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Scanning calorimetry with various inducing variables and multi-output signals

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Abstract – Scanning calorimetry controlled by an independent thermodynamic variable is further developed by simultaneous measurements of the rate of heat evolution and of the variations of the dependent variable. An instrument of this type is presented for use over the pressure interval from 0.1 to 400 MPa at temperatures from 213 to 503 K. The calorimeter is automated on the basis of digital feedbacks by the use of a 8255 I/O card and a PC. The typical low scanning rates of the three basic thermodynamic variables are as follows: P: 5 kPa/s, T: 8 10^{-4}K/s, and V: 2 10^{-5}cm^3/s. Measurements can be made under isothermal, isobaric or isochoric conditions. The direct output signals are: the rate of heat evolution and the variations of the dependent variable or their rate. The total volume of the sample can be varied from 0.5 to 2.5 cm^3 depending on the kind of measurement. The sample can be loaded once into the calorimeter and the phenomenon under investigation observed on different thermodynamic planes. The performence of the instrument is exemplified by investigation of the first-order phase transition in benzene, and phase transitions in 4-n-pentyl-phenylthiol-4′-decyloxybenzoate ($\bar{1}\bar{0}$S5) liquid crystal.

INTRODUCTION

The thermodynamic functions of a system are most often determined by measuring their derivatives against an independent thermodynamic variable. Calorimetry can be easily used to measure the rate of heat evolution of a physicochemical change induced by a known variation of one such variable, whereas the second is kept constant. This procedure allows direct measurements of the most important thermodynamic derivatives (ref. 1). Temperature - controlled scanning calorimeters (TCSC), in which temperature is taken as the inducing variable and varied as a linear (ref. 2) or stepwise (ref. 3) function of time, are the best known instruments of this type and allow measurements of $(\partial H/\partial T)_p$ or $(\partial U/\partial T)_V$. Unfortunately, their construction is such that it is very often difficult to state which variable is being kept constant (pressure or volume), and it is not uncommon for both to change during a given temperature programme, so that the thermodynamic significance of the calorimetric output signal is not clear. Pressure-controlled scanning calorimeters (PCSC) in which pressure is taken as the inducing variable and is varied as a linear (ref.4,5) or stepwise (ref. 6,7) function of time are examples of isothermal scanning calorimeters allowing the measurement of $(\partial S/\partial p)_T$. Calibration of the pump piston displacement as a measure of the volume change inside the cell (ref.8) enables volume to be used as the inducing variable under isothermal conditions so as to construct a volume - controlled scanning calorimeter (VCSC) to measure $(\partial S/\partial V)_T$. However, the proper metrological procedures become more difficult to attain, because volume is an extensive parameter. The three techniques are mostly concerned with the closed systems, any change in the composition of a system can only be a result of the pertubation of its thermodynamic state by a variation of the inducing independent variable. When speaking about the therminology of scanning calorimetry, the thermodynamic reasoning described enables the mixing-flow calorimeters and injection (or titration) calorimeters to be called as composition - controlled scanning calorimeters (CCSC), in which composition, expressed in proper units, is taken as the inducing variable and is varied as a linear (ref. 9) or stepwise (ref. 10) function of time. However, this paper focuses on closed systems and presents further developments of scanning calorimetry controlled by an independent thermodynamic variable. At the IUPAC Conference on Chemical Thermodynamics in 1988 in Prague, we presented this technique as a tool in the investigation of dense liquids. An account will now be given of its new possibilities in investigation of physicochemical transitions in which both the thermal response of the induced change and variations of the dependent variable (or their rate) are simultaneously measured.

INSTRUMENT

An "artistic view" of a calorimetric system allowing the use of pressure, temperature or volume as independent or dependent thermodynamic variables is presented in Fig.1. Its temperature range is 213 to 503 K and its pressure range is 0.1 to 400 MPa. The total volume of the sample under atmospheric pressure can be varied from 0.5 to 2.5 cm^3, depending on the kind of measurements performed. Typical low scanning rates are: T: 8 10^{-4}K/s, V: 2 $10^{-5}cm^3/s$, and p: 5 kPa/s. These allow measurement near the equilibrium state for many processes. The sample can be loaded once into the calorimeter and the phenomenon under investigation observed on various thermodynamic planes. The calorimeter is automated by digital feedbacks, using an 8255 I/O card and a PC. One of the important problems is attainment of the inducing variables as given functions of time without transient overshoots. A relatively new problem in scanning calorimetry in this respect is pressure programming. This can be done with a classical PID controller by heating or cooling an additional hydraulic tank connected to the controlled system in such a way that the pressure in it corresponds to the given set function (ref. 4). Unfortunately, this technique only gives satisfactory results up to not much more than 100 MPa. For higher pressures, we use a piston pump driven by a stepping motor and a gearbox (Fig.1). Fig.2 is a schematic diagram of the software for this digital pressure programmer (ref. 11). The control variable CV is composed of two parts, PR, which is a constant proportional to the chosen speed of pressure variations, and COR, which is a dynamic correction obtained using the control function (CF), based on the difference between the actual pressure in the system and the value resulting from the set function. PR is determined at the beginning of the programme from the limiting speed characteristic (LSC) of the controlled system, which gives its maximal rates of pressure variations over the whole pressure range. Thus the programme starts with the control variable equal to PR, which is sent to the stepping motor via I/O card 8255 and a suitable power amplifier. Any change in the internal volume of the system is detected by the correction term of the CV, which is varied in such a manner as to

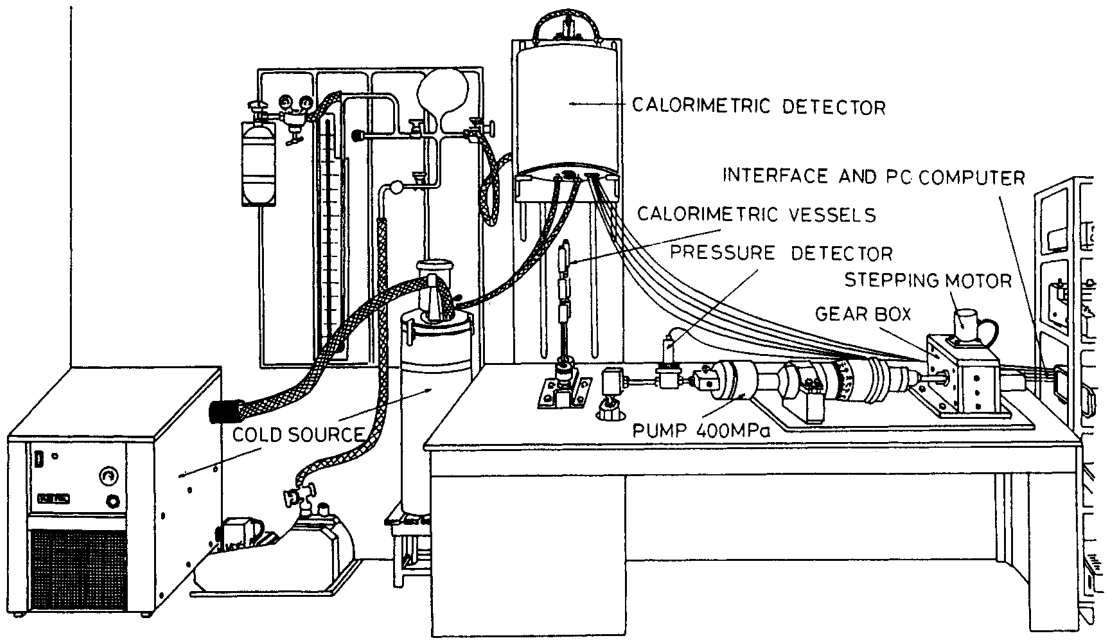
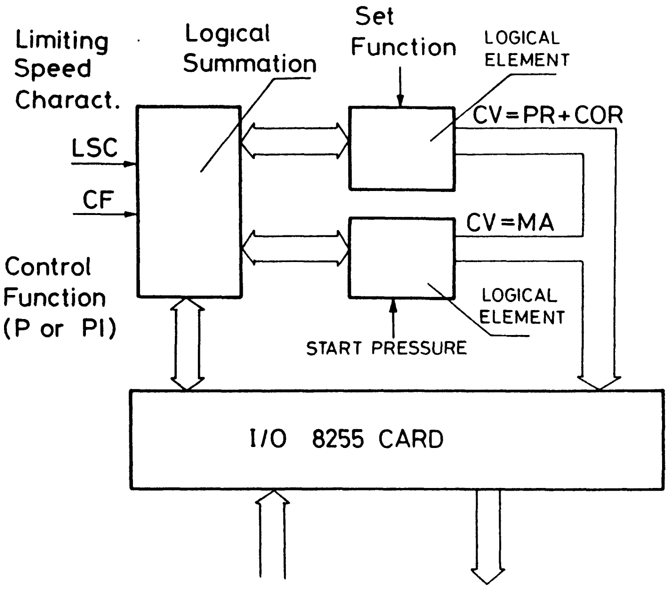


Fig.1. An "artistic view" of the scanning calorimeter with various inducing variables and multi-output signals.



compensate for volume changes and to reach the pressure set function without disturbances.The start pressure can be obtained with CV=MA, which sets the maximal admissible rate of pressure variations over the whole pressure range.A detailed description of the instrument will be given elsewere.

Fig.2. The digital pressure programmer software.

STUDY OF PHASE TRANSITIONS

First-order transitions

The new possibilities of the instrument will first be demonstrated by investigation of a typical 1st-order transition, namely fusion of a sample of benzene (99.95%) under various thermodynamic conditions.

Isothermal fusion of benzene at 303 K induced by the linear reduction of pressure is illustrated in Fig.3. Pressure was varied at 10 kPa/s over the pressure range 140-40 MPa. It can be seen that the linearity of the pressure programme is not disturbed by volume variations. It is known that when pressure is varied without a proper feedback loop, volume changes disturb linear pressure variations and disturbances slower the rate of fusion, and the thermogram is deformed (ref. 4). The thermogram of fusion and the volume changes in Fig.3 are presented in arbitrary units with no correction for the compressibility of the liquid transmitting the pressure. The techniques for calibration of the output signals in investigation of phase transitions will be described later.

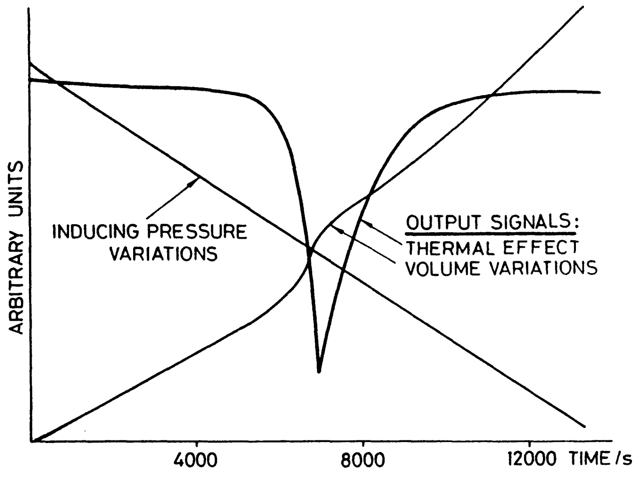


Fig.3. Isothermal fusion of benzene at 303 K induced by linear pressure variations.

Fig.4 shows fusion of the same sample induced by linear variations of volume at 303 K. The pressure in the system remains practically constant. The volume changes and the corresponding thermogram of fusion for a variation of temperature from 303.1 to 314.8 K at 8.3 10^{-4}K/s under a constant pressure of 89.8 MPa are presented in Fig.5.

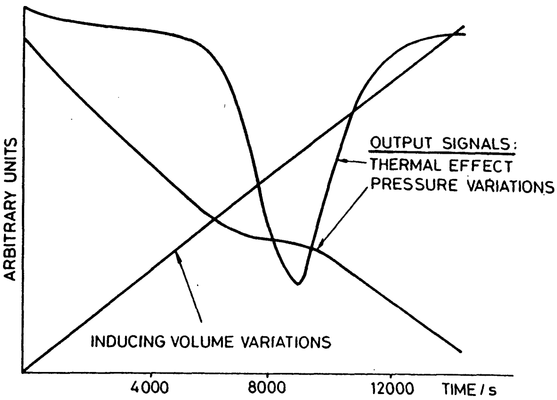


Fig.4. Isothermal fusion of benzene at 303 K induced by linear volume variations.

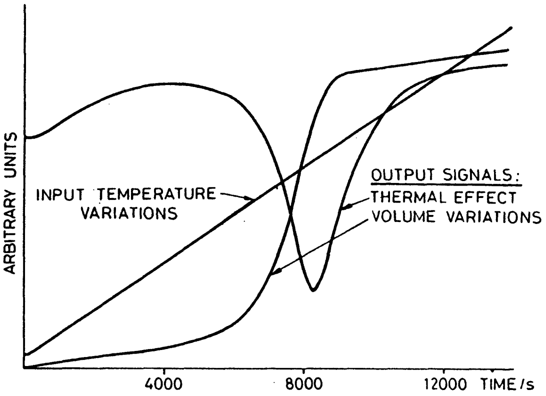


Fig.5. Isobaric fusion of benzene at 89.8 MPa induced by linear temperature variations.

Transitions in liquid crystals

Application od scanning calorimetry in investigations of liquid crystals is interesting because of the multiplicity and variety of their phase transitions. Especially fascinating is the pressure inducing variable. It is known that for such substances the density fluctuations in a single-component system and the concentration fluctations in a multi-component system can produce the same topological distortions of the phase diagram, so that the T-p phase diagram is topologically equivalent to the T-x diagram (ref.12). In previous investigations of liquid crystals the pressure variable was mainly used in the pressurized TCSC (ref. 13). An attempt to use pressure as the inducing variable in the stepwise mode has also been reported (ref. 6). A few examples of direct results obtained with continuous inducing pressure variable will now be described. The substance was 4-n-pentyl-phenylthiol-4′-decyloxybenzoate ($\overline{10}$S5). Its transition from the liquid isotropic to the solid phase passes through the nematic and three smectic phases, A, C and B (ref.14). It has also been suggested that on heating under near-atmospheric pressure the solid phase goes dirctly to the smectic-A phase (ref. 15).

Our measurements were performed at 370 K, i.e. about 11 K higher than the temperature of the nematic-isotropic transition under atmospheric pressure (ref. 14, 15). Fig.6 and Fig.7 illustrate compression and decompression at 10 kPa/s. The volume changes from the previous figures are here replaced by the rate of volume variations, which are much more sensitive in the detection of weak transitions. The output signals are again presented in arbitrary units. It can be seen that in both cases the beginnings of the main transitions are observed at approximately the same pressures independently of the direction of the pressure variations. However, the shapes of the solid-smectic A and smectic A-solid transition are complex and completly different from each other, i.e. the transition cannot be simple. For closer invesgation, the experiments

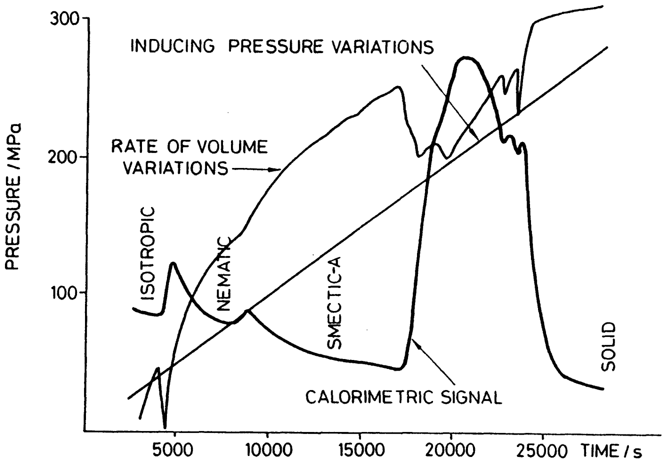


Fig.6. Isothermal compression of $\overline{10}$S5 liquid crystal at 10 kPa/s and 370 K.

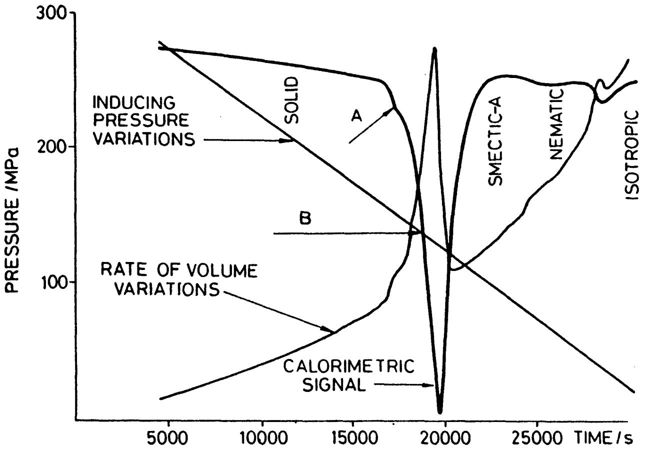


Fig.7. Isothermal decompression of $\overline{10}$S5 liquid crystal at 10 kPa/s and 370 K.

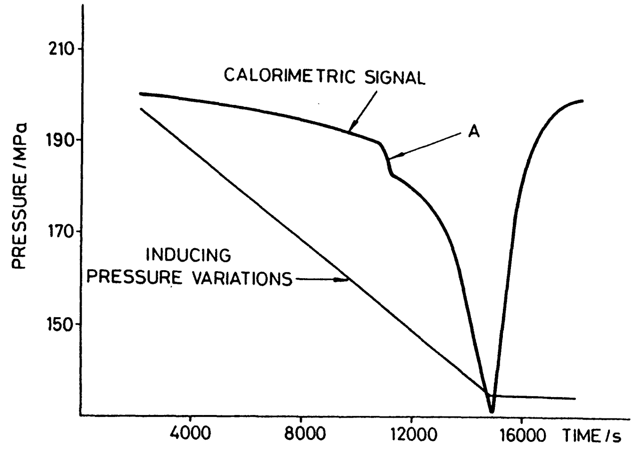
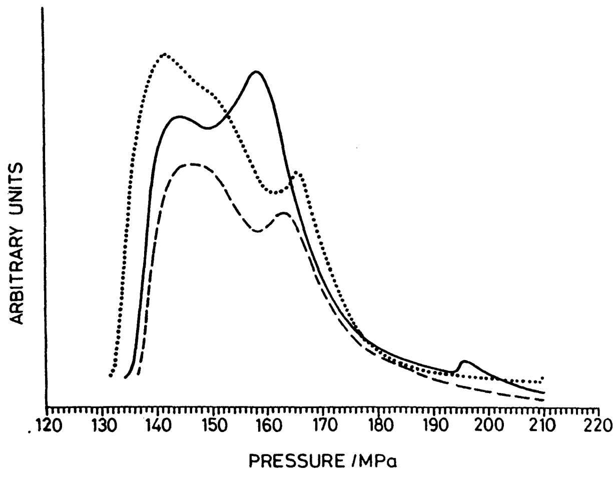


Fig.8. Isothermal decompression of $\overline{10}$S5 liquid crystal at 5 kPa/s and 370 K. Stopped during the solid to smectic-A phase transition.



were repeated at a rate of 5 kPa/s in both directions. In the case of decompression, small deformation of the thermogram at point A was reproducible. In the case of compression, the form of the thermogram was not very different from that in Fig. 6. In the next experiments decompression was stopped somewhere in the middle of the transition between the solid and smectic-A phases, followed by recompression after several hours of rest. Such isothermal decompression stopped at 134.4 MPa (point B, Fig.7) is shown in Fig.8. The small deformation obtained at 10 kPa/s (point A, Fig.7) now becomes a distinguishable step (point A, Fig.8), although the calorimetry alone cannot indicate what process is involved. The thermograms of recompressions started at 131.5, 134.4,and 136.1 MPa 5 kPa/s presented in Fig.9 make it clear that the transition is really complex and at least three processes can already be distinguished.

This paper is not concerned with complicated behaviour of liquid crystals at high densities. Its aim is to demonstrate the new possibilities of scanning calorimetry in such investigations. This technique can be used not only in making phase diagrams, but is also very useful in investigation of the mechanisms of different physicochemical transitions. The pressure variable is of great interest for many reasons. The main experimental advantage is much easier control of transitions induced by pressure than by temperature, due to its fast propagation and the larger phase-coexistence pressure intervals of coexistance of phases.

←Fig.9. Isothermal compressions of $\overline{10}$S5 liquid crystal at 5 kPa/s and 370 K started at various pressures of the coexistence of phases.

CONCLUSIONS

Scanning calorimetry with various inducing variables and two output signals (the rate of heat evolution, and mechanical dependent variable or its rate), is especially helpful in investigation of the mechanism of physicochemical transitions. It can also be of interest in teaching chemical thermodynamics, because phenomena can be observed on various thermodynamic planes and the influence or behaviour of particular thermodynamic variables clearly demonstrated. The pressure and temperature intervals covered by the instrument described are suitable for the investigation of various processes.

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