. For discogens the series are listed by inceasing sophistication of the central cores and, secondly, by inceasing chemical diversity of the side chains. For the plastogens the following geometrical classification for the molecules is used:

- regular tetrahedron (four equal substituents),
- irregular tetrahedron,
- regular octahedron,
- irregular octahedron,
- monocyclic molecule,
- bicyclic molecule,
- molecule with more than three cycles,
- other molecules.

The structural formulae are given for each series. The numbers of carbon atoms in chains are marked by the letters m or n. In absence of indication the alkyl chains are normal (no branched chains). We have not named each compound individually, only the chemical name is given for a series. In some cases, for briefness, we have used the denomination common in the literature in disaccordance with the International Union of Pure and Applied Chemistry rules. The frequency of occurrence of a particular chemical structure in the table is not indicative of that structure's ability to conduct to a mesophase. These frequencies depend on the synthesis feasibilities, on the specializations of the laboratories equipped with DSC apparatus or on the commercialization.

NATURE OF THE PHASES

This book is not a compilation of the identification works for the mesophases, however, the related informations are often contained in the cited references.* But for numerous mesophases their nature is deduced only from texture observations and is not sure. The results are indicated on the top

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*References or copies of binary phase diagrams from a collection of about 1600 samples can be requested freely from J. Billard, Laboratoire Central des Ponts et Chaussées, F 75732 Paris Cedex 15.

of the columns by letters: K for crystal, I for liquid state, N for nematic, BP for blue phase, S for other calamitic mesophases, D for discotic phases and KP for plastic crystalline phases. The twisted mesophases of chiral compounds are mentioned by an asterisk. As far as possible the usual roman letters are used to distinguish the different smectic[4-7] and discotic[8-1] phases. Generally hexatic and crystal B phases.[9-10] are listed as smectic B and S_G', S_G[11] or S_H' and S_H[12] phases are not distinguished. If their true nature is known they are given in a footnote. If two or more mesophases of a compound are not identified they are arbitrarily numbered. The same procedure is used for the solid polymorphism. Points beneath the preceeding symbols indicate the existence of the indicated phases. The absence of a phase written at top of the column is mentioned by a dash. Data concerning monotropic phases are placed between brackets.

FIRST PART: MOLAR ENTHALPY CHANGES

In this first part transition temperatures (in Celsius degrees) are listed and, if available, in italic molar enthalpy changes (in kcal/mole). References for those are given at the end of the first part. Because of the experimental uncertainties we have used in the scales conversions 273 °K for 0 °C. In the International System (S.I.) the heat unit is the joule but the most frequently used is the calorie. To convert from kcal to kJ multiply the former by 4.184. To obtain the molar enthalpy changes from data expressed in grams we have calculated the molar mass using 16g for atomic mass of the oxygen. The purity of the sample can be determined from precise measurements of heat exchanged versus the temperature.[13] For the ordinary DSC measurements the uncertainty of the temperature is about ± 1 °C and, for the enthalpy depends on the magnitude of the latent heat: about ± 6% for large values and to 100% or more for small values from older studies.[14] For recent apparatus the values are ± 0.3 °C and ± 3% respectively.[15] Sometimes the values given in our table (for example for terephthal-bis-butylaniline[16] are not in accordance with Hess' law[17]: the sum of the molar enthalpies for transitions involving monotropic phases is not equal to the molar enthalpy change for the enantiotropic transition. The given explanation[16] is that crystals obtained by cooling are very small and the surface energy is important. From very precise density versus the temperature measurements pretransition behavior can be observed. Similar results are obtained from precise calorimetric measurements [15-24,13], high resolution heat-capacity studies[25-27] or other physical properties.[28] The DSC measurements cannot distinguish latent heat from the precursor effects on heat-capacity.[29] This explains the unfitness for the DSC to discern between first- and second-order transitions for a pure compound. In our table the heat capacity anomalies near the transitions are included in the enthalpy changes, consequently these values are too large. The difference between the DCS signal and the rare fine heat capacity measurement can give the true transition enthalpy change.[30]

In order to calculate phase diagrams the slopes at the departure of the coexisting curves are given by the true molar enthalpy changes and differences between the heat capacities of the phases in equilibrium lead to variations of these enthalpy changes versus the temperature. For mesogens which can form polymers the proportion of monomers and dimers can change at the transitions.[31] In all cases our data are calculated for the molecular mass of the monomer. Generally the enthalpy changes increase with pressure, but one exception is quoted.[32] No observable decrease of the enthalpy change for the nematic-liquid transition on 4-octyl-4′-cyanobiphenyl was observed with magnetic fields up to 187 kOe.[33] Because of the availability of the programmable calculators we have not printed the entropy changes. In agreement with Le Chatelier's principle[34] (in fact a theorem: ref. 17 p. 486), all the enthalpy changes for phase transitions observed by increasing the temperature, including reentrant mesophases, are non negative.

SECOND PART

In the second part the transition temperatures (in Celsius degrees) and, if available, in italic the molar enthalpy changes (in kcal/mole), are repeated. The slopes of the pressure dependence of the transition temperatures (in bar/°C) are given, and, in bold faced type, the molar volume changes (in cm^3/mole) and in bold faced type preceded by the letter R the relative volume changes (in % of the molar volume of the phase stable at the lower temperature). Under the letter indicating the nature of the phase we give successively: preceded by the character α the thermal expansion (in $10^{-4}/°C$), preceded by χ the isothermal compressibility (in $10^{-10} m^2 N^{-1}$), preceded by χ_{ad} the adiabatic compressibility (in $10^{-10} m^2 N^{-1}$), and preceded by ϱ the density in g/cm^3. As often as possible the temperature for which these phase data are given is indicated. Two columns indicate the sources, one with Ph for the phases data and a second with Tr for the transitions data. References are listed at the end of this part. When several different data are reported in the first part for the molar enthalpy change, we report the one that corresponds to the highest transition temperature (probably related to the highest purity sample). The lines without reference for the transition give the slope of the pressure dependence of the transition temperature calculated from the molar volume change by Clapeyron's relation[35] or the result of the inverse calculation for the volume change form the mean value of the slope. An asterisk indicates data collected from a figure. Data obtained under pressure different from atmospheric are signaled by footnotes. The molar volume increases generally at a transition observed with increasing temperature, but negative volume changes can be observed (for example between smectic and reentrant nematic under sufficient pressure.[36,37] Sometimes for highly viscous phases an important decrease of the molar volume change can be detected with a microscope; at the transition cracks appear in the preparations.

In a first approximation the transition temperature is proportional to the pressure, consequently, if for a phase the slope dP/dT for the transition at lower temperature is lower than the one for the transition at higher temperature this phase disappears at a sufficient pressure: a triple point can be foreseen.[38] The appearance of a stable phase at high pressure[39] can be foreseen from values at low pressure only if data on monotropic or virtual[40] transition can be obtained. The pressure coefficient β can be deduced from the following relation involving the thermal expansion α, the pressure P and the isothermal compressibility χ, resulting from the existence of equation of state f (P, T, ρ) = 0 for each phase:

$$\beta = \frac{\alpha}{P\chi}$$

The heat capacities at constant pressure (C_p) and constant volume (C_v) can be deduced from their ratio related to the isothermal (χ) and adiabatic (χ_{ad}) compressibilities by:

$$\frac{C_p}{C_v} = \frac{\chi}{\chi_{ad}} \quad ^{41}$$

and their difference obtained from:

$$C_p - C_v = \frac{\alpha^2 T}{\rho \chi} \quad \text{(ref. 17 p. 104)}$$

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